

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Influence of Certain Alloying Elements on the Creep Activation Energy of Platinum

N. YUANTRIO and W. YONGLI, *Acta Metall. Sin.*, 1979, **15**, (4), 548-556

The influence of certain alloying elements, such as Rh, Au, Mo, W, Zr and Hf on the activation energy of creep of Pt alloys at high temperatures was investigated. The presence of Rh, Zr and/or Hf in the alloys may cause an increment in the activation energy of creep, but W, Mo and/or Au may decrease them. Based on the behaviour of these alloying elements, the mechanism of the creep rupture of the Pt alloys is discussed.

Ordering Kinetics and Domain Structure Formation Mechanism during Isothermal Tempering of Quenched Ni-Pt Alloy

I. N. SAKHANSKAYA, E. I. TEYTEL, N. I. TIMOFFEV, YU. P. DENISOV and P. N. SYUTKIN, *Metalloved. Term. Obrab. Met.*, 1980, **49**, (2), 363-371

X-ray microscopic studies of the ordering kinetics and domain structure formation mechanism were performed at 550°C in Ni-Pt quenched to 800°C. It is shown that the relaxation of internal tension which arises in the grains of the alloy during transition can be accomplished by a number of methods. The effect of the structural changes on the electroresistance of the alloys during ordering is determined.

Segregation and Increased Dopant Solubility in Pt-Implanted and Laser-Annealed Si Layers

A. G. CULLIS, H. C. WEBER, J. M. POATE and A. L. SIMONS, *Appl. Phys. Lett.*, 1980, **36**, (4), 320-322

Q-switched laser irradiation was used to melt and recrystallise amorphous Pt-implanted layers formed on the surface of Si single crystals. While the Pt segregated to the surfaces, the final impurity depth distribution depended on substrate temperature in the range 77-620K. This is correlated to calculations of changing melt dwell times and resolidification velocities. The non-uniform lateral distribution of the segregated Pt at the Si surface may be controlled by constitutional supercooling occurring in the resolidifying melt.

Influence of Yttrium Additions on the Properties of Platinum

K. SCHWARZ, *Neue Huette*, 1980, **25**, (4), 145-148

Adding Y to Pt gives desirable property changes to high temperature deposits. Grain growth is reduced and time stability and creep strength increase. With an Y content of 0.04% at 1200°C the $\sigma_{B/1000h}$ value is larger than for Pt-20Rh. For high temperature

working in air internal oxidation forms Y oxide particles. For an Y content of ~0.08% the time breaking elongation is not perceptibly reduced. Thus Pt-Y alloys are promising materials for glass technology.

Growth Rates for Pt₂Si and PtSi Formation under UHV and Controlled Impurity Atmospheres

C. A. CRIDER and J. M. POATE, *Appl. Phys. Lett.*, 1980, **36**, (6), 417-419

Pt silicides were prepared by depositing Pt thin films under UHV and controlled impurity atmospheres, including various O₂ partial pressures. The substrates and silicide films were analysed. Growth of the silicide films was observed under UHV in real time. The growth rates for Pt₂Si and PtSi formation were observed to be one to three orders of magnitude higher than previously obtained values. Increasing O₂ partial pressure during Pt deposition caused growth rates to decrease by up to a factor of 20 and caused disruption in the normal phase growth sequence. N₂ and Ar partial pressures had no effect.

Magnetic Properties and Structures of Equiatomic Rare Earth-Platinum Compounds RPt (R = Gd, Tb, Dy, Ho, Er, Tm)

A. CASTETS, D. GIGNOUX and J. C. GOMEZ-SAL, *J. Solid State Chem.*, 1980, **31**, (2), 197-207

The magnetic properties and structures of RPt compounds are presented. Below their Curie temperature the compounds have ferromagnetic behaviour. In GdPt the spontaneous magnetisation at 4.2K (6.7 μ_B /Gd) and the small superimposed susceptibility suggest that the Gd moments are parallel and the exchange interactions are positive. In the three types of non-collinear magnetic structures observed in the other compounds the rare earth atoms are divided into two sublattices with different magnetisation directions. These give rise to a ferromagnetic component associated with an antiferromagnetic component. These structures result from competition between magneto-crystalline anisotropy and positive exchange interactions of the Heisenberg type.

Solution of Hydrogen in Non-Stoichiometric Pd₃P_{1-x} Compounds

T. B. FLANAGAN, G. E. BIEHL, J. D. CLEWLEY, S. RUNNQVIST and Y. ANDERSSON, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, (1), 196-208

The solution of H₂(D₂) in a series of Pd₃P_{1-x} compounds for x from 0-0.20 was studied. H₂ solubility is significant for compounds with a large degree of non-stoichiometry and not important for the stoichiometric compounds. H₂ solubility falls to small values for x values near to those above the anomaly which is <0.08. The maximum solubility observed is H/Pd₃P_{0.80} = 0.15 (296K, 93.3kPa).

