

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Metastable Phase Formation and Decomposition in a Rapidly Solidified Aluminium-Platinum Alloy

K. CHATTOPADHYAY and P. RAMACHANDRARAO, *Mater. Sci. Engng.*, 1979, **38**, (1), 7-17

X-ray diffraction and electron microscopic studies of the metastable phase formation and decomposition of a rapidly solidified 2% Pt-Al alloy were performed. Two metastable phases were detected. The first one was of a cubic structure with $a=5.67\text{\AA}$ and was a metastable extension of the equilibrium Al_3Pt phase. The second phase, of the composition Al_2Pt , was orthorhombic with $a=15.762$, $b=12.103$ and $c=8.318\text{\AA}$.

Silicide Formation with Bilayers of Pd-Pt, Pd-Ni, and Pt-Ni

T. G. FINSTAD and M.-A. NICOLET, *J. Appl. Phys.*, 1979, **50**, (1), 303-307

X-ray diffraction studies of the silicide formation of evaporated two-layered thin films of Pd-Ni, Pt-Ni and Pt-Pd on single-crystal Si, vacuum annealed at 200-900°C, were carried out. The silicide layers were highly inhomogeneous for annealing below 600°C but became homogeneous at $>700^\circ\text{C}$. The silicide-substrate interface showed varying sharpness depending upon substrate orientation and evaporation sequence. The existence of ternary monosilicides of the type $\text{Pt}_{1-x}\text{Pd}_x\text{Si}$, $\text{Pt}_{1-x}\text{Ni}_x\text{Si}$ and $\text{Pd}_{1-x}\text{Ni}_x\text{Si}$ is reported. The $\text{Pt}_{1-x}\text{Pd}_x\text{Si}$ ternary silicide was stable up to 900°C.

Magnetic Properties of CePt_3 between 4.2 and 295 K

H. LUEKEN, M. MEIER, G. KLESSEN, W. BRONGER and J. FLEISCHHAUER, *J. Less-Common Metals*, 1979, **63**, (1), P35-P44

The magnetic susceptibility of CePt_3 was measured between 4.2 and 295K by the Faraday method. The deviation from Curie-Weiss behaviour below 80K can be explained by hexagonal crystal field splitting in the $J=5/2$ ground term of Ce^{3+} .

Phase Transformations in High-Strength Alloy of Palladium with Copper and Gallium

S. Z.-B. KHABLIEV, I. N. SAKHANSKAYA, V. G. CHEREMNYKH and V. S. LITVINOV, *Fiz. Metall. Metalloved.*, 1979, **47**, (1), 217-220

The phase transformations in 79.8 Pd-11.7 Cu-8.5 wt. % Ga alloy were studied after deformation

and annealing at 380°C. The increased strength of this alloy is due to the precipitation of $(\text{Pd}, \text{Cu})_2\text{Ga}$ with a b.c.c. structure.

Investigation of Alloy Systems $\text{Pd}_2\text{AlCu-PdAl}$

L. A. PANTELEIMONOV and D. N. GUBIEVA, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1979, (2), 215-216
Metallographic and differential thermal studies of the $\text{Pd}_2\text{AlCu-PdAl}$ system were performed. No restriction in growth of Pd_2AlCu and PdAl compounds by solutes occurred in liquid or solid compounds immediately after solidification. The character of interactions of high temperature modified compounds of Pd_2AlCu and PdAl are described by a diagram of a eutectoid type with the eutectoid point at 20 mol % PdAl and 770°C. At 556-440°C alloys transform into the solid compounds, subsequently undergoing polymorphous transformation into PdAl compounds and at 290°C into Pd_2AlCu compounds.

