

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Radiation Damage, Its Recovery and Platinum Lattice Location on Pt-Bombarded MgO

H. MATZKE, A. TUROS, P. RABETTE and O. MEYER, *J. Phys. C.*, 1981, **14**, (23), 3333-3344

MgO single crystals with $\langle 100 \rangle$ orientation, implanted with 30keV Pt ions to doses of 9×10^{15} and 8×10^{16} ions/cm² were analysed after bombardment and different annealing treatments. The crystals did not become amorphous, and the lattice disorder reached saturation after implantation with the lower dose. Damage recovery proceeded progressively with increasing temperature. The near-surface Pt gave the unexpected result that the critical angles of the impurity and of the host lattice were different. This was explained by coherent precipitation of Pt.

The Decomposition of Ammonia on the Flat(111) and Stepped(557) Platinum Crystal Surfaces

W. L. GUTHRIE, J. D. SOKOK and G. A. SOMORJAI, *Surf. Sci.*, 1981, **109**, (2), 390-418

NH₃ adsorption, desorption, and decomposition to H₂ and N₂ were studied on flat(111) and stepped(557) single crystal faces of Pt by molecular beam surface scattering. Both surfaces show significant adsorption with sticking coefficients ~ 1 . The stepped surface is 16 times more reactive for NH₃ decomposition than the flat surface. Kinetic parameters were determined from NH₃ decomposition on Pt(111). The mechanism of NH₃ decomposition on (557) was investigated.

The Au-Pt (Gold-Platinum) System

ANON, *Bull. Alloy Phase Diagrams*, 1981, **2**, (1), 66-70

Using cited references which give physical properties, the Au-Pt phase diagram has been constructed. Crystal structures for various ordered phases, equilibrium and metastable phase boundaries, lattice parameters, thermodynamics of the Au-Pt system and graphs of the compositional dependence of the lattice parameter of quenched disordered Au-Pt and miscibility gaps are presented. (45 Refs.)

The Phase Diagram of the Eu-Pt System and the Valence Behaviour of Europium and Ytterbium Intermetallies with Platinum

A. IANDELLI and A. PALENZONA, *J. Less-Common Met.*, 1981, **80**, (2), P71-P82

Differential phase, X-ray and metallographic studies of the binary phase diagram of the Eu-Pt system showed seven intermediate phases: Eu₉Pt, Eu₃Pt₂,

Eu₃Pt₂, Eu₃Pt₄, EuPt₂, Eu₂Pt₇, and EuPt₅. The valence behaviour in these phases together with the phases formed in the Yb-Pt system were studied by magnetic measurements and analysis of lattice dimensions, atomic volumes and ionic radii. The results showed that Eu and Yb can form intermetallic phases with Pt, containing divalent or trivalent ions.

SO₂ Adsorption on Rh(110) and Pt(110) Surfaces

R. C. KU and P. WYNBLATT, *Appl. Surf. Sci.*, 1981, **8**, (3), 250-259

SO₂ adsorption at low pressures ($\sim 6 \times 10^{-8}$ torr) on Rh(110) and Pt(110) surfaces was performed, and the S and O concentrations on the SO₂-saturated surfaces were assessed. Heats of desorption of SO₂ (or of its dissociation products on these surfaces) are $> \sim 225$ kJ/mole, indicating strong adsorption of SO₂ on both surfaces. On Rh the O associated with SO₂ can be titrated, but only $\sim 1/3$ of the O associated with SO₂ on Pt is accessible to titration. Differences between the results on the Rh(110) and Pt(110) surfaces are discussed.

Effect of Alloying Platinum on Structure Dislocation and High Temperature Creep

M. P. USIKOV, G. S. STEPANOVA and E. I. RYTVIN, *Izv. Akad. Nauk SSSR, Met.*, 1981, (5), 150-152

Studies were made of the effect of alloying Pt with 17 at.% Pd, Rh, Ir and Ru on dislocation structure and rate of creep during plastic deformation. The results showed that alloying Pt with Pd had practically no effect on structure dislocation with no increase in high temperature creep resistance. Alloying Pt with Rh, Ir, Ru (in order of increasing effect) substantially changed the structure dislocation with decrease in the rate of creep.

Successive Martensitic Transformations in Fe-Pd Alloys

R. OSHIMA, *Scr. Metall.*, 1981, **15**, (8), 829-833

A study of the relationship between the f.c.c. and b.c.c. martensites in Fe-Pd alloys is presented. Fe-Pd alloys containing 23.6-30.6 at.%Pd were studied, and two successive martensitic transformations were seen in an Fe-29.7 at.%Pd alloy in the temperature range 40 to -196°C. The first was a thermoelastic transition from f.c.c. martensitic to an f.c.c. martensite and the second was a non-thermoelastic type from the f.c.c. martensite to a b.c.c. martensite. The b.c.c. martensite was observed for alloys with 25 and 28.7 at.%Pd quenched from the austenite to room temperature. The b.c.c. morphology suggests that the austenite transformed to martensite, going through a f.c.c. structure.