A Study of the New K_2NiF_4 -Type Solid Solutions $Sr_2Fe_xRu_{1-x}O_4$ by Mössbauer Spectroscopy and Other Techniques

R. GREATREX, N. N. GREENWOOD and M. LAL, *Mater. Res. Bull.*, 1980, **15**, (1), 113-120

The magnetic and structural properties of solutions $Sr_2Fe_xRu_{1-x}O_4$ ($0 \leq x \leq 0.5$) were studied. These phases, which are reported for the first time, have the K_2NiF_4 -type structure. As Ru is replaced by Fe, the weak metallic conductivity and Pauli paramagnetism of Sr_2RuO_4 give way to localised electron behaviour and long-range antiferromagnetic order, despite the longer type structure which is unfavourable for 180° Ru-O-M magnetic exchange interactions.

Formation of Zirconium Rich Alloys of Zr-Ru System

V. N. EREMENKO, E. L. SEMENOVA and T. D. SHTEPA, *Izv. Akad. Nauk SSSR, Met.*, 1980, (2), 212-214

Metallographic, X-ray and thermal studies of the behaviour of 0.5-12 at.% Ru-Zr alloys showed a maximum solubility for Ru in the β -Zr phase of 11 at.% at the eutectic temperature of 1250°C and in α -Zr phase of ~ 1 at.% at 600°C . Ru decreases the temperature of the $\alpha = \beta$ transition of Zr, and eutectoid decomposition of the β -solid solution close to 600°C did not occur. The formation of ω -phase with lattice parameters of $a = 4.997$, $c = 3.134 \text{ \AA}$ occurred during quenching at $1000-800^\circ\text{C}$.

Interaction between RRu_2 (R = Nd, Ho, Er) Intermetallics and Hydrogen

M. E. KOST, A. L. SHILOV, M. V. RAEVSKAYA and N. E. EFREMENKO, *Dokl. Akad. Nauk SSSR*, 1980, **250**, (5), 1155-1157

X-ray studies examined the interaction of H with $NdRu_2$, $HoRu_2$ and $ErRu_2$ during hydrogenation in a steel autoclave. The initial absorption of H at 20°C and at H_2 pressures of 30 atm in 1-5 min ceased after 20-120 min. The end products were metallic but were more brittle than the starting products. The measurements showed that the H content of 1 mole of metallide of $NdRu_2H_{5.5}$ is the highest so far obtained for RM_2 systems.

CHEMICAL COMPOUNDS

Sulfur-Bonded Sulfoxide Complexes of Rhodium(III) and Rhodium(I)

B. R. JAMES and R. H. MORRIS, *Can. J. Chem.*, 1980, **58**, (4), 399-408

Aqueous 2-propanol solutions of $RhCl_3 \cdot 3H_2O$ on treatment with sulphoxides yield mer- $RhCl_3L_3$ complexes, the sulphoxides $L =$ dimethyl(DMSO), tetramethylene(TMSO), etc. With diphenyl sulphoxide (DPSO), a $[RhCl(DPSO)_2]_2$ complex with S-bonded sulphoxide is obtained via the propanol reduction of a Rh(III) intermediate. The cyclooctene precursor $[RhCl(C_8H_{14})_2]_2$ has been used to prepare $[RhCl(DPSO)(C_8H_{14})_2]_2$, $[RhCl(DMSO)_2]_2$, etc.

μ_2 Bridging Carbonyl Systems in Transition Metal Complexes

R. COLTON and M. J. McCORMICK, *Coord. Chem. Rev.*, 1980, **31**, (1), 1-52

A review is given of crystal structures involving μ_2 carbonyl bridges between two transition metal atoms and of the wide variety of structural features involved, including structures of homonuclear Rh and Ru metals. (162 Refs.)

Studies of Osmium(IV) Thiochloride Complex Structure

S. V. VOLKOV, Z. A. FOKINA, N. I. TIMOSHENKO and V. I. PEKHNYO, *Ukr. Khim. Zh. (Russ. Ed.)*, 1980, **46**, (2), 213-215

A new Os(IV) thiochloride complex $OsCl_4(SCl_4)_2$ was prepared and analysed by the X-ray technique. From the data obtained by quantitative analysis, magnetic susceptibility and spectral studies ($100-700\text{cm}$), the structure of the complex was $[OsCl_4]^{2-}[SCl_4]^{+2}$.

ELECTROCHEMISTRY

The Development of an Energy Efficient Insoluble Anode for Nickel Electro-winning

A. J. SCARPELLINO and G. L. FISHER. The Electrochemical Society 157th Spring Meeting, St. Louis, Missouri, May 11-16, 1980, **80-1**, 1029-1030

Electrodes were developed for Ni electro-winning from electro-deposits of Pt, Pd, Ir, Ru, Au and Ru-Ir plated onto Ti substrates. Heat-treated Ru-Ir deposits had an oxygen over-potential comparable to that of Ru and RuO_2 , but lower than those of other precious metal coatings. Their suitability as anode coatings was $Ir > Ru-Ir > Pt > Pd \triangle Ru > Au$, but plating considerations precluded Ir. A $1 \mu\text{m}$ thick Ru-Ir coating was tested at $300-500 \text{ A/m}^2$ and 70°C to failure. It failed after ~ 2100 h. Interlayers $0.05-0.5 \mu\text{m}$ thick of Pt, Pd, Ir and Au electrodeposits were tested to failure. Pd, Pt and Ir interlayers exceeded their minimum life targets, and Pd was the best interlayer.