Indentation Recovery of Amorphous Materials

B. T.-A. CHANG and J. C. M. LI, *Scripta Metall.*, 1979, **13**, (1), 51-54

Samples of $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$ amorphous alloy, polystyrene and pyrex glass were indented by a cone shaped diamond, measured, and then annealed at various temperatures to allow the indentations to disappear. It was found that for $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$ an indentation of 0.5 μm deep did not change in depth after 24 minutes at 389°C. Since the crystallisation temperature is 410°C, annealing could not be carried out at higher temperatures or longer times without risking the uncertainty of crystallisation. This recovery was much slower than polystyrene or pyrex.

Dynamics of Laser-Induced Formation of Palladium Silicide

M. VON ALLMEN and M. WITTMER, *Appl. Phys. Lett.*, 1979, **34**, (1), 68-70

The formation of Pd silicide by laser irradiation of a thin Pd film evaporated on single crystal Si was studied. Silicide formation takes place through interdiffusion of the molten elements, followed by thermal quenching. A diffusion constant of $4 \times 10^{-4} \text{ cm}^2/\text{s}$ was estimated. The reacted layer consisted of a mixture of different metal-Si compounds, including PdSi , Pd_2Si , Pd_3Si and Pd_5Si . By appropriate choice of Pd film thickness and laser pulse parameters either complete mixing of Pd and Si or tailored concentration profiles can be achieved. Pd_2Si is a commonly used silicide for ohmic contacts to Si semiconductor devices.

Behaviour of Rhodium and Iridium during Carbonylation of Copper-Nickel Sulphidised Alloys

A. S. MNUKHIN, V. I. BADER and A. F. SIDOROV, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1979, (2), 38-44

The behaviour of Rh and Ir was studied during synthesis of Ni carbonyl from Cu-Ni sulphide materials. Rh and Ir were present only in the metallic phase with Rh uniformly dispersed throughout while Ir was concentrated in localised sections, isomorphically replacing Cu. Rh reacted with Cu sulphide yielding RhS₂. Phases containing > 5 at. % Ir did not go through any changes, passing over into the solid residue of the synthesis.

Thermodynamic Investigations in the Thorium-Osmium and Thorium-Iridium Systems

H. KLEYKAMP, *J. Less-Common Metals*, 1979, 63, (1), P25-P33

The Gibbs energies of formation of the three intermetallic phases, ThOs₂, Th₃Os₂ and Th₇Os₃ occurring in the Th-Os system, and the ThIr₅ and ThIr₃ phases of the Th-Ir system, were determined by e.m.f. measurements using solid galvanic cells with a CaF₂ electrolyte. The enthalpies of formation were correlated with calculated values based on thermodynamic models. The regions of the phase diagrams rich in noble metals for both systems were supplemented by pyrometric melting point determinations: ThOs₂, 2480°C; ThIr₅, 2260°C; and ThIr₃, 2280°C.

CHEMICAL COMPOUNDS

The Interaction of Pt(II) *cis*- and *trans*-diaciddiammine with Sulphur Containing Dipeptides

M. F. MOGILEVKINA, V. I. RAR, G. L. NIKIFOROVA and I. M. CHEREMISINA, *Zh. Neorg. Khim.*, 1979, 24, (2), 425-430

The interactions of *cis*- and *trans*-[Pt(NH₃)₂Cl₂], and also *cis*-[Pt(NH₃)₂(H₂O)₂](NO₃)₂ with S containing dipeptides (LH₂)-glycyl- and α -alanyl-methionine with molar ratio 1:2, were studied. The chemical properties of the obtained complexes and also their molecular electrical conductivity and absorption spectra were given.

A New Cationic Binuclear Trihydrido Complex Containing One Four- and One Five-Coordinate Platinum Atom

G. BRACHER, D. M. GROVE, P. S. PREGOSIN and L. M. VENANZI, *Angew. Chem. Internat. Ed. En.*, 1979, 18, (2), 155-156

An unusual binuclear Pt trihydrido complex was synthesised. This complex contains both a dihydrido bridge and a terminal hydride ligand.

This is the first example of a class of binuclear Pt hydrides containing one four- and one five-coordinate metal centre.

