

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

An XPS Study of Carbon Monoxide and Nitric Oxide Adsorption on Platinum(410): Unusual Dissociation Activity

Y. O. PARK, R. I. MASEL and K. STOLT, *Surf. Sci.*, 1983, **131**, (1), L385-L389

The adsorption of NO and CO on Pt(410) was studied by XPS. The (410) surface showed unusual activity for NO and CO bond breaking. CO adsorbed molecularly on Pt(410) at 30K but partially dissociated on heating to 500K. NO adsorbed dissociatively under all conditions studied. Low index Pt faces and stepped surfaces previously considered give negligible CO dissociation and negligible NO dissociation up to 450K. Woodward-Hoffman ideas predicted that the surface would be unusually active for NO and CO bond breaking.

The Total Anodization of Copper Films on Platinum: Use as Selective Surface Absorbers at High Temperature

A. A. MILGRAM, *J. Appl. Phys.*, 1983, **54**, (8), 4692-4693

Anodic Cu films were formed from a layer of Cu metal 150-250nm thick and deposited on Pt. The solar absorbance and total thermal emittance were measured. These totally anodised Cu oxide films have the superior selective surface properties of the usual passivated anodic Cu oxide films, and in addition they are stable at temperatures up to 600°C.

Palladium-Based Metallic Glasses Containing Beryllium and Boron

A. LUCCI and G. VENTURELLO, *Gazz. Chim. Ital.*, 1983, **113**, (5-6), 301-304

The ability of Pd-Be alloys to form metallic glasses by melt-spinning was examined. An alloy, amorphous up to 98% of its volume was obtained and compared to Pd-B metallic glasses. B displays a stronger stabilising effect on the amorphous condition than Be, since Pd₇₆Be₂₄ crystallises at a temperature 70°C higher than Pd₇₂Be₂₈.

The Magnetic Properties of Some R₅Pt₃ Compounds (R=Gd, Tb, Dy, Ho)

H. GAMARI-SEALE and A. YAZDANI, *J. Magn. & Magn. Mater.*, 1983, **38**, (1), 57-60

The magnetic susceptibility and magnetisation of the R₅Pt₃ intermetallic compounds have been studied. Gd₅Pt₃ is ferromagnetic, while Tb₅Pt₃, Dy₅Pt₃ and Ho₅Pt₃ possess a non-linear magnetic structure, with strong ferromagnetic interaction and high anisotropy effects at low temperatures.

TEM Observations of Laser-Induced Pt and Au Deposition on InP

D. BROSEN, R. F. KARLICEK and V. M. DONNELLY, *J. Electrochem. Soc.*, 1983, **130**, (7), 1473-1479

Laser-induced deposits of Pt or Au on (001)InP surfaces were studied by TEM. It was found that Pt deposition results in the formation of Pt(P, In)₂; whereas, in the case of Au, Au and Au₄In were observed. A description of the general morphology is presented.

Thermal Oxidation of Transition Metal Silicides: The Role of Mass Transport

M. BARTUR, *Thin Solid Films*, 1983, **107**, (1), 55-65

Thin films of transition metal silicides including Pt and Pd, on a Si substrate oxidise and form SiO₂ on their surface when they are annealed in an oxidising ambient atmosphere. The oxidation characteristics of the silicides, which are used as interconnects in integrated circuits, and the SiO₂ growth rate and major steps controlling silicide oxidation are reviewed. The diffusing species during the oxidation of PdSi, Pd₂Si and PtSi are also discussed.

A Simultaneous Voltammetric and Dilatometric Study of Hydrogen Absorption in Pd Amorphous Pd₈₀Si₂₀

B. M. GEERKEN, I. A. M. CORBIÈRE and R. GRIESSEN, *J. Phys. Chem. Solids*, 1983, **44**, (8), 793-799

By simultaneously measuring the length change of a Pd electrode and the current through the electrolytic cell when a triangular voltage is applied across the cell the surface and bulk processes during H uptake in Pd can be distinguished. The diffusion of H into the bulk of the samples takes place mainly along dislocation lines. Dilatometric and voltammetric measurements in magnetic fields up to 10T show that the absorption of well annealed Pd electrodes increases up to 1T and saturates at higher fields.