Stabilization and Strengthening of Pd₈₀Si₂₀ Metallic Glass

J. MEGUSAR and N. J. GRANT, *Mater. Sci. Eng.*, 1981, **49**, (3), 275-283

The effect of composition on thermal and mechanical stability of Pd₈₀Si₂₀ glass was studied after adding B and Zr. The addition of B destabilises Pd₈₀Si₂₀. Adding 3 at.%B and 1.5 at.%Zr gives an amorphous structure with increased thermal stability (T_g increases by 73K). Stabilised (Pd₈₀Si₂₀)_{0.955}B_{3.0}Ar_{1.5} glass behaves substantially elastically, as does Pd₈₀Si₂₀ when tested under identical conditions at 433K and slow strain rates. Controlled decomposition of Pd₈₀Si₂₀ also has an effect on general yielding and fracture strength at elevated temperatures.

Equilibrium Silicides of Palladium

J. A. WYSOCKI and P. E. DUWEZ, *Metall. Trans. A*, 1981, **12**, (8), 1455-1460

The Pd-Si system was examined in the 13-25%Si range by X-ray diffraction, thermal analysis and metallography. The existence of compounds Pd₃Si, Pd₉Si₂ and Pd₃Si was confirmed. Pd₃Si is monoclinic, while the other two are orthorhombic. These compounds form defect structures with low symmetry and large unit cells. No evidence for the existence of Pd₄Si or Pd₉Si₄ was found.

Observation of the Coexistence of Superconductivity and Long-Range Magnetic Order in TmRh₄B₄

H. C. HAMAKER, H. B. MACKAY, M. S. TORIKACHVILI, L. D. WOOLF, M. B. MAPLE, W. ODOM and H. ROTT, *J. Low Temp. Phys.*, 1981, **44**, (5/6), 553-568

The a.c. electrical resistance, heat capacity, static magnetic susceptibility, thermal conductivity and linear thermal expansion coefficient were measured for superconducting TmRh₄B₄. The results indicate that the Tm³⁺ magnetic moments order at about 0.4K, while bulk superconductivity, which occurs at 9.8K, persists to temperatures below 60mK, which was the low temperature limit of the apparatus. Possibilities for the magnetic order are examined.

CHEMICAL COMPOUNDS

Formation of σ -Aryl Pt(II) Complexes in the Reaction of Aromatic Compounds with Pt(II) Salts and Their Oxidation by H₂PtCl₆

G. B. SHUL'PIN and G. V. NIZOVA, *Kinet. Katal.*, 1981, **22**, (4), 1061-1063

Heating of aromatic compounds (benzene, toluene, etc.) with Na₂PtCl₄ in the mixture CF₃COOH-H₂O resulted in the formation of a σ -aryl Pt(II) complex which could be converted in the presence of H₂PtCl₆ to the well-known anionic σ -aryl Pt(IV) complex. The discovered σ -formed Pt(II) appears to be the intermediate compound in the H-D bulk of aromatic hydrocarbons catalysed by Pt(II) salts during hydrocarbon oxidation in the presence of H₂PtCl₆.

Platinum(0) and Palladium(0) Carbenoid Insertion into Mercury Salts of Metal Carbonyls

V. I. SOKOLOV, A. A. MUSAEV, K. V. BASHILOV and O. A. REUTOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, (10), 2409-2411

The insertion of Pt(0) and Pd(0) into Hg salts of Mn, Re and Co carbonyls produced Pt and Pd compounds containing chains of various metals of the type: Re-Hg-Pt, Mn-Hg-Pd-Mn and Co-Hg-Pd-Co. Pd(IV) products stabilised by two electron-acceptors of metal carbonyl groups were prepared by double oxidative addition of Pd(PPh₃)₄ to BrHgMn(CO)₅.

Interaction of Tin Chloride Platinum Metal Complexes with Triphenylphosphine and Triphenylphosphin oxide

P. G. ANTONOV, IU. N. KUKUSHKIN, V. F. SHKREDOV and V. I. ANUFRIEV, *Khim. Khim. Tekhnol.*, 1981, **24**, (8), 941-945

Studies were made of the compounds prepared by interaction of [M(SnCl₃)₅Cl]^{m-} where M is Ru(II), Os(II), Rh(III) or Ir(III), with Ph₃P and Ph₃PO. The reaction with Ph₃PO yielded [M(SnCl₂OPPh₃)₅Cl]_{n-1} whereas with Ph₃P it yielded (PPh₃PH)_n[M(SnCl₃)₅Cl] which changed after heating in air at 460K to [M(SnCl₂OPPh₃)_n(SnCl₃)_{5-n}Cl]. Spectroscopic and electroconductivity measurements were made.

