

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Adsorption of Oxygen on Pt(III) and Its Reactivity to Hydrogen and Carbon Monoxide

D. R. MONROE and R. P. MERRILL, *J. Catal.*, 1980, **65**, (2), 461-469

O₂ adsorbed on Pt with an initial sticking coefficient of 0.048 ± 0.006 and linear adsorption kinetics. The surface saturated at an O₂:Pt ratio 1:4. The reactivity of adsorbed O₂ to H₂ and CO was determined from steady-state O₂ coverages for H₂-O₂ and CO-O₂ mixtures. From the reactivity data, which show reaction probabilities of 1.0 for CO and $\frac{1}{2}$ for H₂ over a wide range of O₂ coverages, it is concluded that both H₂ and CO are reactive in mobile states which may be precursors to adsorption.

Corrosion Resistant Alloys and the Prospects for Their Development

N. D. TOMASHOV, *Zashch. Met.*, 1981, **17**, (1), 16-33

The conditions for the production of high corrosion resistant alloys, such as stainless steel cathodically modified by Pt, Pd, Ru, Ir, Rh, Os or Au, are given. Some ways of obtaining new Ti based corrosion resistant alloys containing platinum group metals are reviewed. (47 Refs.)

Homogeneous Flow of Amorphous Pd_{77.5}Cu₆Si_{16.5}

A. I. TAUB and F. SPAEPEN, *Scr. Metall.*, 1980, **14**, (11), 1197-99

A study of the flow and relaxation behaviour of amorphous Pd_{77.5}Cu₆Si_{16.5} is presented. This system has relatively easy glass forming ability. The glass was initially heated at 500K under load for 3 days. Its flow was then monitored at different temperatures. On returning to 510K at the end of one temperature cycle its viscosity had increased by nearly 50%. The glass was also heated from 510 to 534K and its flow monitored. After the increase in temperature to 534K where it was held for 6 days while the temperature was then cycled, there was no significant change in the observed viscosity.

Solid Solution Decomposition in Fe-33 at.% Pd Single Crystal Alloy

G. V. IVANOVA, G. M. MAKAROVA, L. M. MAGAT and N. N. SHCHEGOLEVA, *Fiz. Met. Metalloved.*, 1980, **50**, (4), 788-794

Eutectic decomposition of a high temperature solid solution in monocrystalline Fe-33 at.% Pd alloys proceeded through three stages. In the first stage, α -Fe is formed whereas in the second, and third stages the formation of α - and γ -phases, and atomic ordering in the γ -phase occurred, respectively.

The Effect of Plastic Deformation of Amorphous Pd-Si Alloys on Their Thermal Properties

T. KULIK and H. MATYJA, *J. Mater. Sci.*, 1980, **15**, (12), 3169-3172

The effect of plastic deformation of metallic Pd_{100-x}Si_x (x = 16, 18, 20, 22 at.%) glasses on their thermal stability was examined. Plots of crystallisation temperature against x revealed that plastic deformation causes a decrease in the crystallisation temperature, and that the magnitude of changes in crystallisation temperature is a function of the chemical composition of the alloy.

Solid Solutions of RuO₂ and IrO₂

E. N. BALKO and C. R. DAVIDSON, *J. Inorg. Nucl. Chem.*, 1980, **42**, (12), 1778-1781

Studies were made of mutual solubility and morphological changes of the RuO₂ and IrO₂ system during thermal stabilisation. X-ray diffraction studies showed the presence of a single rutile phase (Ru_{1-x}Ir_x)O₂ over the entire range of composition. There was no evidence of a discrete IrO₂ or RuO₂ phase. The (Ru_{0.87}Ir_{0.13})O₂ system was studied for thermal stabilisation effects. Increasing temperature and increasing time at temperature causes a less fine porosity and leads to the loss of all defined pore structure below 500Å.