Hydrogen Chemisorption on Palladium Foil and Palladium Films

YU. A. ZUBAREV, I. I. MIKHALENKO and V. D. YAGODOVSKII, *Kinet. Katal.*, 1983, **24**, (5), 1194-1199

Studies of the H₂ chemisorption on Pd foil or Pd films showed that the transfer of H₂ through the Pd membrane coexists with negatively and positively contaminated forms of atomic H. The limiting stages of the transfer process was the recombination of desorbed negatively contaminated H. The degree of surface coverage of H⁻ and H⁺ forms ranges from 0.05-0.06 and 0.04-0.08, respectively. Three Pd forms with activation desorption of 33.5, 84.0 and 117 kJ/mol were observed on Pd films at 100-430°C.

Superconducting Tunnel Junctions on Oxidized Zr₂Rh Films

M. LEVINSON and M. GURVITCH, *J. Appl. Phys.*, 1983, **54**, (8), 4683-4685

High quality superconducting Zr₂Rh films were produced by d.c. diode sputtering in Ar. Superconducting films were obtained for substrate temperatures of ~350-650°C, with maximum values of T_c = 11.2K and resistance ratio ~26 falling in the range 550-600°C. Oxidations were performed without breaking the vacuum. The best tunnelling characteristics occurred for 180 Torr s O₂ exposure and pre- and post-oxidation anneals. An ~10Å sputtered Zr overlayer improved the performance.

pH Dependent Voltammetry of Iridium Oxide Films

M. F. YUEN, I. LAUKS and W. C. DAUTREMONT-SMITH, *Solid State Ionics*, 1983, **11**, (1), 19-29

Studies of anodic Ir oxide films (AIROFs) and sputtered Ir oxide films (SIROFs) by voltammetric analysis and open-circuit pH response are reported. The voltage and pH dependent double injection of ions and electrons into the films are described by a model of an equilibrium change in electronic Fermi level and ionic chemical potential. Electronic densities of states derived from quasi-static voltammograms indicate that AIROFs perform a pH sensitive structural transformation which is not shown by SIROFs.

Ferromagnetism and Superconductivity Down to 0K in b.c.t. ErRh₄B₄

J. L. GENICON, A. SULPICE, R. TOURNIER, B. CHEVALIER and J. ETOURNEAU, *J. Phys.-Lett. (Paris)*, 1983, **44**, (17), L-725-L-732

ErRh₄B₄ compounds with b.c.t. structure of CuRu₄B₄ type using C doping were prepared. The superconductivity exists from 7.5K down to 0K. The simultaneous presence of ferromagnetism is shown by a jump in the thermal variation of the frozen flux obtained after decreasing the magnetic field from above H_{c2}, and by the rectangular shape of the magnetisation hysteresis. These effects give new tools for finding ferromagnetic superconductors.

Magnetic Behaviour of the Kondo-Lattice System CeRu₂Si₂

L. C. GUPTA, D. E. MACLAUGHLIN, C. TIEN, C. GODART, M. A. EDWARDS and R. D. PARKS, *Phys. Rev. B.*, 1983, **28**, (7), 3673-3676

The intermetallic compound CeRu₂Si₂ exhibits low temperature magnetic properties similar to those of heavy-fermion superconductor CeCu₂Si₂. Magnetic susceptibility and ²⁹Si NMR measurements establish that the ground state of CeRu₂Si₂ is nonmagnetic and electric resistivity reflects Kondo-type spin fluctuations. The observed proportionality between the Ce contributions to the ²⁹Si NMR shift K and magnetic susceptibility χ distinguishes CeRu₂Si₂ from mixed-valence Ce- and Yb-based systems found previously to exhibit anomalous nonlinear dependence of K on χ.