Palladium(II) and Platinum(II) Complexes with Nucleobases and Nucleosides. Crystal Structure of *trans*-Bis(adeninato)bis(tri-n-butylphosphine)palladium(II)

W. M. BECK, J. C. CALABRESE and N. D. KOTTMAIR, *Inorg. Chem.*, 1979, 18, (1), 176-182

The synthesis and degradation of novel dinuclear and tetranuclear complexes [L(n-Bu₃P)MCl]₂ and [Cl₂(n-Bu₃P)M(L)M(P-n-Bu₃)Cl]₂, [M = Pd(II), Pt(II)] with the anion of adenine (L) have been studied. These complexes have nucleobases and nucleosides.

Planar Complexes of Asymmetrically Substituted Alkyl and Aryl- α , β -dionedioximes with the Ions Nickel(II), Palladium(II) and Platinum(II)

H. J. KELLER and R. LEHMANN, *Z. Naturf. B*, 1979, 34, (2), 245-250

New planar bis(α , β -dionedioximato)metal(II) complexes of the ions Pd(II), Pt(II) and Ni(II) with asymmetrically substituted glyoximes as ligands are reported. These are found to crystallise in columnar stacks. Compared with the known symmetrical derivatives the solubility of the isolated neutral compounds greatly increased in organic solvents.

On the Synthesis and Characterization of Pd(CO)(PPh₃)₃

F. MORANDINI, G. CONSIGLIO and F. WENZINGER, *Helv. Chim. Acta*, 1979, 62, (1), 59-61

Pd(CO)(PPh₃)₃ could be isolated from the reaction mixture arising from cyclohexene hydrocarboxylation by PdCl₂(PPh₃)₂ as the catalyst precursor and also through direct reaction of Pd(PPh₃)₄ with CO in benzene. ³¹P- and ¹³C-NMR studies of this complex suggest a rapid dissociation of PPh₃ at room temperature and tetrahedral structure at -70°C in solution.

Kinetics of Olefin Arylation with bis-(Triphenylphosphine) Palladium(II) Diacetate and Its *trans*→*cis*-Isomerisation

A. D. RYABOV and A. K. YATSIMIRSKII, *Kinet. Kataliz*, 1979, 20, (1), 106-112

Studies of the kinetics of Pd(PPh₃)₂(OAc)₂ decomposition with formation of Pd⁰ and of the kinetics of arylation of substituted styrene in the presence of Pd(PPh₃)₂(OAc)₂ in freezing HOAc were carried out. A mechanism of arylation is proposed, including intermediate reduction of Pd(II) to Pd⁰ with formation of σ -phenylpalladium particles and a fast phase of transmission of phenyl groups from these particles onto olefins. Kinetics and conditions of *trans*→*cis*-isomerisation of Pd(PPh₃)₂(OAc)₂ are discussed.

Synthetic Aspects of Rhodium(III) Chemistry. I. A High Yield Route to *cis*-Bis(1, 2-diaminoethane)rhodium(III) Complexes

M. P. HANCOCK, *Acta Chem. Scand., Ser. A*, 1979, **33**, (1), 15-18

A crude, 1:1 mixture of *trans*- and *cis*-[RhCl₂(en)₂]ClO₄ (en = 1, 2-diaminoethane) was obtained in ~80% yield following the pH controlled reaction of RhCl₃·3H₂O with en (as en·2HCl). The crude mixture was converted to [Rh(ox)en₂]⁺(A) (ox = oxalate) isolating oxalato complex as pure perchlorate on bromide salts in ~80% yield. The *cis*-dihalo complex was synthesised in an almost quantitative yield by the reaction of (A) in boiling 6M HCl. The entire reaction sequence thus permitted the synthesis of the *cis*-dihalo complexes in ≥60% overall yield based on RhCl₃·3H₂O.