Electronic Absorption Spectra of Trivalent Rhodium in Chloride Melts

E. P. ALEXANDROV, B. D. VASIN, V. A. IVANOV and S. P. RASOPIN, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 1981, **23**, (5), 86-89

Systematic studies of absorption spectra of Rh containing chlorides (RhCl₃, Na₃[RhCl₆], etc.) were performed over a wide temperature range. Octahedral symmetry of RhCl₆³⁻ and spectroscopic parameters are determined. The use of the spectral method for controlling the Rh(III) concentration in dilute chloride solutions is suggested.

ELECTROCHEMISTRY

Polymer Films on Electrodes. 5. Electrochemistry and Chemiluminescence at Nafion-Coated Electrodes

I. RUBINSTEIN and A. J. BARD, *J. Am. Chem. Soc.*, 1981, **103**, (17), 5007-5013

The electrochemical behaviour of 10-15 μ m thick films of the cation-exchange Nafion on substrates of Pt-containing Ru(bpy)₃²⁺ (bpy = 2,2'-bipyridine), pyrolytic graphite or glassy C is described. The reaction of electrogenerated Ru(bpy)₃³⁺ with oxalate dissolved in the solution leads to production of Ru(bpy)₃^{2+*} and light emission. Information about the mechanism of excited-state production, with evidence for penetration of the polymer film by oxalate, and also possible quenching of Ru(bpy)₃^{2+*} by Ru(bpy)₃³⁺ is provided.

Oxidation State Changes of Palladium Oxide Films

J. GENESCA, M. RIUS DE RIEPEN and L. VICTORI, *Extended Abstracts, 160th Electrochemical Society Meeting, 81-2*, Denver, Colorado, Fall 1981, 1477-1478

Coloured films, whose thicknesses increased with polarisation time, were made on Pd electrodes by anodic treatment in HClO_4 and NaOH at potentials above that for O_2 evolution. The films were analysed. Films were golden or dark brown and the colour intensified as polarisation time increased. Under anodic oxidation at high potentials an oxide is formed indistinguishable from PdO_2 . The reduction of PdO_2 was observed when the oxidised electrode underwent a galvanostatic process. The coloured film vanished in air.

Effect of Ruthenium on the Anodic Behaviour of Ductile Chromium in Sulphuric Acid

N. D. TOMASHOV, G. P. CHERNOVA and E. N. USTINSKI, *Zashch. Met.*, 1981, 17, (4), 401-407

Studies of the corrosion and electrochemical behaviour of 0.1-0.4wt.% Ru-Cr alloy were performed in 40% H_2SO_4 at 65°C. It is shown that Ru inhibits active dissolution of the alloys by two mechanisms: by blockage (Ru is the solid solution) and by screening (Ru accumulates on the surface of the alloy).

Ruthenium-Based Mixed Oxides as Electrocatalysts for Oxygen Evolution in Acid Electrolytes

R. S. YEO, J. OREHOTSKY, W. VISSCHER and S. SRINIVASAN, *J. Electrochem. Soc.*, 1981, 128, (9), 1900-1904

Ru oxide, prepared by thermal decomposition, has the highest known initial electrocatalytic activity for O_2 evolution in acid electrolyte. However, the Ru oxide is unstable in the electrolyte and exhibits an increase in O overpotential with time, probably due to a chemical transformation of the oxide from a lower to a higher valence state. The Ru was stabilised by preparing mixed oxides with Ir and/or Ta, by thermal decomposition. Electrocatalytic activities for O evolutions were determined, and were improved for these mixed oxides.

The Increase of the Passivation Ability and Corrosion Resistance of Stainless Steels by Surface Alloying with Palladium

G. P. CHERNOVA, T. A. FEDOSEEVA, L. P. KORNENKO and N. D. TOMASHOV, *Zashch. Met.*, 1981, 17, (5), 513-519

Studies of electrochemical behaviour and corrosion resistance of steels 15X25T and 08X18H10T alloyed with Pd, by electrodeposition of thin layers of Pd from an electrolyte and subsequent diffusion, were performed in 20% H_2SO_4 at 100°C. It is shown that corrosion resistance of Pd surface alloyed steels was increased by several orders.

Dynamics of Light-Induced Water Cleavage in Colloidal Systems

D. DUONGHONG, E. BORGARELLO and M. GRÄTZEL, *J. Am. Chem. Soc.*, 1981, 103, (16), 4685-4690

A transparent TiO_2 sol (particle radius 200 Å) was produced and then loaded simultaneously with ultrafine Pt and RuO_2 deposits. These had extremely high activity as water decomposition catalysts. Band-gap excitation of TiO_2 generates H_2 with a quantum yield of 30 + 10%, and O_2 is produced stoichiometrically. When $\text{Ru}(\text{bpy})_3^{2+}$ or rhodamine B was used as sensitizer H_2O was decomposed by visible light. Adding MV^{2+} significantly increases H_2 yield.