A Study of the Potential Oscillations of the Alloys on the Basis of Chromium Alloyed with the Metals of the Platinum Group in Solutions of Sulphuric Acid

N. D. TOMASHOV, E. N. USTINSKY and G. P. CHERNOVA, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, (4), 383-387

A study of the spontaneous periodic potential oscillations under corrosion of ductile Cr with admixtures of 0.1-0.4 wt.% Pt, Pd, Ir, Os or Ru was performed in still, aerated 40-55% solutions of H_2SO_4 at $40-120^\circ\text{C}$. A mechanism is given for the formation of potential oscillations in Cr alloys. It is assumed that oscillations appear when the alloy is in a passive-active state, due to the change in the value of pH in the near-electrode layer. The cathodic additives Pt, Pd, Ir, Os and Ru differ in their effect on the appearance of potential oscillations in Cr alloys.

Electrooxidation of Methanol on a Platinum-Tin Oxide Catalyst

A. KATAYAMA, *J. Phys. Chem.*, 1980, **84**, (4), 376-381
Electro-oxidation of methanol was done on a Pt-Sn oxide electrode in an aqueous acidic solution of the same catalytic activity as a Pt-Sn binary system. Pt^{4+} and Pt^{2+} occurred in the Pt-Sn oxide, showing that Pt was frozen in the catalyst in ionic forms. The times of polarisation of electro-oxidation were compared using Pt-Sn oxide and Pt after anodic activation, the deactivation on Pt-Sn oxide was less than on Pt, thus leading to enhanced catalytic activity; solid state current density is therefore greater on Pt-Sn oxide than on Pt. Pt deactivation was caused by an accumulation of adsorbed species from methanol.

Film Thickness Effect on Hydrogen Sorption at Palladium Electrodes

J. HORKANS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, **106**, 245-249
The sorption behaviour of H at thin film evaporated Pd electrodes is quite different from that at bulk Pd. Diffusion of dissolved H in the thin films is slow. Thin films sorb a greater quantity of H than bulk Pd. Annealing the evaporated films, due to an increase in grain size, results in H sorption behaviour resembling that of bulk Pd and a decrease in the charge due to sorbed H. The dependence of sorption charge on Pd morphology is explained by segregation of sorbed H at grain boundaries.

Corrosion and Mechanical Properties of High Chromium Ferrite Steels Alloyed with Molybdenum and Palladium

N. D. TOMASHOV, S. A. GOLOVANENKO, E. A. UL'YANIN, G. P. CHERNOVA and A. D. GORONKOVA, *Zashch. Met.*, 1980, **16**, (2), 105-112
The effect of additions of 0.3% Pd and 2% Mo on the corrosion and mechanical properties of high Cr ferrite steels containing 25% Cr implanted with C+N was studied in H_2SO_4 and HCl solutions. Steels alloyed with Pd showed higher corrosion stability in 10-50% H_2SO_4 and in 1-2% HCl at 80-100°C. The steels alloyed both with Pd and Mo showed a considerable increase in the stability of their passive layers in both the H_2SO_4 and HCl solutions.

The Anodic Rhodium Oxide Film: A Two-Color Electrochromic System

S. GOTTESFELD, *J. Electrochem. Soc.*, 1980, **127**, (2), 272-277
The oxide film grown on a Rh substrate in alkaline solutions by potential multipulsing behaves as a fast two-colour electrochromic system. In 1M or 5M KOH reversible yellow \rightleftharpoons dark green or yellow \rightleftharpoons brown-purple occurs. After 10^5 cycles the films suffer very small charge losses. In 5M KOH the response is faster but the open-circuit memory is shorter. The response time of the film is comparable to that of the Ir oxide electrochromic in acid solution, but its open-circuit memory is shorter. Excessive pulses cause a loss of electrochromic activity.

Chemical and Light-Induced Catalytic Water Oxidation

V. YA. SHAFINOVICH, N. K. KHANNANOV and V. V. STRELETS, *Nouv. J. Chim.*, 1980, **4**, (2), 81-84
The first example of the homogeneous photocatalytic water oxidation by visible light is reported. The catalytic water oxidation by one-electron oxidants IrCl_6^{2-} and $\text{M}(\text{bpy})_3^{3+}$ (M = Os, Fe and Ru; bpy = 2,2'-bipyridine) with Co(II), Fe(II), Fe(III), Ni(II) and Cu(II) hydroxocomplexes as catalysts is reported. Irradiation of $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ solution by visible light ($\lambda = 436\text{nm}$) forms O_2 .