U.V. Photoelectron Spectral Studies on the Metal Carbonyl Cluster Compounds Os₃(CO)₁₂, Ru₃(CO)₁₂, and Os₆(CO)₁₈

J. C. GREEN, E. A. SEDDON and D. M. P. MINGOS, *J. Chem. Soc., Chem. Commun.*, 1979, (3), 94-95

The photoelectron spectra of Os₃(CO)₁₂ and Ru₃(CO)₁₂ have been recorded and are consistent with the molecular orbital scheme proposed for such molecules. The first ionisation energies of these compounds, and of Os₆(CO)₁₈ were compared with the work functions of the corresponding metals and found to be ~3eV higher.

Ternary Metal Borides [La, Ce, Pr, Nd, Sm] Os₃B₄ and [Y, La, Ce, Pr, Nd, Sm, Gd, Tb] Ir₄B₄ with NdCo₄B₄-Type Structure

P. ROGL, *Monatsh. Chem.*, 1979, **110**, (1), 235-243

New ternary metal borides with composition R.E.T₃B₄ (R.E. = rare earth metal, T = transition metal) were prepared within the systems [La, Ce, Pr, Nd, Sm]-Os-B and [Y, La, Ce, Pr, Nd, Sm, Gd, Tb]-Ir-B. All compounds crystallised in the NdCo₄B₄-type structure.

ELECTROCHEMISTRY

The Measurement of Strong Adsorption on Platinum Film Electrodes by Surface Conductance

L. MÜLLER, G. N. MANSUROV and O. A. PETRIL, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **96**, (2), 159-164

The adsorption of thiourea (TU), urea and sulphide on Pt-film electrodes was measured at 25 ± 1°C with 0.5M H₂SO₄ as supported electrolyte. The small dependence of Δφ on the potential for a monolayer of chemisorbed O₂ (1.6-0.8V), S(0.05-1.0V) or I(0.05-0.4V) shows that for these chemisorption monolayers the partial charge transfer coefficient does not depend on electrode potential.

Two Forms of Chemisorbed Sulphur on Platinum and Related Studies

A. Q. CONTRACTOR and H. LAL, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **96**, (2), 175-181

The effect of temperature on the potentiodynamic oxidation of adsorbed S layers on Pt, by H₂S or SO₂ was studied. The broad oxidation peak at 1.2-1.3V observed at room temperature changed at 80°C. Two distinct peaks were observed: oxidation peak I (at 0.97V) and oxidation peak II (at 1.10V) corresponding to the weakly and strongly bound S, respectively. An extension of the H region was observed at higher temperatures during cathodic charging in the presence of adsorbed S.

Purification of Acetic Acid

Res. Discl., 1979, (177), 8

To reduce the by-product propionic acid formed when H is present during the production of acetic acid from methanol, a membrane, selectively permeable to H is employed. The membrane can be made of Pd or Pd-Ag foils, or organic materials, or may be a multicomponent membrane. This effectively reduces H content after recycling the gases.

ELECTRODEPOSITION AND SURFACE COATINGS

A New Method for Coating Metals with Hydrogen-Transparent Pd Layers

T. SCHÖBER and A. KARL, *J. Less-Common Metals*, 1979, **63**, (1), P53-P56

A new technique for coating metals with H-transparent Pd layers consists of spot welding a thin 25 μm foil onto the metal which is to be charged with H or D. The advantages of this method include: not having to use UHV equipment or degassing units for applying the Pd layer.

HETEROGENEOUS CATALYSIS

Evaluation of Catalysts for Vapour Phase Oxidation of Odorous Organic Compounds

A. K. WASFI, G. P. MATHUR, C. C. S. PIERRE and A. W. GNYP, *Atmos. Environ.*, 1978, **12**, (12), 2389-2398

The oxidation of four organic odorants: n-butanol, n-butyraldehyde, n-butyric acid and toluene was carried out over four commercially available catalysts: 0.1% Pt/γ-Al₂O₃, 0.5% Pd/γ-Al₂O₃, 0.5% Pt/γ-Al₂O₃ and 10% CuO/γ-Al₂O₃, at 116-497°C. The results show that the Pt catalysts are more effective in terms of chemical conversion as well as odour removal efficiency than the Pd and Cu catalysts which required much higher temperatures than the Pt catalysts for comparable performance.