Photoproduction of I_2 , Br_2 and Cl_2 on n-Semiconducting Powder

B. REICHMAN and C. E. BYVIK, *J. Phys. Chem.*, 1981, 85, (15), 2255-2258

Cl_2 , Br_2 and I_2 were photoproduced in O_2 -saturated aqueous solutions containing halide ions and platinised semiconducting n- TiO_2 powder. The platinised TiO_2 powders are considered as many short-circuited Pt-semiconductor electrodes on which the photoassisted reactions take place. All oxidation rates were increased or started by using Pt- TiO_2 powder and u.v. radiation. These reactions indicate that Pt- TiO_2 powders can lead to a net conversion of solar energy to storable chemical energy.

Palladium-Silver-Oxygen-Cesium Photocathode

X. HOU, W. SIBBETT and B. WEEKLEY, *Rev. Sci. Instrum.*, 1981, 52, (10), 1487-1489

A low surface-resistivity, semitransparent photocathode, consisting of a Pd-Ag-O-Cs layer, has been developed. It has near i.r. response which extends to cut-off wavelengths of $\sim 1.5 \mu\text{m}$. The processing scheme and its effect on the photoemission characteristics of this photocathode are described.

Photo-Oxidation of Water on the Surface of Hectorite Using *trans*-Diaquabis-(2,2'-bipyridine) ruthenium(2+) as Catalyst

H. NIJS, M. CRUZ, J. FRIPIAT and H. VAN DAMME, *J. Chem. Soc., Chem. Commun.*, 1981, (20), 1026-1027

trans- $\text{Ru}(\text{bpy})_2(\text{H}_2\text{O})_2^{2+}$ (bpy = 2,2'-bipyridine) was shown to be an efficient redox catalyst for the oxidation of H_2O , and enabled a catalytic water photo-oxidation system within an adsorbed layer to be constructed.

Two-Way Split Generates Hydrogen More Efficiently

New Sci., 1981, 92, (1274), 100

A practical H_2 generating system from sun-powered H_2O -splitting is based on particles of the semiconductor CdS and the catalyst RuO_2 . The particles split H_2O to give H_2 and OH^- , forming H_2O again and S. The new process could convert the H_2S into useful H_2 fuel and a marketable S product.

ELECTRODEPOSITION AND SURFACE COATING

Preparation and Surface Characteristics of Platinized Antimony-Doped Tin Oxide Films

G. B. HOFLUND, F. F. COX and H. A. LAITINEN, *Thin Solid Films*, 1981, **83**, (2), 261-265

Thin Sb-doped Sn oxide films were platinised electrochemically from a $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution. Spectroscopic studies of the surface composition and electron structure showed that Pt appears predominantly as Pt^0 with a small amount of $\text{Pt}(\text{OH})_2$, whereas the Sn was predominantly SnO_2 with some SnO present.

Palladium-Nickel: An Alternative to Gold

K. SCHULZE-BERGE, *Galvanotechnik*, 1981, **72**, (9), 932-936

Pd-Ni alloy electrodeposited coatings were compared to Au electrodeposited coatings. Organic additives have been developed for the Pd-Ni deposits; making them fully bright and only needing to be levelled. Technical properties for Pd-Ni coatings are similar to those for Au.

Electrolytic Rhodium Deposition

M. BRANIK and F. KUMMER, *Galvanotechnik*, 1981, **72**, (11), 1175-1180

Commercially available Rh electrolytes used for decorative and technical applications have a sulphate or phosphate base. The relationships between deposition parameters and their influence on the Rh deposits are discussed. A new method for measuring the lightness of colour of the Rh deposit used in decorative applications is proposed. Good quality electrolytes have no effect with regard to the lightness of the Rh deposits.

LABORATORY APPARATUS AND TECHNIQUE

Microsampling Technique in Flame Atomic Absorption. Application in Preparation of Platinum-Ruthenium Alumina Catalysts

H. URVAIN and N. MARTIN, *At. Spectrosc.*, 1981, **2**, (4), 127-129

Microsamples of catalysts prepared by impregnating Al_2O_3 pellets by an active-element species, such as PtCl_6H_2 or RuCl_6H_2 in HCl acid media, were drawn from the solution and the decreases in Pt and Ru concentrations were determined as a function of time. The analysis has advantages over continuous sampling methods in that very small samples, 100 μl , can be withdrawn, several elements can be determined from the same sample, or a wide working range (50-2000 mg/l) can be used with reproducible sensitivities and no memory effects. The tolerance for solutions with high salt content and residual solid particles is improved without clogging.