Photoelectrochemical Production of Oxygen Based on Electron Transfer Quenching of $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$

D. P. RILLEMA, W. J. DRESSICK and T. J. MEYER, *J. Chem. Soc., Chem. Commun.*, 1980, (5), 247-248
A photoelectrochemical cell based on electron transfer quenching and the excited state $\text{Ru}(2,2'\text{-bipyridine})_3^{2+}$, in which visible photolysis gives both O_2 and an appreciable photocurrent, is described.

Preparation and Properties of Bismuth Ruthenate Thin Film Electrodes for Chlorine Evolution

P. F. CARCIA, R. B. FLIPPEN and P. E. BIERSTEDT, *J. Electrochem. Soc.*, 1980, **127**, (3), 596-599
Thin film electrodes in a compositional range about $\text{Bi}_2\text{O}_3 \cdot 2\text{RuO}_2$ were prepared by r.f. sputtering directly onto heated Ti substrates. $\text{Bi}_2\text{Ru}_2\text{O}_7$ was specifically prepared with the pyrochlore structure, $\text{Bi}_3\text{Ru}_3\text{O}_{11}$, and non-crystalline Bi ruthenate films. The resistivity of all films at 300K was $< 10^{-2} \Omega \text{cm}$. Electrochemical measurements on anodes of $\text{Bi}_2\text{Ru}_2\text{O}_7$ and $\text{Bi}_3\text{Ru}_3\text{O}_{11}$ show high activity for Cl_2 evolution. $\text{Bi}_2\text{Ru}_2\text{O}_7$ anodes lost some Bi.

Alloying of Co_3O_4 -Film Anodes with Ruthenium

V. V. SHALAGINOV, O. V. MARKINA and D. M. SHUB, *Elektrokhimiya*, 1980, **16**, (2), 270
Studies on $\text{TiCo}_3\text{O}_4(\text{Ru})$ anodes, prepared by thermal decomposition from mixed aqueous Ru and Co salt solutions on the surface of a Ti substrate, showed an increase in their electrocatalytic activity during electrolysis of chloride solutions yielding Cl_2 . Maximum activity occurred when the anodes contained 2.5 at.% Ru. In the 4M NaCl + 0.01M HCl electrolyte at 25°C, the current density is $\sim 0.1 \text{ A/cm}^2$ at 1.4V. Alloying the anode with Ru increases the electroconductivity and catalytic activity.

Proton Diffusion in Crystalline Ruthenium Dioxides

J. E. WESTON and B. C. H. STEELE, *J. Appl. Electrochem.*, 1980, **10**, (1), 49-53
A potential-step technique was employed to measure the chemical diffusion coefficient for protons in porous powder electrodes of RuO_2 with varying Cl contents, and correlated with published data.

Electrochemical Reduction of $\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2^+$ and Nature of Coupled Homogeneous Reactions

G. INNORTA and G. PIAZZA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, **106**, 137-147

Studies of the mechanism of the electrochemical reduction of the $\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2^+$ complex showed a reduction into two mono-electric steps: a reversible process and an irreversible one. The product of the reaction is either a stable compound $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$ produced by a bimolecular equilibrium reaction or a labile compound which slowly decomposes. In the second reduction process the anion formed reacts in a very fast reaction with the parent compound, giving rise to a product similar to those obtained in the reaction following the first charge transfer.

LABORATORY APPARATUS AND TECHNIQUE

Platinum-Zirconia Oxygen Sensors

R. J. REED, *Glass Ind.*, 1980, **61**, (2), 32-34

The structure and working of a Pt-ZrO₂ O₂ sensor is described. Pt on the inside and outside of the ZrO₂ converts O₂ to O ions inside the probe. The ions then travel to the outside of the probe and are converted back to free O₂ and free electrons. The difference in O₂ concentrations between inside and outside causes a millivoltage difference between the probe surfaces which is detectable. The probe must be at least 1200°F to function. This probe gives "wet" O₂ readings, as compared to others which remove H₂O vapour from the O₂ before analysis.

JOINING

A Review of Wafer Bumping for Tape Automated Bonding

T. S. LIU, W. R. RODRIGUES DE MIRANDA and P. R. ZIPPERLIN, *Solid State Technol.*, 1980, **23**, (3), 71-76

A review of tape automated bonding technology, beginning with the historical background, making use of the tri-metal system, Pd-Ni, Ag-Au and plated Au, then the Ti-Pd-Au metallisation system using plated bumps, is presented. Current bumping technology, such as using barrier metallisation of Ti, Pd and Au deposited on the wafer to provide a diffusion barrier between original Al bonding pads and the Au bump is examined. Other bumping technologies, future trends and the current status of bumping technology are briefly mentioned. (50 Refs.)