Effect of Carbon on the State of Platinum in Aluminium Oxide Supported Bimetallic Catalysts

V. A. USHAKOV, E. M. MOROZ, N. R. BURSIAK, S. B. KOGAN and E. A. LEVITSKII, *Kinet. Kataliz*, 1979, **20**, (1), 177-180

The effect of C on the state of Pt in 2 wt.-% Pt/ γ -Al₂O₃ bimetallic catalysts promoted by 0.8 wt.-% Ir, 0.8 wt.-% Re and 0.3 wt.-% Ga was studied, on samples prepared by saturation in solutions of H₂IrCl₆, NH₄ReO₄ or Ga(NO₃)₃, before and after coking. The promoter was found to react with the support, filling vacant positions in the spinel structure of Al₂O₃.

Fluorinated Alumina-Platinum Catalysts in Decane Isomerisation

L. B. GAL'PERIN, B. KH. GOKHMAN, E. G. LIRINA and I. D. YAKOVLEVA, *Neftekhimiya*, 1979, **19**, (1), 22-25

Studies of the effect of the method of the introduction of F on the catalytic activity and physico-chemical properties of fluorinated Pt/ γ -Al₂O₃ catalysts prepared by treatment of γ -Al₂O₃ with HF followed by saturation with Pt, and by treatment of Pt/ γ -Al₂O₃ with HF or with a fluororganic compound were performed during decane isomerisation at 40 atm and 325-400°C. Dispersion of Pt increased in Pt/ γ -Al₂O₃ catalysts treated with F but their acidity was not effected. The Pt/ γ -Al₂O₃ catalysts treated with HF were most active.

Poison-Resistant Catalysts for the Simultaneous Control of Hydrocarbon, Carbon Monoxide, and Nitrogen Oxide Emissions

L. L. HEGEDUS, J. C. SUMMERS, J. C. SCHLATTER and K. BARON, *J. Catalysis*, 1979, **56**, (3), 321-335

The operation of Pt, Rh and Pd catalysts in automobile exhausts near the stoichiometric air:fuel ratio (A/F) was investigated. The extent of intrapellet diffusion limitations as a function of feedstream stoichiometry, poisoning mechanisms, the effects of Pt, Rh and Pd impregnation profiles on activity and poison resistance, and the effects of A/F oscillations on catalyst performance were examined. A pellet configuration containing an external shell of Pt and internal rings of Rh and Pd had improved poison resistance and light off characteristics. The addition of Ce improved the initial performance of the catalysts.

Rhodium Oxide Formation on the Surface of Pt-Rh Gauzes Used in the Catalytic Oxidation of Ammonia

M. PSZONICKA, *J. Catalysis*, 1979, **56**, (3), 472-474
90% Pt-Rh gauzes were used for NH₃ oxidation and then examined. The spent catalyst wires were found to be sheathed with a Rh oxide film of 8-10 μ m thickness, much thicker than previously observed, of three different layers. This oxide layer explains the decrease of catalyst activity.

Study of Irradiated Pd/ γ -Al₂O₃ Using the ESR Method

K. K. KUZEMBAEV, D. V. SOKOL'SKII, G. T. TUGEL'-BAEVA and L. M. KURASHVILI, *Dokl. Akad. Nauk S.S.S.R.*, 1979, **244**, (5), 1165-1168

Spectroscopic studies of the mechanism of activity of γ irradiated 0.5-10% Pd/Al₂O₃ catalysts were performed during reduction at 500°C. Sorption ability of the catalyst increased due to the formation of ionic centres of activity after irradiation. The formation of Pd⁺ ions in the catalysts was found to have a fundamental effect on their activity and selectivity.