The Fe-Ru (Iron-Ruthenium) System

L. J. SWARTZENDRUBER and B. SUNDMAN, *Bull. Alloy Phase Diagrams*, 1983, **4**, (2), 155-160

A provisional paper on the Fe-Ru system is presented, covering the Fe-Ru equilibrium diagram for 400 to 2400°C, crystal structures, magnetic properties and a thermodynamic model.

CHEMICAL COMPOUNDS

Chemistry of Bis(diphenylphosphino) Methane

R. J. PUDEPHATT, *Chem. Soc. Rev.*, 1983, **12**, (2), 99-127

A review of bis(diphenylphosphino) methane, especially with metal-P bonds is presented. Many platinum group metal complexes are discussed. Topics covered include related ligands, complexes with monodentate dppm, chelate dppm and bridging dppm; compounds with metal-metal bonds but no other bridging groups, compounds with other bridging groups, cluster complexes with dppm, complexes with deprotonated dppm and catalysis with the dppm complexes. (149 Refs.)

[H₃NCH₂CH₂NH₃]_{0.82}[Pt(C₂O₄)₂].2H₂O —A New Partially Oxidised Bis(oxalato) Platinite

A. E. UNDERHILL, M. MIZUNO, K. KROGMANN and M. ROSCH, *J. Phys. (Paris), Colloq. C3*, 1983, **44**, (6), C3-1331-C3-1334

The preparation of a new one-dimensional conductor is described together with the results of structural and electrical conductivity studies. The Pt subshell is triclinic. At room temperature electrical conductivity σ₁₁ in the Pt chain direction, lay in the range 9.6-0.3/Ω cm with an average of 4/Ω cm.

The Synthesis, X-Ray Crystal Structure and Vibrational Characterisation of the Mixed-Valence, Iodine-Bridged Complex [Pt^{II}(dien)I][Pt^{IV}(dien)I₃]I₂

R. J. H. CLARK, M. KURMOO, A. M. R. GALAS and M. B. HURSTHOUSE, *J. Chem. Soc., Dalton Trans.*, 1983, (8), 1583-1586

The complex [Pt(dien)I][Pt(dien)I₃]I₂ (dien = diethylenetriamine) can be obtained as bronze crystals by partial oxidation of [Pt(dien)Cl]Cl with I₂ in dilute hydroiodic acid. X-ray analysis shows it has orthorhombic space group Pmcn. The complex is the first to be characterised in which each Pt ion is coordinated to a tridentate ligand.

PrPd₅ A New Intermetallic Compound

N. CHEN, H. XU, J. ZHU and C. YANG, *Acta Metall. Sin.*, 1983, **19**, (3), A251-A252

A new intermetallic compound PrPd₅ (1) has been synthesised from pure metals. Its lattice parameters, by comparison with MoAl₅(2), the WAl₅-type structure are: a 4.98(1), 4.89(2); c 8.996(1), 8.80(2); c/a 1.81(1), 1.80(2).

Preparation, Magnetic and Mössbauer Resonance Investigation of Some Perovskite-Type Oxides Containing Iridium + V

M. WELEWSKI, B. BUFFAT, G. DEMAZEAU, F. WAGNER, M. POUCHARD and P. HAGENMULLER, *Mater. Res. Bull.*, 1983, **18**, (7), 881-887

New Ir(+V) perovskites, $M\text{LaMgIrO}_6$ ($M = \text{Ca, Sr, Ba}$) were prepared under high O_2 pressures. The stabilisation of Ir(+V) is discussed and compared to that of $\text{La}_2\text{LiIrO}_6$. Ir in the materials is characterised. Weak Li-O bonds stabilise Ir(+V).