Superconductivity of New Ternary Borides with the LuRuB₂-Type Structure

H. C. KU and R. N. SHELTON, *Mater. Res. Bull.*, 1980, **15**, (10), 1441-1444

A new group of superconducting ternary borides, with a general formula MTB₂ (where M is Sc, Y or Lu and T is Ru or Os) has been found. The superconducting transition temperature range is from 1.3K for ScOsB₂ to 10.0K for LuRuB₂. Isomorphous compounds with M = Tb, Dy, Ho, Er or Tm order magnetically with critical temperatures in the range 2-46K. Superconductivity and magnetism are discussed with respect to analogous data on MT₂B₄ systems.

CHEMICAL COMPOUNDS

Luminescence of K₂Pt(SCN)₄ Single Crystals at High Pressure

I. HIDVEGI, W. TUSZYNSKI and G. G. GLIEMANN, *Chem. Phys. Lett.*, 1981, **77**, (3), 517-519

Single crystal emission spectra of K₂Pt(SCN)₄ were measured at 100K under pressures up to 57 kbar. The observed blue-shift of $\approx 10 \text{ cm}^{-1}/\text{kbar}$ was explained by a reduction of the central ion-ligand distance with pressure.

Co-ordination of Promethazine [10-[2-(Dimethyl)(amino)propyl]phenothiazine] Hydrochloride with Palladium(II): X-Ray Crystal Structure of a Trichloro-Palladium(II) Product

W. J. GEARY, N. J. MASON, L. A. NIXON and I. W. NOWELL, *J. Chem. Soc., Chem. Commun.*, 1980, (22), 1064-1065

The structure of a unique Pd complex, and the first crystallographic evidence for a co-ordinated phenothiazine drug is reported. K_2PdCl_4 reacts with promethazine hydrochloride giving a unique complex in which the protonated promethazine is S-bonded to Pd and takes up a "scorpion" conformation, thus facilitating electrostatic interaction between the quaternary N on the side chain and $PdCl_3$.

Luminescence of Some $Ru(bipy)_3^{2+}$ Compounds

D. M. KROL and G. BLASSE, *Chem. Phys. Lett.*, 1981, 77, (2), 253-256

The luminescence of $Zn_{0.999}Ru_{0.001}(bipy)_3SO_4$, $Ru(bipy)_3Br_2 \cdot 6H_2O$ and $Ru(bipy)_3(CIO_4)_2$ was studied in the range 4.2-300K. The luminescence of $Zn_{0.999}Ru_{0.001}(bipy)_3SO_4$ and $Ru(bipy)_3Br_2 \cdot 6H_2O$ were described with a single centre model. In $Ru(bipy)_3(CIO_4)_2$ energy transfer between different types of Ru complexes was observed.

ELECTROCHEMISTRY

Electrochemical Polymerization of Aromatic Amines. IR, XPS and PMT Study of Thin Film Formation on a Pt Electrode

A. VOLKOV, G. TOURILLON, P.-C. LACAZE and J.-E. DUBOIS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, 115, (2), 279-291

Films obtained by the anodic oxidation of various monosubstituted aromatic amines were grafted on Pt electrodes in a $CH_3CN-NaClO_4$ -pyridine medium. The studies showed that these films are organic polymers of emeraldine basic structure and are formed by the coupling of electrochemically formed ϕNH radicals with monomer. The films are homogeneous, very adherent, thermally stable and free of ionic impurities.

Electrochemical Oxidation of Aqueous Solutions of Ammonia on Platinum Group Metals

N. I. CHEKNOUSOVA, G. A. BOGDANOVSKII and G. D. VOVCHEENKO, *Vestn. Mosk. Univ., Khim.*, 1980, 21, (4), 389-390

Electrochemical oxidation studies of aqueous solutions of NH_3 on Pt/Pt, Rh/Pt and Pd/Pt electrodes were performed in a solution containing 0.1N NaOH + NH_3 . The adsorption of NH_3 occurred at the expense of dehydrogenation forming particles of the NH and NH_2 type. These difficult to oxidise intermediate products block the active centres and so drop the current on the polarised curves.