Carbonylation of Olefins in the Presence of Supported Palladium Catalysts

A. L. LAPIDUS, S. D. PIROZHKOVA, A. R. SHARINOVA and K. V. PUZITSKII, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1979, (2), 371-376

Carbonylation of olefins on supported Pd/C, Pd/zeolites, Pd/0.8 CaNaY and Pd/SiO₂ catalysts was performed at various temperatures and pressures. Pd/C and Pd/zeolites catalysts containing 0.25-1% Pd were active and selective during carbonylation of ethylene, propylene and hexene-1 yielding carboxylic acid.

Activity of RhNaX Catalyst Promoted by Some Transition Metal Oxides in the Carbonylation of Methanol by Carbon Monoxide at Atmospheric Pressure

B. K. NEFEDOV, R. V. DZHAPARIDZE, O. G. MAMAEV and N. S. SERGEEVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1979, (2), 376-381

Studies of the effect of addition of Cr, Mn, Fe, Co, Ni and Cu on the catalytic activity and selectivity of Rh/zeolite NaX catalysts were performed during carbonylation of methanol by CO at atmospheric pressure. The formation of methyl acetate was observed at 210-240°C over catalysts promoted by Fe, Cu and Mn oxides with the selectivity of 92-100% and methanol conversion of >90%. The reaction was zero order for CO and CH₃OH and first order for CH₃I.

Versatile Polymer-Bound Hydrogenation Catalysts. Rhodium(I)-Catalyzed Hydrogenation

N. L. HOLY, *J. Org. Chem.*, 1979, **44**, (2), 239-243

The bidentate ligand anthranilic acid was anchored to polystyrene beads and its Rh(I) complex prepared. This polymer catalyst has exceptional hydrogenation activity, long-term stability, and insensitivity to poisoning. Hundreds of catalytic cycles per metal atom are demonstrated without substantial loss of activity. The Rh catalyst reduces various olefinic and aromatic hydrocarbons and carbonyl, nitrile and nitro functional groups. Catalytic activity depends on retention of beads, if fragmentation occurs the activity is diminished.

Adsorption Properties of Osmium Catalysts

G. D. ZAKUMBAEVA, D. KH. CHURINA and KH. G. OMASHEV, *Kinet. Kataliz*, 1979, **20**, (1), 136-141
Microcalorimetric, thermal desorption and electron microscopy studies of the H₂ adsorption on Os catalysts were performed. The adsorption temperature of H₂ increases over Os/Al₂O₃ catalysts compared to that over Os/black catalysts. The adsorption temperature of H₂ on Os catalysts was higher in the gaseous phase than in the liquid phase due to the chemisorption effect of H₂O.

Kinetics of the Methanation Reaction over Ru, Ru-Ni, Ru-Cu, and Ni Clusters in Zeolite Y

D. J. ELLIOTT and J. H. LUNSFORD, *J. Catalysis*, 1979, **57**, (1), 11-26

Clusters of Ru, Ni and Ru-Ni, and Ru-Cu bimetallics in a Y-type zeolite were investigated as catalysts for the reaction of CO with H₂ to form CH₄. Ni clusters had smaller turnover numbers than the Ru clusters. Adding Ru to the bimetallic clusters caused average particle size to decrease, and Ru-Ni zeolite turnover numbers decreased linearly as Ni was added.

Catalysis by a Ruthenium Complex Heterogenized in Faujasite-Type Zeolites: the Water Gas-Shift Reaction

J. J. VERDONCK, P. A. JACOBS and J. B. UYTTERHOEVEN, *J. Chem. Soc., Chem. Commun.*, 1979, (4), 181-182

The Ru(NH₃)₆³⁺ complex, exchanged as such in faujasite-type zeolites, can be converted into another kind of complex of the form [Ru(NH₃)_x(OH)_y(CO)_z]ⁿ⁺ with n < 3; this complex, which is stable up to 280°C, has no homogeneous equivalent. It is very active for the water gas shift reaction and it has greater activity than a Cu based low-temperature shift catalyst.