$\text{PPh}_3\text{Me}[\text{Os}(\text{NO})\text{Cl}_4]$; a Penta Coordinate Osmium Nitrosyl Complex

B. CZESKA, K. DEHNICKE and D. FENSKE, *Z. Naturforsch. B*, 1983, **38**, (8), 1031-1033

$\text{PPh}_3\text{M}_4[\text{Os}(\text{NO})\text{Cl}_4]$ was prepared by the reaction of $(\text{NO})_2[\text{Os}(\text{NO})\text{Cl}_5]$ with methyltriphenylphosphonium chloride in CH_2Cl_2 solution. The structure consists of $[\text{P}(\text{C}_6\text{H}_5)_3\text{CH}_3]^+$ cations and disordered $[\text{Os}(\text{NO})\text{Cl}_4]^-$ anions; the latter have approximate C_{4v} symmetry with a linearly co-ordinated nitrosyl ligand in the axial position.

ELECTROCHEMISTRY

Studies of Hydrogen Production by the Water Gas Shift Reaction and Related Chemistry

R. EISENBERG, *NTIS Energy*, 20 Sept. 1983, 1743

Noble metal complexes Pt, Rh and Ir have been investigated for the water gas shift reaction at atmospheric pressures and 80-100°C. The catalysts have also been examined as electrocatalysts for the anode reaction of CO fuel cells. The best water gas shift catalysts observed include $\text{Rh}(\text{CO})_2\text{C}_{12}$, PtC_{17} , 4PbC_{12} and $\text{PtC}_{13}(\text{C}_2\text{H}_4)$. None of these electrocatalytically oxidised CO; however $\text{RhCl}(\text{PPh}_3)_3$, $\text{Rh}(\text{dppe})(\text{mnt})$ and $\text{Rh}(\text{dppe})^{2+}$ complexes, which bind CO, exhibited some limited electrocatalytic CO oxidation behaviour.

An X-Ray Photoelectron Spectroscopic Study of Electrocatalytic Activity of Platinum Group Metals for Chlorine Evolution

M. HARA, K. ASAMI, K. HASHIMOTO and T. MASUMOTO, *Electrochim. Acta*, 1983, **28**, (8), 1073-1081

A correlation between the catalytic activity for anodic Cl^- evolution on Pt group metals and the nature of the surface film formed during Cl^- evolution in a NaCl solution was studied by XPS. The change in the surface film with increasing potential was found on Pt, including an increase in the cationic valence. This appears to be responsible for the decrease in Cl^- evolution on Pt in the high potential region. Replacement of OH^- in the surface film by Cl^- becomes easier in the order of Rh, Ir, Pd and the activity for anodic Cl^- evolution increased in this order due to an increase in the Cl^- in the film.

Metal Electrodes Bonded on Solid Polymer Electrolyte Membranes (SPE)—The Behaviour of Platinum Bonded on SPE for Hydrogen and Oxygen Electrode Processes

A. KATAYAMA-ARAMATA, H. NAKAJIMA, K. FUJIKAWA and H. KITA, *Electrochim. Acta*, 1983, **28**, (6), 777-780

The electrochemical characteristics of a Pt electrode directly bonded to one side of a solid polymer electrolyte membrane (Pt-SPE) were studied. Hydrogen evolution, ionisation and O reduction were examined when the Pt side of the Pt-SPE was free from liquid but filled with the gases concerned. The electrode lightly bonded on the SPE gives great promise, especially in fuel cell applications.

Radiotracer and Electrochemical Study of the Adsorption and Electrocatalytic Oxidation of Glycerol at a Platinised Platinum Electrode.

G. HORÁNYI and E. M. RIZMAYER, *Acta Chem. Scand., Ser. B*, 1983, **37**, (5), 451-457

Adsorption and electrocatalytic oxidation of glycerol at a platinised Pt electrode was studied in acidic medium by a radiotracer method using ^{14}C -labelled glycerol. An attempt was made to explain the role of strongly chemisorbed organic species and chemisorbed O_2 in the observed polarisation behaviour. It was assumed that the shape of the polarisation curve is determined by two main factors: reactions on free metal sites and processes taking place on the top of the chemisorbed O_2 .