The A-C Response of Iridium Oxide Films

S. H. GLARUM and J. H. MARSHALL, *J. Electrochem. Soc.*, 1980, 127, (7), 1467-1474

The dependence of the a.c. response of IrO_2 films upon thickness, potential and pH was examined in H_2SO_4 and perchloric acid solutions. For concentrations >0.1 M the response function closely resembled that for an injection process, diffusively spreading from one interface throughout the film. The response time shifted by a factor of 10^5 with the potential drop across the film. A porous film model is suggested in which the response is determined by the mobility of reduced lattice sites, the diffusion coefficient being controlled by a H ion exchange current within the pores.

PHOTOCONVERSION

Photocatalytic Production of Hydrogen from Water and Texas Lignite by Use of a Platinised Titania Catalyst

S. SATO and J. M. WHITE, *Ind. Eng. Chem., Prod. Res. Dev.*, 1980, 19, (4), 542-544

Studies of the photocatalytic production of H_2 from H_2O and powdered Texas lignite containing 64% C, 17% O, 5% H, 1% N and 0.1% S were performed over platinised TiO_2 prepared by platinising (2wt.% Pt) by the photolysis at 55°C of a hexachloroplatinic acid solution containing suspended TiO_2 . The results obtained in the presence of H_2O vapour and u.v. light showed a catalytic reaction occurring at 23°C forming H_2 and CO_2 .

Heterogeneous Photocatalytic Oxidation of Hydrocarbons on Platinised TiO_2 Powders

I. IZUMI, W. W. DUNN, K. O. WILBOURN, F.-R. F. FAN and A. J. BARD, *J. Phys. Chem.*, 1980, 84, (24), 3207-3210

The photodecomposition of hydrocarbons in O_2 -containing solutions at platinised TiO_2 yields mostly CO_2 as the reaction product, with intermediate production of hydroxylated compounds. The hydrocarbons react readily with $\cdot OH$ to form the CO_2 . This hydrocarbon destruction may be useful in treating waste streams or spills.

Photochemical Cleavage of Water by Photocatalysis

E. BORGARELLO, J. KIWI, E. PELIZZETTI, M. VISCA and M. GRÄTZEL, *Nature (London)*, 1981, 289, (5794), 158-160

A bifunctional redox catalyst of RuO_2 and Pt co-supported on colloidal TiO_2 and sensitizer $Ru(bipy)_3^{2+}$, without any electron relay system, was found to exhibit extremely high activity in promoting water cleavage into H_2 and O_2 . Adsorption of the sensitizer at the TiO_2 particle-water interface and electron ejection into the TiO_2 conduction band are used to explain the observations. Exposure to u.v. radiation leads to efficient water cleavage in the absence of sensitizer.

Light-Induced Hydrogen Generation Catalysed by Ruthenium Dioxide

E. AMOYAL, P. KELLER and A. MORADPOUR, *J. Chem. Soc., Chem. Commun.*, 1980, (21), 1019-1020

RuO₂ which catalyses water oxidation to O₂ also efficiently catalyses H₂ formation from water in a model system containing Ru(2,2'-bipyridyl)₃²⁺, methyl viologen and EDTA. It has a higher efficiency above pH = 5 than previously observed with colloidal Pt.

Is There a Particle-Size Dependence for the Mediation by Colloidal Redox Catalysts of the Light-Induced Hydrogen Evolution from Water

P. KELLER and A. MORADPOUR, *J. Am. Chem. Soc.*, 1980, **102**, (24), 7193-7196

Particle size effects for the catalysis of light induced H₂ evolution from H₂O using the (Ru(bpy)₃²⁺/methyl viologen/EDTA) system were investigated with widely polydispersed colloidal Pt hydrosols, and samples with narrower size distributions obtained from the former hydrosols by centrifugation. The optimum values for the H₂ formation rates were similar for all catalysts studied, and for particles of sizes <100 Å and >1000 Å. No Pt size effects were seen.