Weldability and Hot Cracking in Thorium-Doped Iridium Alloys

S. A. DAVID and C. T. LIU, *Met. Technol. (London)*, 1980, **7**, (3), 102-106

Modified Ir alloys containing ≥ 100 ppm Th are susceptible to cracking during gas tungsten-arc and electron-beam welding; but the latter is better, especially for Ir-0.3W doped with 200 ppm Th and

50 ppm Al. The weldability of this alloy is sensitive to the beam-focus condition and welding speed. Successful welds were made at low speeds over a narrow range of beam-focus conditions, while, at high speeds, an extended range of focus could be used. Weld-metal cracking was caused by HAZ liquation cracking and solidification cracking, and patches of low melting eutectic were seen. In cracked welds a Th region occurred near the fusion boundary, and it is suggested that this may be a source for the nucleation of liquation cracks.

HETEROGENEOUS CATALYSIS

On the Kinetic Instabilities during the CO-Oxidation on Platinum Catalysts

W. KEIL and E. WICKE, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, (4), 377-383

The kinetic instabilities during CO oxidation on a Pt catalyst under jumps of "ignition" and "extinction" as well as oscillations were studied in a tubular reactor under normal pressure at 100-300°C. The instabilities occur at mean CO contents of ~0.1% to a few % of CO in air. At lower and higher CO contents the kinetics of the reaction can be described uniformly by a Langmuir-Hinshelwood relationship, taking into account the different chemisorption sites for CO and O₂ at the Pt surface. The unstable behaviour of the reaction in the middle range is due to a reversible CO blocking of the Pt surface.

Study of n-Hexane Aromatisation on Platinum-Alumina Catalyst by the Method of Labelled Molecules

G. V. ISAGULYANTS, A. A. GREISH, L. I. KOVALENKO, N. N. ROZHDESTVENSKAYA and M. I. ROZENGART, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, (4), 864-870

Study of n-hexane aromatisation on a Pt/Al₂O₃ catalyst by a labelled molecule technique showed two parallel reaction stages with the intermediates of hexane and methylcyclopentane. No direct cyclisation of hexane to cyclohexane occurs. The presence of the Pt/Al₂O₃ catalyst in the reaction increased the amount of hydrocarbon conversion yield without the formation of the intermediate reaction products.

Catalytic Combustion of Methane: Comparison between the Kinetics with Different Catalysts

S. SICARDI, V. SPECCHIA, F. FERRERO and A. GIANETTO, *Riv. Combust.*, 1980, **34**, (1), 32-40

Reaction rates for catalytic combustion of CH₄ were studied using Al₂O₃ fibre-supported Pt or Pd catalysts, with and without Cr₂O₃ activators. Different techniques were used for the reduction of Pt and fibre impregnation. Different reactant concentrations, temperatures and gas flow rates were measured. Pd was more active than Pt and the Pd-containing catalysts can give rise to much higher chemical rates (up to 300 fold) than those of a good commercial catalyst.

On the Mechanism of Catalytic Cracking of Hydrocarbons on Zeolites

L. KH. SHAKIROVA, M. F. PLUZHNIKOVA and A. M. TSYBULEVSKII, *Neftekhimiya*, 1980, **20**, (2), 229-236

The mechanism of catalytic cracking of hydrocarbons on the zeolites A($\text{SiO}_2:\text{Al}_2\text{O}_3 = 1.8$), X(2.5) and Y(3.90; 4.35; 4.90) containing 0.5 wt.% Pd and on 0.6% Pt/CaY catalysts heat treated in air at 450-500°C was studied in H_2 at 350°C. The addition of Group VIII metals into the zeolites increased their cracking activities with no changes in the activity of the H spillover effect. The cracking of n-heptane in H_2 increased the rate of the reaction on CaY 2.5 times and on the Pt/CaY catalyst 30 times.

Poisoning of Platinum-Rhodium Automotive Three-Way Catalysts: Behavior of Single-Component Catalysts and Effects of Sulfur and Phosphorus

W. B. WILLIAMSON, H. K. STEPIEN and H. S. GANDHI, *Environ. Sci. Technol.*, 1980, **14**, (3), 319-324

The activity and selectivity of Pt, Rh and Pt + Rh Al_2O_3 -supported catalysts for NO, CO, hydrocarbon(HC) and CH_4 conversion were investigated as functions of catalyst composition, feed-gas composition, temperature and S and P fuel levels. The three-way conversion of Pt-Rh catalysts closely resembled the activity of pure Rh catalysts. Steady-state activities of the individual components of three-way catalysts (TWC) indicated that the net NO activity of Pt-Rh results from the high NO activity and selectivity of Rh. Pt-Rh catalysts have good HC oxidation activity and behave like Rh catalysts in rich gas mixtures and like Pt catalysts in lean conditions. The Pt-Rh TWCs were poisoned by S but not by fuel P. Removing S from the fuel increased net NO conversions and improved conversions of HC and CO. Removing fuel P substantially decreased NO reduction and HC conversions.