Study of the Electrocatalytic Reduction of Allyl Chloride and Chloral Hydrate at a Platinised Platinum Electrode in Acidic Medium

G. HORÁNYI and K. TORKOS, *J. Electroanal. Chem. Interfacial Electrochem.*, 1983, **154**, (1/2), 181-191

Electrocatalytic reduction and polarisation behaviour of allyl chloride and chloral hydrate were studied at a platinised Pt electrode in acidic medium. Polarisation behaviour shows that the rate-determining step of the reaction is a charge-transfer process connected with the splitting of the C-Cl bond in allyl chloride.

Precipitation of Pd^{II} as $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ and the Behaviour of Various Impurities

M. KNOTHE, *Z. Anorg. Allg. Chem.*, 1983, **503**, (8), 213-223

The dependence of $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$ precipitation upon reaction conditions such as pH, Cl content, reaction time and temperature were studied. The increase of Pd concentration was due to the formation of $[\text{Pd}(\text{NH}_3)\text{Cl}]^-$. The coprecipitation of the Pt group metals and of Au was highly dependent on the previous formation of ammine complexes of these metals. The considerable coprecipitation of Pt^{IV} was probably due to the formation of mixed Pd/Pt compounds, whereas the other impurities were adsorbed by $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$.

Study of the Electrochemical and Corrosion Behaviour of Titanium Surface Alloyed with Palladium by the Ionic Implantation Method

N. D. TOMASHOV, M. I. GUSEVA, G. P. CHERNOVA, A. E. GORODETSKII, B. G. VIADIMIROV, O. A. ZHILTZOVA, D. B. BOGOMOLOV and R. KH. ZALAVUIDINOV, *Zashch.Met.*, 1983, 19, (6), 872-878

Study of the electrochemical and corrosion behaviour of Ti surfaces alloyed with Pd by ionic implantation was made in 20% H₂SO₄ at 20-100°C. The effects of the implantation on the stability of saturated compounds and on the electrochemical properties of the samples were studied. The dependence of the electrochemical and corrosion properties of Ti implanted with Pd on the total amount of implanted Pd and on the character of its distribution in the surface layer is established.

PHOTOCONVERSION

Photo-Kolbe Reaction at Gas-Solid Interfaces

S. SATO, *J. Phys. Chem.*, 1983, 87, (18), 3531-3537

Photocatalytic decarboxylation of carboxylic acids, i.e. the photo-Kolbe reaction, occurred in the gas phase over platinised anatase (TiO₂). Platinised rutile was much less reactive. For acetic acid the reaction rate and relative yield ethane: methane increased with increasing acetic acid pressure, ethane selectivity being up to 50%. Adding gas-phase water accelerated the reaction and improved ethane selectivity up to 90% but had no effect on the reaction over anatase.

Photocatalytic Hydrogen Production from Solutions of Sulfite Using Platinized Cadmium Sulfide Powder

M. MATSUMURA, Y. SAHO and H. TSUBOMURA, *J. Phys. Chem.*, 1983, 87, (20), 3807-3808

H₂ was efficiently produced from platinised CdS powder suspended in a sodium sulphite solution, by visible light. Sulphite ions were oxidised to sulphate and dithionate ions.

Supported Palladium Catalysts for the Reduction of Sodium Bicarbonate to Sodium Formate in Aqueous Solution at Room Temperature and One Atmosphere of Hydrogen

C. J. STALDER, S. CHAO, D. P. SUMMERS and M. S. WRIGHTON, *J. Am. Chem. Soc.*, 1983, 105, (20), 6318-6320

The reduction of the aqueous NaCO₃H to aqueous Na formate, NaHCO₂, can be performed at 298K and 1 atm H₂ using various Pd catalysts, such as 5% Pd/C, Pd black, 5% Pd/BaSO₄ and W/polymer/Pd. The results suggest that photoproduction of CO₂ in aqueous solution could be efficient, since H₂ generation at semiconductor photocathodes has been shown to be efficient under visible light.