Electron-Transfer Quenching of the Luminescent State of the Tris-(bipyridyl)ruthenium(II) Complex in Micellar Media

M. A. J. RODGERS and J. C. BECKER, *J. Phys. Chem.*, 1980, **84**, (21), 2762-2768

Observations of the orange luminescence from the excited state of Ru(bpy)₃²⁺ ions were used to follow its photoredox reaction with methyl (and other N-alkyl) viologen ions in aqueous and micellar media in heptane and cyclohexane. The luminescence always decayed exponentially, even when the quencher distribution about micelles should require non-exponential decay. Electron transfer and reverse transfer occurred very rapidly when the reactants were co-associated with the aggregates.

Quantum Yield and Electron-Transfer Reaction of the Lowest Excited State of Uranyl Ion

T. ROSENFELD-GRÜNWARD and J. RABANI, *J. Phys. Chem.*, 1980, **84**, (22), 2981-2985

The pulsed photoreduction of UO₂²⁺ in its ground state and lowest excited state at pH2 and in aqueous 2M H₃PO₄ was studied. Excited UO₂²⁺ was quenched by Ru tris(bipyridine) ions, Ru(bpy)₃²⁺ and Ru(bpy)₃³⁺ is formed, namely excited UO₂²⁺ is an electron-acceptor species. Excited Ru(bpy)₃²⁺ is quenched by UO₂²⁺ and again Ru(bpy)₃³⁺ is formed, UO₂²⁺ being an electron acceptor in its ground state. In steady-state experiments the absorption and emission spectra of the UO₂²⁺-Ru(bpy)₃²⁺ system remained unchanged after 2 × 10⁴ photoelectron transfer-back reaction cycles. This shows a relatively high stability which is required for a use in solar conversion and storage.

Ruthenium(II) Tris(bipyrazyl) Dication - A New Photocatalyst

R. J. CRUTCHLEY and A. B. P. LEVER, *J. Am. Chem. Soc.*, 1980, **102**, (23), 7128-7129

Ru(bipyrazyl)₃²⁺ was found to be a new and superior photosensitiser to Ru(bpy)₃²⁺ for the production of MV⁺ (methyl viologen). Ru(bpz)₃²⁺* is reductively quenched by triethanolamine forming Ru(bpz)₃⁺ which is oxidised by MV²⁺. When exposed to air Ru(bpz)₃⁺ is oxidised to reform Ru(bpz)₃²⁺.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Rhodium-Nickel Alloy

L. I. KADANER and G. N. IARMOLENKO, *Khim. Khim. Tekhnol.*, 1980, **23**, (10), 1277-1279

Studies of electrodeposition of Rh-Ni alloys containing 5-70% Rh were performed in an electrolyte of Rh + Ni sulphamates, pH 3.5-4.0 and current density of 1-4 A/dm² at 50°C. The conditions for obtaining dense finely crystallised deposits of 5-10 μm in thickness containing 10-30% Rh were reported. The studied physico-chemical and physico-mechanical properties of the alloys showed them suitable for use in electric contacts.

The Determination of Ruthenium in Plating Solutions and Electroplated Deposits

T. Y. KOMETANI and L. D. BLITZER, *Plat. Surf. Finish.*, 1980, **67**, (10), 57-60

Atomic absorption spectroscopy was developed for determining Ru in plating solutions and electrodeposits. The electrodeposits were made on sealed reed contacts. Methods for determining Ru thickness and cathode current efficiency and methods of monitoring K₃Ru₂NCl₈(H₂O)₂ plating solutions were also developed for process control.

LABORATORY APPARATUS AND TECHNIQUE

Gas Sensors Using Semiconductors. I. Sensitivity of Zinc Oxide Impregnated with Palladium Salts for Hydrogen

W. B. LI, H. YONEYAMA and H. TAMURA, *Denki Kagaku*, 1980, **48**, (10), 570-573

The change in the electrical conductance of ZnO in contact with H₂ gas pulse was studied at up to 120°C. Porous ZnO sinters impregnated with PdCl₂ solution followed by drying at 120°C showed high sensitivities for H₂. The same was true for porous samples prepared by mixing PdCl₂ with ZnO in a molar ratio of Pd : Zn = 3.7 × 10⁻⁴, followed by pressing into pellet form. The impregnation with PdBr₂ was less effective, and that with PdI₂ ineffective, suggesting that the ionicity of Pd salts is important for the appearance of the sensitivity.