HETEROGENEOUS CATALYSIS

Platinum on Carbon-Fibre Paper Catalysts for Methanol Electro-Oxidation. Part 2. Role of Platinum Surface Area in Determining Catalytic Activity for Methanol and Formic-Acid Electro-Oxidation

B. D. MCNICOL, D. ATTWOOD and R. T. SHORT, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, (9), 2017-2028

The intrinsic catalytic activity of Pt supported on pre-oxidised C-fibre paper depended on the Pt surface area for both methanol and formic acid electro-oxidation. The activity for formic acid oxidation decreases as the Pt surface area decreases, whereas that of methanol initially increases then decreases with decreasing Pt area, thus producing a maximum in the activity/surface area relationship. The effects are explained in terms of the mode of adsorption of the fuels on Pt and their oxidation mechanism.

Deuterium Exchange between Water Mists and Hydrogen Gas in a Hydrophobic Catalyst Bed

Y. ASAKURA, H. TSUCHIYA, H. YUSA and S. MATSUDA, *Nucl. Sci. Eng.*, 1981, **79**, (1), 49-55

The deuterium exchange reaction between D-enriched water mist and H_2 was studied with a hydrophobic Pt/porous Teflon supported catalyst. The water mists and H_2 moved downward co-currently, through the catalyst bed. This new method improved the poor contact efficiency between water and H_2 gas in the catalyst bed. The reaction rate increased an order of magnitude over the conventional method where liquid water and H_2 react countercurrently. The increased rate was due to the increase of D transfer at the water/gas interface. The reaction rate determining process changed with H_2 gas flow.

Effect of Platinum Concentration in Pt/ Al_2O_3 Catalysts on Dehydrogenation Reaction of High Molecular Weight n-Paraffins

E. A. TIMOFEEVA, A. P. TIUNAEV and G. V. ISAGULIANTS, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1981, (9), 2067-2071

Studies of the effect of concentration of 0.05-1.0% Pt on the dispersity of Pt/ Al_2O_3 catalysts with and without 1% Li were performed during n-dodecane dehydrogenation at 480°C under H_2 pressure. The increase in Pt concentration in the catalysts was followed by a decrease in their dispersity. The selectivity of the catalysts was not affected by Pt concentration but depended on the Li present. Catalysts containing 0.25-1.00% Pt had similar specific activity during n-dodecane dehydrogenation. The catalysts containing 0.05% Pt showed higher specific activity than catalysts with higher Pt concentrations.

Influence of Temperature and Thermal Processing Atmosphere on Properties of Platinum Catalysts Used for Complete Oxidation

S. KULAK and J. WRZYSZCZ, *Przem. Chem.*, 1981, **66**, (6), 326-328

Pt/Al₂O₃ catalysts were heated in oxidising and reducing atmospheres, in CO₂ and combustion gases at up to 1300K. The heating resulted in a decrease of Pt dispersion in the catalyst, dependant on the atmosphere. An increase of catalyst activity was observed during the complete oxidation of hydrocarbons after heating in combustion gases and CO₂, as well as after heating in air or H₂.

Studies on the Isomerization of n-Pentane on γ -Al₂O₃ Supported Pt Catalyst Modified by Adsorbed Bi and Pd

M. HEGEDUS, S. GOBLOS, S. SZABO, D. MOGER and F. NAGY, *Magy. Kem. Foly.*, 1981, **87**, (7), 324-328

The isomerisation of n-pentane on Bi-Pt/ γ -Al₂O₃ and Pd-Pt/ γ -Al₂O₃ catalysts was investigated by pulse and continuous flow reactors. The activity of the catalysts was smaller than that of the base Pt/ γ -Al₂O₃ catalyst. The selectivity of Bi-Pt/Al₂O₃ for isomerisation was higher than that of the other two catalysts investigated. The behaviour of the Bi-Pt catalyst gradually approaches that of the base catalyst. The selectivity and stability for the Pd-Pt catalyst were the smallest, but the extent of cracking on this catalyst was larger than that of the other two.

The Effects of the Nature and the Structure of Platinum Group Catalysts on Their Poisoning and Regeneration

A. A. SUIYAGINA and G. D. VOVCHEKNO, *Surf. Technol.*, 1981, **13**, (3), 257-264

The poisoning of Pt, Pd, Rh, Os, Ru and Rh-Os alloys by Hg, S and Pb was investigated. The capacity for being poisoned depends not only on the nature of the catalyst, but also on its structure and surface morphology. Chemical compounds are formed when Pt, Pd and Rh catalysts are poisoned, but not for Os and Ru. Different types of interactions and surface distribution of poison were seen for poisoning of Pt and Rh with S and Pb. Electrochemical methods were found for regeneration of the poisoned catalysts.