Photochemistry of Iodopentaammine-rhodium(III) in Zeolite Y

M. J. CAMARA and J. H. LUNSFORD, *Inorg. Chem.*, 1983, 22, (18), 2498-2501

The photoaquation of iodopentaammine-rhodium(III) in fully and partially hydrated zeolite Y was studied as a model reaction to examine the photochemistry of transition metal complexes in zeolites. The reaction was followed by i.r. spectroscopy by observing the production of the NH₄⁺ ion. The quantum yield was only 15-20% of that observed in aqueous solution, and this drop is attributed to the decrease in mobility of water in the zeolite and to the exclusion of water from the ligand-exchange site by the zeolite lattice. Light scattering by zeolite reduces the efficiency of the photochemical reaction.

Surface Enhanced Resonance Raman Spectroscopy of Adsorbates on Semiconductor Electrode Surfaces: Tris(bipyridine)ruthenium(II) Adsorbed on Silver-Modified n-GaAs(100)

R. P. VAN DUYN and J. P. HAUSHALTER, *J. Phys. Chem.*, 1983, 87, (16), 2999-3003

The first observations of surface-enhanced resonance Raman scattering from Ru(bdy)₃²⁺ at monolayer (or less) coverage on n-GaAs(100) semiconductor electrodes modified by the electrodeposition of ~100 monolayers of Ag are reported. The photoelectrochemical and surface microstructural properties of Ag/GaAs/Ru(bpy)₃²⁺ electrodes were studied by cyclic voltammetry and SEM.

Kinetic Mechanism of Water Oxidation by Ru(dipy)₃²⁺ Complex in the Presence of Cobalt Salts

N. K. KANNANOV, A. V. KHRAMOV, A. P. MORAVSKII and V. YA. SHAFIROVICH, *Kinet. Katal.*, 1983, 24, (4), 858-864

Studies of the kinetic reduction of Ru(dipy)₃²⁺ to Ru(dipy)₃¹⁺ in the presence of Co hydroxy complex showed that the oxidiser [Ru(dipy)₃²⁺] in the system acts in two ways: first by oxidative-reductive destruction of Ru(dipy)₃²⁺ accompanied by the formation of Ru(dipy)₃¹⁺ and oxidation of small co-ordination molecules of dipyridyl to CO₂ and secondly by oxidation of H₂O forming O₂ which is catalysed by Co complex.

Effect of Applied Potential on Photoinduced Charge Separation at Metal Complex Thin-Film Electrodes

Y. UMEZAWA and T. YAMAMURA, *Nippon Kagaku Kaishi*, 1983, (6), 929-932

The effect of applied potentials on photocurrents at metal thin film electrodes was studied. 1 × 10¹⁵ Molecules of tris(2,2'-bipyridine)Ru(II) complex or one of four metalloporphyrins was coated onto a Pt electrode. Only water and electrolyte were in the sample solutions. Light of range 400-800 nm was focused onto the electrodes. Photocurrent versus applied potential I/p was divided into three groups.

Highly Efficient Photoreduction of Methylviologen by Tris(bis-Diazadiimine) Ruthenium(II) Complexes

N. KITAMURA, Y. KAWANISHI and S. TAZUKE, *Chem. Lett. Jpn.*, 1983, (8), 1185-1188

Photoreduction of methylviologen by several Ru(II)L₃ (L = bisdiazadiimine) complexes was studied in the presence of triethanolamine in aqueous solution. The quantum yield for MV⁺ formation was as high as 0.98 or 0.85 in vacuo, when L = 2,2'-bipyrazine or 2,2'-bipyrimidine, respectively.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Pt and Os Targets for Nuclear Reaction Experiments

A. E. STUCHBERY, *Nucl. Instrum. Methods Phys. Res.*, 1983, 211, (2,3), 293-295

Procedures for electrodeposition of bright, well-adhered elemental targets of Pt and Os, ~1-2 mg/cm² thick on Fe, Co, Cu and Ag substrates are described. The preparation of the electrolytic solutions and the plating procedures are described. The plating efficiency is strongly temperature dependent.