HOMOGENEOUS CATALYSIS

Oxidative Dehydrogenation of Cyclohexene with Oxygen to Benzene Catalysed by a Palladium Cluster

A. S. BERENBLIUM, A. G. KNIZHNIK, S. L. MUND and I. I. MOISEEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, (12), 2700-2704

The mechanism of the oxidative dehydrogenation of cyclohexene with O₂ to benzene over a (PPh)₂Pd₅ cluster catalyst is presented. This included reversed complex formation of cyclohexene with (PPh)₂Pd₅, breaking the C-H bond of co-ordination cyclohexene, reaction of the formed complex and O₂ with the reaction products and reversed interaction of (PPh)₂Pd₅ with benzene.

Propene Hydroformylation with Rhodium Carbonyls and Triphenylphosphine. III. Kinetics of By-products Formation

G. MONTRASI, G. PAGANI, G. GREGORIO, P. C. D'ORO and A. ANDREETA, *Chim. Ind. (Milan)*, 1980, **62**, (10), 737-742

The formation of by-products from butyraldehydes during propene hydroformylation catalysed by Rh carbonyls and triphenylphosphine was studied by empirical correlations useful for both the choice of reaction design and operating conditions. The amount of heavy products was sharply dependent on temperature, aldehyde concentration and time, but did not depend on the presence of Rh complexes, PPh₃, OPPh₃ and reagents CO, H₂ and propene.

Hydrogenation of Carbon Monoxide in Methanol and Ethylene Glycol by Homogeneous Ruthenium Catalysts

B. D. DOMBEK, *J. Am. Chem. Soc.*, 1980, **102**, (22), 6857-6858

Studies of Ru catalysts at pressures of 340 atm and below and for homogeneous CO hydrogenation under moderate conditions, are presented. Carboxylic acids solvents had a remarkable promoter effect forming ethylene glycol besides methanol. Ru catalysts used included Ru₃(CO)₁₂.

HETEROGENEOUS CATALYSIS

Influence of the Chlorine Content on the Behaviour of Catalysts for n-Heptane Reforming

N. S. FIGOLI, M. R. SAD, J. N. BELTRAMINI, E. I. JABLONSKI and J. M. PARERA, *Ind. Eng. Chem., Prod. Res. Dev.*, 1980, **19**, (4), 545-551

The effect of Cl content on the activity, selectivity and stability of Pt/Al₂O₃ reforming catalysts was studied during n-heptane reforming. The activity and selectivity of the catalyst was well balanced for 0.8-0.9% Cl. At this concentration the coke formation was a minimum. The minimum is interpreted as being produced by a maximum in Pt to Al₂O₃ H₂ spillover, which eliminates coke precursors.

Germanium Modification of Platinum Catalysts for Hydrocarbon Aromatisation

B. M. PAVLIKHIN and M. E. LEVINEV, *Khim. Khim. Tekhnol.*, 1980, **23**, (10), 1260-1264

The addition of GeO₂ on the aromatisation properties of Pt/γ-Al₂O₃ catalysts increased dehydrocyclisation activity, stability and selectivity of the catalysts and decreased their coking. The optimal catalyst for n-heptane aromatisation was 0.5% Pt + 0.4% Ge + 1.2% Cl/γ-Al₂O₃ at 85-180°C. The reaction over this catalyst increased aromatic hydrocarbon yield.

The Reduction of Nitric Oxide by Hydrogen over Pt/γ-Al₂O₃ as a Function of Metal Loading

K. OTTO and H. C. YAO, *J. Catal.*, 1980, **66**, (1), 229-236

The reduction of NO by H₂ on Pt/γ-Al₂O₃ was evaluated as a function of Pt concentration between 273 and 373K. Product distribution and apparent activation energy remained constant as Pt atoms changed from a dispersed to a particulate phase of distinct clusters. Atoms in the particulate phase were more reactive per chemisorption site than dispersed atoms. Optimum efficiency was at ~5 wt.% Pt load.