Investigations on Metal Catalysts. XXII. Chemisorption of Hydrogen on Pt-Ru and $\eta\text{-Al}_2\text{O}_3$ Supported Pt-Ru Catalysts

S. ENGELS, N. P. KHUE and M. WILDE, *Z. Anorg. Allg. Chem.*, 1980, **461**, (2), 155-164

Studies of the H_2 chemisorption on a series of Pt-Ru and Pt-Ru/ $\eta\text{-Al}_2\text{O}_3$ catalysts were made by a volumetric technique. Addition of Ru to Pt greatly affects the sorption behaviour of the samples. A H-spillover effect was found in Pt-Ru unsupported catalysts and in $\eta\text{-Al}_2\text{O}_3$ and Pt-Ru/ $\eta\text{-Al}_2\text{O}_3$ catalysts.

Magnetic, Infrared and Catalytic Studies of PtFe/SiO₂ Catalysts

L. GUCZI, G. KIMÉNY, K. MATUSEK, J. MINK, S. ENGELS and W. MÖRKE, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, (4), 782-789

Magnetic studies of the PtFe/SiO₂ system showed a totally reduced form of Fe in Pt-Fe clusters at up to 40 at.% Fe but at 70 at.% Fe, a part of the Fe was not reduced. The i.r. spectra of CO absorbed on the catalyst were measured and a shift was found in the

lower characteristic band, which is due to strongly adsorbed Pt + CO species. Catalytic reactions of propane showed methane formation over the Pt-rich catalyst while the reaction over the Fe-rich catalyst showed a high selectivity for benzene formation and hydrogenation.

Liquid-Phase Catalytic Hydrogenation of 1,4-Cyclohexanedione: Activity and Selectivity

M. BONNET, P. GENESTE and M. RODRIGUEZ, *J. Org. Chem.*, 1980, **45**, (1), 40-43

Liquid phase catalytic hydrogenation of 1,4-cyclohexanedione was carried out using Pd, Pt, Ir, Ru, Ni and Cu catalysts supported on SiO_2 in 2-propanol under 6.2 bar H_2 pressure at 20°C. A kinetically consecutive process, diketone→ketol→diol is obtained, but with Ru 4-hydroxycyclohexanone was obtained by hydrogenation in a single step from diketone with a 70% yield.

Hydroisomerisation of Diesel Fuel on Modified Palladium Zeolite-Containing Catalysts

M. A. SHARIKHARA, V. G. DYRIN, A. N. LOGINOVA, M. E. LEVINTER and R. A. BAKULIN, *Neftekhimiya*, 1980, **20**, (2), 237-241

The effect of the degree of exchange of Na^+ and H^+ on the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio in mordenites, and in the modification of 1 wt.% Pd/zeolite catalysts by Ca^{2+} and Mg^{2+} cations on their physical and catalytic properties, was studied during hydroisomerisation of diesel fuel in the presence of H_2 at 340-380°C. The catalysts prepared on the dealuminised zeolites were more acidic with higher activity compared with decationised zeolites. The addition of Ca^{2+} and Mg^{2+} cations into the catalysts increased their catalytic activity. The use of catalysts based on dealuminised mordenite modified by additions of Mg^{2+} cations in the hydroisomerisation reaction allows diesel fuel production at <-35°C.

Noble Metals Supported on Phillips-Type Catalysts: Preparation, Characterization, and Activity for Ethane Hydrogenolysis

G. C. BOND and G. HIERL, *J. Catal.*, 1980, **61**, (2), 348-358

Electron-transfer reactions between $\text{PdCl}_2(\text{PhCN})_2$, $\text{Rh}(\text{CO})_2\text{Cl}_2$ and AgClO_4 in aprotic solvents with Cr(II) ions on the surface of SiO_2 were examined with various metal:Cr(II) ratios. When molar Pd(II):Cr(II) ≤ 0.5 most Pd(II) was reduced to Pd^0 by electron transfer from Cr(II). Oxidation of Cr(II) by electron transfer to Rh(I) was complete only when Rh(I):Cr(II) = 5. The Pd metal area (m^2/g metal) increased as the molar Pd(II):Cr(II) ratio decreased from 2.5 to 0.18. In Rh-containing products Rh was only moderately well dispersed. Pd^0 formed from electron transfer from Cr(II) showed transient specific activity for ethane hydrogenolysis 300 times higher than that shown by larger particles. Specific activities for Rh catalysts were 100 times larger than previously reported values.

Structure and Catalytic Activity of Deposited Palladium Catalysts

S. A. G. ZAIDA, *Zh. Obshch. Khim.*, 1980, **50**, (1), 111-115

X-ray diffraction and electron microscopy studies of the structure and catalytic activity of Pd catalysts were performed. The catalysts were prepared by saturation by Pd chloride of C layers deposited on Cu screen, followed by reduction in H₂ at 200°C for 4h, and activated in N at 300°C for 10 h. The formation of new catalytic centres on the surface of deposited Pd catalysts occurred during the oxidation reaction with propylene. The catalytic centres were formed when the hydrocarbon enriched portion of the substance was passing through the catalyst.