HOMOGENEOUS CATALYSIS

Selective Codimerization of Acetylenes and Allyl Halides Catalyzed by Palladium Complexes

K. KANEDA, T. UCHIYAMA, Y. FUJIWARA, T. IMANAKA and S. TERANISHI, *J. Org. Chem.*, 1979, **44**, (1), 55-63

The reaction of various acetylenes and allyl halides with Pd complexes selectively gives substituted 1,4-diene codimers. The PdX₂(PhCN)₂ complex is the most active catalyst. In contrast to substituted acetylenes, the reaction of acetylene and allyl halides gives a cotrimer besides codimers. The catalysis proceeds initially by acetylene inserting into a Pd-halogen bond and subsequently allyl halide inserts into a Pd-vinyl bond, followed by β-halogen elimination to give a codimer.

Hydrogenation Catalysts—Their Effect on Selectivity

J. I. GRAY and L. F. RUSSELL, *J. Am. Oil Chem. Soc.*, 1979, **56**, (1), 36-44

A review of the effects of heterogeneous (including the platinum group metals) and homogeneous catalysts including a mixture of chloroplatinic acid and tin (II) chloride, [Pt(PPh₃)₂(SnCl₃)H], RuCl₂(PPh₃)₃ in isopropylalcohol and other Pt and Pd catalysts, etc. on the hydrogenation of edible oils is discussed. (107 Refs.)

Effect of Partial Pressures of Hydrogen and Carbon Monoxide on Hydroformylation of Cyclododecene in the Presence of Hydrocarbonyl-tris(Triphenylphosphine) Rhodium (I)

V. M. USHAKOV, D. B. KAZARNOVSKAYA, L. L. KLINOVA and N. M. MALYGINA, *Neftekhimiya*, 1979, **19**, (1), 62-66

Studies of the effect of partial pressures of H₂ and CO on hydroformylation of cyclododecene in the presence of RhH(CO)(PPh₃)₃ with and without surplus PPh₃ at 11.5-120 atm and 100°C were performed. An increase in the reaction rate with an increase in H₂ and CO partial pressures when the Rh catalyst contained no surplus PPh₃ was observed. The rate of the hydroformylation reaction in the presence of the Rh catalyst containing excess PPh₃ depends only on the partial pressure of H₂ but not on the partial pressure of CO.

Infrared and Kinetic Study of Polymer-Bound Rhodium Cluster Catalysts for Hydrogenation

M. S. JARRELL, Ph.D. Thesis, University of Delaware, *Diss. Abstr. Int. B*, 1978, **39**, (6), 2900-2901
Polymers prepared by ligand exchange of poly(styrenedivinylbenzene) membranes containing bond PPh₂ groups and Rh₆(CO)₁₆ were found to be active cluster catalysts for the hydrogenation of ethylene and cyclohexene at 75°C and 1 atm. The kinetics of the cyclohexene hydrogenation were second order in cyclohexene partial pressure and one-half order in H₂ partial pressure.

GLASS TECHNOLOGY

Phase Separation and Crystallization in Amorphous Pd-Si-Sb

M. A. MARCUS, *J. Non-Cryst. Solids*, 1979, **30**, (3), 317-335

Replacing some of the Si in a Pd-Si-Sb glass with Sb makes it more resistant to crystallization than binary Pd-Si. This is shown by an increase in crystallisation temperature and a decrease in glass temperature as Sb content is increased. Alloys such as Pd₈₀₋₃Si₁₆₋₅Sb₃ may be quenched into amorphous rods up to 0.5 mm thick.

Drawing of Pd_{77.5}Cu₈Si_{16.5} Metallic Glass Wires

S. TAKAYAMA, *Mater. Sci. Engng.*, 1979, **38**, (1), 41-48

Wires of Pd_{77.5}Cu₈Si_{16.5} metallic glass were cold drawn using diamond dies. A total area reduction of up to about 93% was obtained after multiple passes through appropriate dies. Tensile tests conducted on both drawn and undrawn wires show fracture in planes that always deviate from the 45° maximum shear phase. The fracture stresses of drawn wires are found to be slightly increased; the macroscopic elongation to break increases considerably after cold drawing.