Hydrogenation of Coal Oil from Coal from the Saar to Petroleum

T. JACOBSEN and E. GALLEI, *Erdoel Kohle Erdgas Petrochem.*, 1981, **34**, (10), 447-450

Hydrogenation of coal oil by liquefaction of coal is described. The three stages of raffination, hydrocracking and reforming are explained. Because the coal oil has a high N content raffination is operated at higher pressures than refining the petroleum fraction, to achieve the high level of N in the middle oil fraction which is needed for hydrocracking feedstocks (5-10 ppm). Zeolite

supported noble metals were used at the hydrocracking stage, Pt-Re is mentioned. For reforming, the catalyst and operating conditions are similar to those for petroleum naphtha reforming. The product is gasoline with premium gasoline quality without Pb additives. It has higher specific gravity than commercial gasoline.

The Effect of SMSI (Strong Metal-Support Interaction) Behavior on CO Adsorption and Hydrogenation on Pd Catalysts. I. IR Spectra of Adsorbed CO Prior to and during Reaction Conditions. II. Kinetic Behavior in the Methanation Reaction

M. A. VANNICE, S.-Y. WANG and S. H. MOON, *J. Catal.*, 1981, **71**, (1), 152-166, 167-174

Infrared spectra and kinetic data were measured under steady-state conditions on Pd/support catalysts. The i.r. spectra of CO adsorbed on Pd/TiO₂, Pd/SiO₂-Al₂O₃, Pd/Al₂O₃ and Pd/SiO₂ were obtained. H₂ reduced the CO band intensities for Pd/TiO₂ (SMSI) catalyst, but under reaction conditions no CO bands were detected, while all other Pd catalysts had observable i.r. bands. Only a small fraction of the Pd surface atoms are active sites and the large CO surface concentrations detected by i.r. are not directly involved in the rate-determining step for methanation. Specific activity of Pd in methanation can show a 200-fold variation depending upon the support used. But CH₄ turnover frequencies were independent of Pd crystallite size. Turnover numbers increase Pd/SiO₂ \ll Pd/SiO₂-Al₂O₃, Pd/Al₂O₃ \approx Pd/TiO₂ < Pd/TiO₂ (SMSI).

Kinetics of Hydrogenation of Benzene on Deposited Palladium Catalysts

O. V. BAIDUS, T. N. MASLIANSKII, V. P. GIL'CHENOK and A. C. MOSHKEVICH, *Neftekhimiya*, 1981, **21**, (4), 508-514

Studies of benzene hydrogenation were performed on deposited Pd catalysts supported on Al₂O₃-SiO₂, γ -Al₂O₃ and γ -Al₂O₃ + A (A is an additive which increases the acidity of the support) at 190-270°C and 2.0-4.0 MPa. The order of the reaction near zero did not depend on the nature of the supports, whereas the order of the reaction in H₂ did depend on the nature of the support, changing in the range 1.0 to 1.6. The values for the apparent activation energy are similar and are between 59.6-65.0 kJ/mole.

Effects of Metal-Support Interactions on the Synthesis of Methanol over Palladium

YA. A. RYNDIN, R. F. HICKS, A. T. BELL and YU. I. YERMAKOV, *J. Catal.*, 1981, **70**, (2), 287-297

The synthesis of methanol and other products from CO and H₂ was studied over Pd catalysts prepared by adsorption of Pd(π -C₃H₅) on various supports and Pd/SiO₂ prepared from PdCl₂ and Pd black. Both the activity and selectivity of Pd were affected strongly by the support and composition of the Pd precursor. The specific activity for methanol synthesis

decreased in order Pd/LaO₃ » Pd/SiO₂ (derived from PdCl₂) > Pd/ZrO₃ > PdZnO ≈ Pd/MgO > PdTiO₂ > Pd/Al₂O₃ ≈ Pd/SiO₂ (derived from Pd(π -C₃H₅)₂) » Pd black. Pd/TiO₂ had highest specific activity for hydrocarbon synthesis, and the order of activity for this and for dimethyl ether production were found.

Supported Liquid Phase Hydroformylation Catalysts Containing Rhodium and Triphenylphosphine. Effects of Additional Solvents and Kinetics

J. HJORTKJAER, M. S. SCURRELL, P. SIMONSEN and H. SVENDSEN, *J. Mol. Catal.*, 1981, **12**, (2), 179-195

Catalysts containing HRh(CO)(PPh₃)₃ and excess PPh₃ supported on SiO₂ show some modification in behaviour during hydroformylation of propene if additional solvents are present. The effect of PPh₃ loading on the kinetic parameters is discussed in terms of an increasing tendency for PPh₃ to become highly mobile at sufficiently high loadings.