The Reactions of Acetaldehyde, Ethanol and Acetic Acid on a Rhodium/Silica Acid Catalyst

U. BOS, W. HERZOG and E.-I. LEUPOLD, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, (2), 182-186

Thermal desorption and spectrometric studies of the reactions of CH₃CHO, C₂H₅OH and CH₃COOH on a promoted Rh/SiO₂ catalyst were performed. The catalyst was bifunctional in the reaction of CH₃CHO, when the support catalysed the formation of crotonaldehyde, etc. and the Rh was responsible for the decomposition of CH₃CHO to CO and CH₄. The support also catalysed hexadiene to benzene.

HOMOGENEOUS CATALYSIS

Syngas Reactions. II. The Homogeneous Catalyzed Carbonylation and Cyclization of Allylic Substrates

J. F. KNIFTON, *J. Organomet. Chem.*, 1980, **188**, (2), 223-236

CO insertion and/or addition to allylic precursors may lead to the formation of both linear and cyclic carbonylation products. Pt, Pd, Rh and Ni-based homogeneous catalysts have been developed and are particularly useful for selective synthesis of γ -butyrolactam, N-alkyl-2-pyrrolidones, vinylacetate and phenylacetate esters and diesters from a variety of allylic and benzylic substrates.

A New Catalytic Reaction of Sulphur Dioxide with Butadiene

U. M. DZHEMILEV, R. V. KUNAKOVA, YU. T. STRUCHKOV, G. A. TOLSTIKOV, F. V. SHAPIROVA, L. G. KUZMINA and S. R. RAFIKOV, *Dokl. Akad. Nauk SSSR*, 1980, **250**, (1), 105-108

A new catalytic reaction between SO₂ and butadiene in the presence of Pd(acac)₂-PPh₃-Al(C₂H₅)₃ catalyst (of the ratio 1:3:4 prepared by reduction at 100°C for 10 h) yielded *trans*-2,5-divinylsulpholane (I) and 3-sulpholene(II). The total yield of (I) was 10-15% and the content of (II) in the sulphone medium was \leq 10%. Various unlimited sulphones can also be prepared from 1,3-dienes and SO₂ in a similar reaction.

Palladium(II)tert-Butyl Peroxide Carboxylates. New Reagents for the Selective Oxidation of Terminal Olefins to Methyl Ketones. On the Role of Peroxymetalation in Selective Oxidative Processes

H. MIMOUN, R. CHARPENTIER, A. MITSCHLER, J. FISCHER and R. WEISS, *J. Am. Chem. Soc.*, 1980, **102**, (3), 1047-1054

A new family of Pd(II)tert-butyl peroxidic complexes of general formula (RCO₂PdOO-t-Bu)₄ was synthesised and characterised. These complexes were highly efficient reagents for the selective stoichiometric oxidation of terminal olefins to methyl ketones at ambient temperatures, and catalysts for ketonisation of terminal olefins.

Polymer-Bound Phosphine-Substituted Tetrairidium Carbonyl Clusters: Catalysts for Olefin Hydrogenation

J. LIETO, J. J. RAFALCO and B. C. GATES, *J. Catal.*, 1980, **62**, (1), 149-156

Unique tetrairidium carbonyl clusters, analogues to [Ir₄(CO)_{21-x}(PPh₃)_x]_n (x = 1, 2 or 3), were anchored to phosphine functionalised poly(styrene-divinyl benzene). The predominant metal species in each catalyst was the tetrairidium cluster. The catalysts were stable with unchanged i.r. spectra and undiminished activity for as many as 5000 turnovers for ethylene and cyclohexene hydrogenations, at temperatures <90°C; but at temperatures >120°C, the i.r. clusters aggregated to form crystallites.

Homogeneous Catalytic Hydrogenation of Free Carboxylic Acids in the Presence of Cluster Ruthenium Carbonyl Hydrides

M. BIANCHI, G. MENCHI, F. FRANCALANGI, F. PIACENTI, U. MATTEOLI, P. FREDIANI and C. BOTTEGHI, *J. Organomet. Chem.*, 1980, **188**, (1), 109-119

Saturated monocarboxylic acids up to C₆, several bicarboxylic acids and some of the corresponding anhydrides are hydrogenated in the homogeneous phase with H₄Ru₄(CO)₈(PBu₃)₄ as catalyst. This gives the corresponding alcohols (present among the reaction products as esters) or lactones at 100-200°C under a pressure of 100-200 atm H₂. Anhydrides react at temperatures lower than those needed for acids. Esters are not reduced.

The Mechanism of Hydrogenation of Activated Olefins, Including Prochiral Ones, Using *trans*-Chlorohydridobis-(diop)ruthenium(II)

B. R. JAMES and D. K. W. WANG, *Can. J. Chem.*, 1980, **58**, (3), 245-250

Solutions of *trans*-HRuCl(diop)₂, where diop is an optically active chelating ditertiary, hydrogenate under mild conditions activated olefinic substrates in high optical yield. Kinetic and spectroscopic studies indicate an "unsaturate" mechanism involving rapid co-ordination of the substrate. A diop ligand dissociates to give co-ordination sites.