ELECTRICAL AND ELECTRONIC ENGINEERING

Contact Reactions in Pd/GaAs Junction

J. O. OLOWOLAFE, P. S. HO, H. J. HOVEL, J. E. LEWIS and J. M. WOODALL, *J. Appl. Phys.*, 1979, **50**, (2), 955-962

X-ray diffraction studies of the solid-state reaction of thin Pd films with GaAs substrates were performed. Fast diffusion and dissolution were observed for both As and Ga into Pd, which slowed down after the formation of distinct compound layers. These were identified as PdAs₂ and PdGa at 250°C, PdAs₂, PdGa and Pd₂Ga at 350°C and PdGa at 500°C.

NEW PATENTS

METALS AND ALLOYS

Palladium-Containing Alloys

INTERNATIONAL BUSINESS MACHINES CORP.

British Patent 1,539,686

Improved ferromagnetic alloys for use such as in bubble domain devices have the general formula Ni_{100-x-y}Fe_xPd_y, where x is 25-80 at. % and y is 25-65 at. %.

Nickel Glow Plug Alloys

NGK SPARK PLUG COMPANY LTD.

British Appl. 2,003,501

An alloy for use in a glow plug heater used in I.C.E., particularly diesel engines, contains Ni and between 0.05 and 2.0% of Y, Zr and/or Ru. The additions prevent grain coarsening and high temperature degradation without affecting the electrical resistance of the material.

Amorphous Alloys

SONY CORP.

British Appl. 2,003,772

A continuous-casting process for the manufacture of amorphous alloys is applicable to Fe-P-C alloys containing minor amounts of Ru, for instance Fe₇₈Ru₂P₁₃C₇.

TEMPERATURE MEASUREMENT

Appraisal of Interpolation Instruments for the International Practical Temperature Scale from 630.74 to 1064.43°C

L. A. GUILDNER, H. J. KOSTKOWSKI and J. P. EVANS, *Metrologia*, 1979, **15**, (1), 1-4

Two replacements for the Pt:10% Rh-Pt thermocouple currently being used as the standard temperature measuring device for IPTS-68 (International Practical Temperature Scale 1968) from 630°C to the gold point are considered. These are a high temperature Pt resistance thermometer (PRT) and a photoelectric spectral pyrometer (PSP). The PRT has many advantages over the PSP, including the fact that essential supporting technology is already widely known.

MEDICAL USES

Synthesis of Spin-Labelled Platinum Drugs and Interaction with Deoxyguanosine

A. MATHEW, B. BERGQUIST and J. ZIMBRICK, *J. Chem. Soc., Chem. Commun.*, 1979, (5), 222-224

Two novel spin-labelled *cis*-Pt drugs have been synthesised, and allowed to react with deoxyguanosine to form a spin-labelled complex. This spin-labelled Pt complex is useful for studying the interaction of Pt drugs with DNA.

Palladium-Containing Brazing Alloy

COMPTOIR LYON-ALEMAND LOUYOT

French Appl. 2,378,601

A "high-temperature" brazing alloy consists of 20-80% transition metal, such as Ni, Fe and/or Co, 0.5-15% Ge and 5-40% Pd.

CHEMICAL COMPOUNDS

Ruthenium and/or Iridium-Containing Pyrochlore Compound

EXXON RESEARCH & ENGINEERING CO.

U.S. Patent 4,129,525

Electrically conductive pyrochlore compounds have the formula A₂(B_{2-x}A_x)O_{7-y} where A is Pb and/or Bi, B is Ru and/or Ir, x is 0-1.0 and y is 0-1.0.

Adhesive Organopolysiloxanes

WACKER-CHEMIE G.M.B.H. *U.S. Patent* 4,130,707

The adhesive compounds contain vinyl-containing organopolysiloxanes, organopolysiloxanes containing Si-H atoms and Group VIII metal