Reaction of Allyl Alcohol with Triorganosilane in the Presence of Ions

T. N. ZASLAVSKAIA, V. O. REIKHSFELD, N. A. FILIPPOV and N. A. SHORNIK, *Zh. Obshch. Khim.*, 1980, **50**, (11), 2478-2482

Studies of the kinetics of the allyl alcohol reaction with triorganosilane in the presence of H₂PtCl₆ fixed on the anions were performed. The immobilised catalysts were highly active and stable during reaction of allyl alcohol with SiH₄ at 20-60°C and two parallel reactions occurred: hydrosilylation and dehydrocondensation. The reaction of allyl alcohol with tetramethyldisiloxane on immobilised catalyst produced a mixture of dehydrocondensation and hydrosilylation products.

Water Gas Shift Reaction with the Aid of Selenium/Platinum Catalyst

N. KAMBE, F. MORIMOTO, K. KONDO and N. SONODA, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, (12), 1007

A new catalyst for the water gas shift reaction is metallic Se/Pt black. Conversion of CO into CO₂ was at most 43% after 20h at 200°C. H₂Se/Pt black is also suitable for use as a catalyst.

Hydrogenation of CO₂ to CH₄ over Alumina-Supported Noble Metals

F. SOLYMOSI and A. ERDÖHELYI, *Magy. Kem. Foly.*, 1980, **86**, (10), 476-478

Catalytic hydrogenation of CO₂ was investigated over Al₂O₃ supported Pt, Pd, Ir, Ru, and Rh. The main hydrogenation product was CH₄ in all cases. Over Rh and Ru, hydrogenation of CO₂ occurred at the lowest temperature of 170-270°C. Specific activities decreased Ru > Rh > Pt > Ir > Pd.

Catalytic Properties of Pt-Ru Catalysis

R. GOMEZ, G. CORRO, G. DIAZ, A. MAUBERT and F. FIGUERAS, *Nouv. J. Chim.*, 1980, **4**, (11), 677-681

Pt-Ru/Al₂O₃ catalysts were prepared and the adsorptions of O₂ and CO on pre-adsorbed H were compared. The percentage of metal exposed was measured and surface enrichment in Pt was found for Ru rich samples. Turnover frequency for benzene hydrogenation increased 30 to 140 s⁻¹ on adding Pt to Ru, but decreased to 20 on Pt/Al₂O₃. However turnover frequency for cyclopentane hydrogenolysis only varied by a factor of 2.

Catalytic Hydrogenation of Graphite by Platinum, Iridium and Platinum-Iridium

R. T. K. BAKER, R. D. SHERWOOD and J. A. DUMESIC, *J. Catal.*, 1980, **66**, (1), 56-64

The interaction of Pt, Ir and Pt-Ir with graphite under H₂ was investigated as the temperature was increased. Three predominant phenomena were observed after initial nucleation of the metal particles. These were: the spread of metal particles over the graphite, renucleation of smaller metal particles on graphite and channelling these particles across the graphite due to catalytic C hydrogenation.

Isomerisation of n-Hexane on Pd-Zeolite Catalyst with Cations of Rare-Earth Elements

B. A. DADASHEV, S. E. MAMEDOV, A. A. SARYDZHANOV, S. M. MAMEDOVA and K. G. DZHAVADOVA, *Neftekhimiya*, 1980, **20**, (5), 655-658

Studies of the effect of rare earth metals on catalytic activity and acidity of 0.5wt.%Pd/Y-zeolite catalysts with molar ratio of SiO₂:Al₂O₃ = 5, were performed during n-hexane isomerisation. The activity and selectivity of the catalysts increased with the increase in numbers of centres with medium acidity. Replacing up to 5% of Ca cations by cations of rare earth metals in Pd/CaY led to an increase in numbers of centres with medium acidity. Replacing >5% of Ca cations increased numbers of strongly acidic centres, so decreasing catalyst activity and selectivity.