Improvement of the Catalytic Performance of a Ruthenium Powder in Ammonia Synthesis by the Use of a Cyclic Procedure

G. RAMBEAU and H. AMARIGLIO, *Appl. Catal.*, 1981, **1**, (5), 291-302

H₂ inhibits the catalytic activity of Ru in NH₃ synthesis. Lowering the H₂ content lowers the temperature at which the reaction is detectable, but does not allow a high NH₃ production rate. This is avoided by alternate N₂ and H₂ feeds. The improvement is higher the larger the catalyst area. With 1 m² active area the average rate of production is eight times higher than the best steady rate of production, and the increase is ~ 10³ at 200°C, if the average rate is compared with the steady state rate corresponding to the stoichiometric mixture. Ru dispersed catalysts at only 300°C and atmospheric pressure could obtain the same industrial performance as Fe catalysts.

Ammonia Synthesis as a Catalytic Probe of Supported Ruthenium Catalysts: the Role of the Support and the Effect of Chlorine

W. K. SHIFLETT and J. A. DUMESIC, *Ind. Eng. Chem. Fundam.*, 1981, **20**, (3), 246-250

The effects of the support and the presence of Cl⁻ on the properties of highly dispersed Ru(γ)-Al₂O₃ and Ru/SiO₂ catalysts were studied during NH₃ synthesis. The rate of NH₃ synthesis was inhibited by NH₃ more strongly on Ru/Al₂O₃ than on Ru/SiO₂. This indicates that the Ru is electron deficient when supported on Al₂O₃ compared to Ru on SiO₂; Cl as an Al₂O₃ support constituent suppressed the synthesis rate, increasing both the apparent activation energy and the inhibiting effect of NH₃ on the reaction rate. The results were consistent with an additional decrease in electron density on the Al₂O₃-supported Ru induced by the presence of chloride on the support.

HOMOGENEOUS CATALYSIS

Terpene Amine Synthesis via Palladium-Catalyzed Isoprene Telomerization with Ammonia

W. KEIM and M. RÖPER, *J. Org. Chem.*, 1981, **46**, (18), 3702-3707

Isoprene and dry NH₃ were converted into a mixture of primary, secondary and tertiary terpene amines via homogeneous catalysis with Pd acetylacetonate and tributyl phosphite, which had the best activities and selectivities for telomerisation. Seven amines were isolated and characterised.

Hydrogenation and Isomerization of Olefins on Heterogenized Rhodium Complexes

T. UEMATSU, T. KAWAKAMI, F. SAITHO, M. MIURA and H. HASHIMOTO, *J. Mol. Catal.*, 1981, **12**, (1), 11-26

The catalytic properties of polymer-bound complexes RhCl(PPh₃)₃, bound to three types of phosphinated polystyrene, were studied during hydrogenation and isomerisation of olefins in the gas-solid heterogeneous system. The results were compared with those for the complex on SiO₂ and those in the homogeneous system. The selectivity for the isomerisation of butene was increased over supported catalysts. Catalytic activity for the hydrogenation was increased by anchoring on the rigid polymer when loading on SiO₂, while it decreased remarkably by anchoring on the inner phosphine groups of the copolymer. The results are explained in terms of the availability of the sites, the structure of the actual species, and the carrier effects caused by binding.

Investigation of Unique Metal Complexes Produced with Polystyrene-2,2'-Bipyridine and Several Hydrogenation Catalysts Derived from this Copolymer

R. S. DRAGO, E. D. NYBERG and A. G. EL AMMA, *Inorg. Chem.*, 1981, **20**, (8), 2461-2466

Cleavage reactions between PS-bound pyridine (py) and 2,2'-bipyridine (bpy) ligands and dimers [Rh(X)(CO)Cl₂], [P], (X = CO, (C₆H₅)₃P or (tol)₃P) were studied. [P]-py cleavages produced products analogous to those found homogeneously and [P]-bpy reactions formed several metal complexes not found in solution. The supported Rh systems [P]-bpy Rh, [P]-bpyPdCl₂ and [P]-bpyPtCl₂ were investigated as hydrogenation catalysts. The [P]-bpy PtCl₂ system is an active catalyst for hydrogenations on substrates.

A Greatly Improved Procedure for Ruthenium Tetraoxide Catalyzed Oxidations for Organic Compounds

P. H. J. CARLSEN, T. KATSUKI, V. S. MARTIN and K. B. SHARPLESS, *J. Org. Chem.*, 1981, **46**, (19), 3936-3938

The addition of acetonitrile to the traditional CCl₄/H₂O system for RuO₄ catalysed oxidations leads to a greatly improved system. Some applications to olefins, alcohols, aromatic rings and others are described.