CATHODIC PROTECTION

Cathodic Alloying of the Surface of Titanium, Chromium, and Stainless Steels as a Method of Increasing Their Passivation and Corrosion Resistance

N. D. TOMASHOV, G. P. CHERNOVA and T. A. FEDOSEVA, *Corrosion (Houston)*, 1980, **36**, (4), 201-207

The electrospark technique and electrochemical deposition from solution followed by annealing were used to alloy the surfaces of Ti, Cr and stainless steels with electropositive metals. The corrosion resistance of Ti in (20-40%) H₂SO₄ and (5-10%) HCl at 100°C is increased by plating the surface with Pd(1-10 μm) with or without subsequent annealing, and by electrospark alloying of stainless steels with Pd(0.5-0.6 μm). Cr deposits, unstable in H₂SO₄ and HCl become stable if modified with Pd by galvanic plating with Cr and Pd layer after layer. Corrosion resistance improves with annealing. Fe-27Cr, and Fe-18Cr-10Ni steels became corrosion resistant in 20% H₂SO₄ when coated with Pd.

The Corrosion Behaviour and Rutherford Backscattering Analysis of Palladium-Implanted Titanium

G. K. HUBLER and E. McCAFFERTY, *Corros. Sci.*, 1980, **20**, (1), 103-116

The corrosion behaviour of Pd-implanted Ti in boiling 1M H₂SO₄ was investigated by Rutherford backscattering profiles of the Pd concentration as a function of corrosion time, and by other methods. The rate of Ti dissolution was reduced by about 3 orders of magnitude for Pd-implanted samples. Soon after immersion the Pd surface concentration rises to 20 at.% because of preferential dissolution of Ti, and Pd is retained in the surface for corrosion times of up to 9h. The steady state corrosion potential of implanted samples is close to that of pure Pd.

NEW PATENTS

METALS AND ALLOYS

Nickel Base Alloy

SPECIAL METALS CORP. *British Patent* 1,565,606

A gamma prime strengthened Ni base alloy contains up to 6% Ru and up to 2% or one or more of the lanthanide metals.

Superplastic Aluminium Alloy

EUROPEAN ATOMIC ENERGY COMMUNITY (EURATOM) *British Patent* 1,565,620

An Al alloy containing 17-30% Pd and not more than 1% of impurities possesses superplastic properties. A preferred alloy has a purity of 99.5% + and a Pd content of 23%. The alloy may replace Pd sponge or powder catalysts in hydrogen/deuterium exchange reactions.

ELECTRICAL AND ELECTRONIC ENGINEERING

A Study on a Palladium-Titanium Oxide Schottky Diode as a Detector for Gaseous Components

N. YAMAMOTO, S. TONOMURA, T. MATSUOKA and H. TSUBOMURA, *Surf. Sci.*, 1980, **92**, (2/3), 400-406

The current through a Schottky barrier formed at the interface between Pd film and n-type TiO₂ single crystal is sensitive to H₂ or other reducing gases in the ambient. This is explained by taking into account the diminished barrier height at the Pd/TiO₂ interface caused by the action of gases, which changes the work function of Pd. The change in Pd work function is confirmed by direct measurements of the metal surface potentials.

Effect of Ruthenium Ions on Grain Boundaries in Gallium Arsenide Thin Film Photovoltaic Devices

W. D. JOHNSTON, H. J. LEAMY, B. A. PARKINSON, A. HELLER and B. MILLER, *J. Electrochem. Soc.*, 1980, **127**, (1), 90-95

Chemisorption of Ru ions decreases the rate of carrier recombination at grain boundaries and the surface recombination velocity on thin film, polycrystalline n-GaAs grown by chemical vapour deposition. There is a pronounced improvement in charge collection at Au n-GaAs Schottky barriers following Ru treatment. After chemisorption of Ru ions a solar to electrical conversion efficiency of 4.8% was reached in the n-GaAs/0.8 M K₂Se-0.1 M K₂Se₂-1 M KOH/C liquid junction cell with semiconductor grains of 3-7 μm diameter. The Ru effect is more dramatic than that shown in single crystal substrates, increasing the power conversion efficiency by up to a factor of four over etched specimens.

CHEMICAL COMPOUNDS

Osmium Tetroxide Complexes

JOHNSON MATTHEY & CO. LTD.

British Patent 1,560,481

Complexes suitable for fixing and staining cells for electron microscopy are obtained from OsO₄ and an aromatic tertiary amine, a cycloaliphatic tertiary amine and/or a compound having a heterocyclic ring containing one or two N atoms, such as quinuclidine.

New Iridium Compounds

INTERNATIONAL NICKEL CO. *U.S. Patent* 4,174,378

Novel Ir compounds are prepared by refluxing a diammonium hexahalogen salt of Ir and sulphamic acid in an aqueous medium for more than thirty hours. The Ir products are useful in electroplating.