Selective Hydrogenation of Diene Hydrocarbons C₅ on the Membrane Catalyst Made from Pd-Ru Alloy

V. M. GRIAZNOV, M. M. ERMILOVA, L. D. GOGUA, N. V. OREKHOVA and L. S. MOROZOVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, (12), 2694-2699

Studies of the selective hydrogenation of diene hydrocarbons C₅ on the Pd-Ru alloy membrane catalyst showed that hydrogenation of 1,3-pentadiene and isoprene over Pd-9.8% Ru membrane catalyst yielded olefins without the formation of paraffin. During intake of H₂ through the membrane catalyst, the rate of hydrogenation of 1,3-pentadiene was higher than during its intake in the mixture with hydrocarbon vapours. Where the ratio of the partial pressures H₂:1,3-pentadiene > 1, the main product was *cis*-pentene-2. The intake of H₂ through the membrane catalyst yielded pentene-1.

Synthesis of Highly Dispersed Supported Metal Catalysts via Chemical Dissolution and Precipitation of Eutectic Alloys

C. S. BROOKS, G. S. GOLDEN and F. D. LEMKEY, *Surf. Technol.*, 1980, **11**, (5), 333-347

A new procedure for preparing highly dispersed supported metal catalysts is described. It involves the controlled solidification (unidirectional or vacuum atomisation) of eutectic or pro-eutectic alloys of Rh, Ni and Al followed by chemical dissolution, and acid precipitation of the Al. This gives a high surface area oxide matrix support for the Rh or Ni. Analysis revealed the Rh and Ni metal phases were in a highly dispersed state on the Al₂O₃ substrate. The Rh/Al₂O₃ and Ni/Al₂O₃ catalysts were evaluated for 3H₂-CO methanation and steam reformation of ethane. The initial methanation catalysis was superior to that of conventional support catalysts.

Effect of Strong Metal-Support Interactions on the Catalytic Reduction of NO by TiO₂-Supported Rhodium

V. RIVES-ARNAU and G. MUNUERA, *Appl. Surf. Sci.*, 1980, **6**, (2), 122-137

Rh/SiO₂ and Rh/TiO₂ catalysts were prepared by thermal decomposition in vacuo from RhCl(PPh₃)₃ impregnated supports. Adsorption of H₂, CO and NO and their activity for the reduction of NO by CO was studied. The same amount of CO was adsorbed on both samples, but the NO adsorbed twice as much on Rh/TiO₂ as on Rh/SiO₂. The activity for the reduction of NO by CO follows the same trend as NO adsorption. Infrared spectroscopy indicated a linear-type Rh-CO adsorption with a single band at 2070 cm⁻¹ for Rh/SiO₂ which shifts to 2020 cm⁻¹ on Rh/TiO₂, indicating a higher electron donor capacity. The enhanced reactivity of the Rh/TiO₂ sample may be due to strong metal-support interactions of Rh with Ti(III) ions.

Preparation of Polymer-Supported Isonitrile Complexes

J. A. S. HOWELL and M. BERRY, *J. Chem. Soc., Chem. Commun.*, 1980, (21), 1039-1040

The preparation of isonitrile ligands bound to polystyrene and SiO₂ supports is reported. These ligands react with [Rh(CO)₂Cl]₂ to yield [Rh(CO)₂Cl(polymeric support-NC)] complexes.

Evidence for an Oxygen Intermediate in the Catalytic Reduction of NO by CO on Rhodium Surfaces

L. H. DUBOIS, P. K. HANSMA and G. A. SOMORJAI, *J. Catal.*, 1980, **65**, (2), 318-327

ELS spectroscopy showed that NO and CO molecules associatively adsorb on Rh(331) single crystal surfaces at 300K. Chemisorbed NO readily dissociates on the surface upon heating to 450K. At 700K only O₂ is present on the catalyst surface, and when CO is added, gaseous CO₂ is formed. Similar results were obtained when O₂ was substituted for NO as a control, thus O₂ is a surface intermediate.

FUEL CELLS

Biochemical Combustion Cells

L. ONICIU and L. BEȘE, *Rev. Chim. (Bucharest)*, 1980, **31**, (10), 947-952

A short review of biochemical fuel cells is presented. Data regarding the exchange current densities and the transfer coefficients on smooth, platinised and palladised platinum and Pt incorporating Rh, determined by the electro-oxidation of glucose are given.