Homogeneous Hydrogenation of Carbon Monoxide by Iodide-Promoted Ruthenium Catalysts

B. D. DOMBEK, *182nd Am. Chem. Soc. Natl. Meeting*, New York, Aug. 23-28, 1981

A new type of homogeneous Ru catalyst has been developed for hydrogenating CO to methanol, ethanol and free ethylene glycol, where glycol is the major product. The system has basic promoters, such as ionic iodide promoters and polar solvents. Typical promoters include NaI, KI or bis(tri-phenylphosphine)iminium iodide and typical solvents are N-methylpyrrolidone, sulfolane and 18-crown-6. The new system has activity, substantially higher than known Ru catalysts.

Triphenylphosphine Ruthenium(II) Complex with Tin(II) Trichloride and Its Catalytic Properties

P. G. ANTONOV, N. V. BORUNOVA, I. N. KUKUSHKIN and L. KH. FRIEDLIN, *Khim. Khim. Tekhnol.*, 1981, **24**, (6), 663-665

The prepared complex catalyst $[\text{Ru}(\text{PPh}_3)_2(\text{SnCl}_3)\text{Cl}]$ was found to be active during hydrogenation of unsaturated hydrocarbons but was inactive during isomerisation. The rate of olefin and diene hydrogenation was very high. The activity of the catalyst was 4-5 fold higher than that of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$. The presence of strongly *trans*-orientating SnCl_3 ligands in the sample increased its catalytic activity and also the stereospecificity of diene hydrogenation.

NEW PATENTS

METALS AND ALLOYS

Platinum-Rhodium Alloys

OWENS-CORNING FIBERGLASS CORP.

British Patent 1,597,659

New alloys having low creep rates, suitable for glass fibre production bushings, contain 10-40% Rh, 0.001-0.01% B, 0.015-1.25% Zr, Mg, Y, La, Ti, Hf, Nb and/or Ta and the remainder Pt.

Electroplated Silver-Palladium Contact Materials

BELL TELEPHONE LABORATORIES INC.

U.S. Patent 4,269,671

Pd-Ag alloys, plated from baths containing Li chloride and other Group IA or IIA metal halides, have improved corrosion resistance over similar wrought alloys, allowing larger amounts of Ag to be used in the alloys. Plated Pd-Ag alloys may be used in applications where Au is the normal contact material and the corrosion of the underlying base metal substrate by the plating solution is avoided by Au-flashing the substrate prior to plating.

ELECTRICAL AND ELECTRONIC ENGINEERING

Contact Resistance Measurements of Platinum-Silicide and Chromium Contacts to Highly Doped n and p Silicon

G. BOBERG, L. STOLT, P. A. TOVE and H. NORDE, *Phys. Scr.*, 1981, **24**, (2), 405-407

A comparison of contact resistivity for Pt silicide contacts and sputtered Cr contacts on heavily doped n- and p-Si was made by a method suitable for contacts of a highly conductive surface layer on a less conductive base material. The results showed less spreading and lower specific contact resistance for PtSi contacts on both n⁺ and p⁺-Si, than for Cr contacts which with p⁺ showed non-ohmic behaviour.

Palladium with a Thin Gold Layer as a Sliding Contact Material

T. SATO, Y. MATSUI, M. OKADA, K. MURAKAWA and Z. HENMI, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1981, **CHMT-4**, (1), 10-14

Two types of electroplated Pd contacts, one with a thin Au layer, were evaluated as substitutes for Au. The Au deposit properties were as good as acid hard gold deposits. Friction coefficients were 0.4-0.7 for electroplated Pt and 0.15-0.3 for electroplated Au. The multilayer contact had friction properties similar to those of Au contacts, and the Au acted as a lubricant between the harder Pd electroplates. Pd had good results in 1000-hour corrosion tests in an 80%N₂-20%O₂ atmosphere containing 10 ppm H₂S.

ELECTROCHEMISTRY

Water Heater Non-Sacrificial Anodes

RHEEM INTERNATIONAL INC. *British Patent* 1,596,839

A water heater tank is protected from corrosion by means of an impressed current supplied from a Ti-Pt non-sacrificial anode and a Pt or Pd water recombination catalyst fitted at the top of the tank.

Photogalvanic Production of Hydrogen

TOKYO INSTITUTE OF TECHNOLOGY

British Appl. 2,071,154 A

H₂ is produced by irradiating an aqueous solution of alkylammonium salt of polytungstic or polyvanadic acid in a photogalvanic cell having Pt, Pd or W electrodes.

Catalytic Electrode

GENERAL ELECTRIC CO.

British Appl. 2,071,157 A

The use of Ru oxide electrodes for the liberation of halogens by the electrolysis of aqueous halide solutions has not been successful because of attack by the acidic electrolyte. Now, by stabilising the oxides by a