CHEMICAL TECHNOLOGY

Ion Flotation Studies and Separation Procedures for the Platinum Group Metals

D. M. DOWNEY, Ph.D. Thesis, Louisiana State Univ. and Agricultural and Mechanical Col., 1980, *Diss. Abstr. Int. B*, 1980, **41**, (4), 1357

Anionic chlorocomplexes of Pt(IV), Pd(II), Ir(IV), Ir(III), Rh(III) and Au(III) were floated from aqueous solutions with cationic surfactants of quaternary ammonium type RNR₃⁺Br. The flotation of each was determined. Most surfactants floated the platinum metals. A general flotation sequence Au(III) > Pd(II), Ir(IV), Pt(IV) > Ir(III) > Rh(III) was observed. Optimum ion flotation conditions were established for recovering the metals.

Reclamation of Palladium from Residual Wastes after Regeneration of Active Carbon Catalysts

M. ŠIROKI, *J. Less-Common Met.*, 1980, **75**, (1), P23-P24

Pd on active C used in catalytic hydrogenation was recovered by digesting the waste with boiling concentrated H₂SO₄, then converting it to Pd(II) sulphate which is dissolved. After dilution and removal of the insoluble portions by centrifugation and filtration, the acidic solution is heated in the presence of oxalic acid to yield a Pd mirror which precipitates. This contains only a few impurities.

NEW PATENTS

METALS AND ALLOYS

CoCrAl(Y) Coated Nickel-Based Superalloy

GENERAL ELECTRIC CO. *British Patent* 1,580,283

Ni-based superalloys coated with CoCrAl(Y) alloys containing less than 10% Al possess outstanding oxidation and corrosion resistance and firm adhesion between the two layers. The coating alloys contain 26-32% Cr, 3-9% Al, and up to 1% of Y, Pt, Rh, and/or other lanthanide metals.

TEMPERATURE MEASUREMENT

A Method for the Measurement of Temperature in a Flame with a Non-Screened Thermocouple

C. CASAROSA, F. DE BELLIS, E. LATROFA and L. PETARCA, *Riv. Combust.*, 1980, **34**, (7-8), 273-280

The true temperature of gases in a flame was determined from the experimental temperature transient of the hot junction of fine SiO₂-coated and uncoated Pt:Pt-13% Rh thermocouples. Two different procedures for elaborating the transient data have been developed on the assumption of instantaneous thermal equilibrium. The temperature values calculated by the procedures agree completely with the temperature measured optically.

MEDICAL USES

Hardening Reactions in a High-Gold Content Ceramo-Metal Alloy

R. M. GERMAN, *J. Dent. Res.*, 1980, **59**, (11), 1960-1965

An 85wt.%Au-5wt.%Pd-5wt.%Pt alloy was studied for its hardening reactions and the hardness developed during the porcelain firing cycle. Ordering of a submicron FePt-type intermetallic phase was responsible for observed ageing behaviour.

Age-Hardening of Dental Ag-Pd-Cu-Au Alloys

M. OHTA, T. SHIRAIISHI, K. HISATSUNE and M. YAMANE, *J. Dent. Res.*, 1980, **59**, (11), 1966-1971

Age-hardening mechanisms of dental Ag-Pd-Cu-Au alloys were investigated by electron microscopy. Hardening was due to the precipitation of the L1₀ type CuPd-ordered platelet in the grain interior and to the discontinuous precipitation at the grain boundary. The characteristics of age-hardening curves were determined by rates of continuous and discontinuous precipitation.

ELECTROCHEMISTRY

Electrodes for Diaphragm Cells

IMPERIAL CHEMICAL INDUSTRIES LTD.

British Patent 1,579,427

Anodes for brine cells are formed from two groups of finger electrodes, the planes of each group facing and diverging from each other, to give an improved current distribution. The electrodes are made from valve metals coated with platinum group metals or metal oxides typically Ru oxide-Ti oxide coated Ti.