LABORATORY APPARATUS AND TECHNIQUE

Semiconductor Detector for the Selective Detection of Atomic Hydrogen

K. C. HARVEY and C. FEHRENBACH, *Rev. Sci. Instrum.*, 1983, 54, (9), 1117-1120

A semiconductor detector, with two Pt electrodes and Pt connections, which responds to the atomic H in an atomic beam but is insensitive to molecular H₂ is described. The H flux is measured through the change in conductivity of the semiconductor material which occurs when the H is chemisorbed. The H₂ is filtered and regulated by a Pd leak. The minimum detectable signal is ~10⁹ H atoms/mm²s and the response time is <2ms.

HETEROGENEOUS CATALYSIS

Activity of Supported Platinum Catalysts for Methane Oxidation

M. NIWA, K. AWANO and Y. MURAKAMI, *Appl. Catal.*, 1983, 7, (3), 317-325

Oxidation of CH₄ was carried out on Pt catalysts supported on Al₂O₃, SiO₂-Al₂O₃ and SiO₂. Catalysts were characterised by TPR. Catalytic activity was related to the TPR profile if the component reducible at relatively low temperature was considered to be the active site. The catalyst was completely oxidised under the experimental conditions and catalyst activity was dependent on the reducibility of Pt oxide. The turnover frequency for the CH₄ oxidation was Pt/SiO₂-Al₂O₃ > Pt/Al₂O₃ > Pt/SiO₂.

Dynamic Behaviour of Automotive Catalysts. 2. Carbon Monoxide Conversion under Transient Air/Fuel Ratio Conditions

R. K. HERZ, J. B. KLELA and J. A. SELL, *Ind. Eng. Chem., Prod. Res. Dev.*, 1983, 22, (3), 387-396

The first analysis of the CO conversion response of three-way automotive catalysts following step-changes in engine air/fuel ratio (A/F) and during individual A/F cycles is presented. Two fresh three-way catalysts were compared: Ce containing Pt/Pd/Rh/Ce/Al₂O₃ beads and similar but Ce free Pt/Pd/Rh/Al₂O₃ beads. The results presented give more understanding of the performance of catalysts.

The Effect of Chloride Ion on the Metal Interaction and Reaction Selectivity of Pt-Sn/Al₂O₃ Catalysts

C. WANG, R. WU and L. LIN, *J. Catal. (Dalian, China)*, 1983, 4, (3), 177-183

A series of Pt-Sn/Al₂O₃-Cl catalysts with a range of Sn:Pt and Cl⁻ contents was prepared. The activity, selectivity and stability of these catalysts were determined in a flow reactor for reforming n-heptane. Selectivities were evaluated at temperature 500°C, H₂:n-heptane 6.6 and 6kg/cm² pressure. Catalysts prepared by incorporating Cl⁻ as a ligand of the Pt-Sn complex are very stable and have better selectivity for aromatisation and isomerisation of n-heptane. Those with Cl⁻ from addition of HCl to the acidic component have much higher hydrocracking activity and lower selectivity for aromatisation and isomerisation, implying that the larger the Pt-Sn to Cl⁻ distance, the lower the selectivity for aromatisation and isomerisation of n-heptane.

Isomerization and Hydrocracking of C₉ through C₁₆ n-Alkanes on Pt/HZSM-5 Zeolite

J. WEITKAMP, P. A. JACOBS and J. A. MARTENS, *Appl. Catal.*, 1983, 8, (1), 123-140

The pure n-alkanes, C₉-C₁₆, were converted on a Pt/HZSM-5 zeolite in the presence of H₂. Products were formed by hydrocracking and isomerisation, probably inside the pores of the catalyst. Product distributions differ substantially for these on Y type zeolites. Monomethyl isomers are mostly formed by isomerisation. Cracked products consist of n- and i-alkanes with single methyl branching. Neither methane nor ethane are formed, which indicates an ionic cleavage mechanism.

Colloidal Noble Metal Catalysts Supported on Inorganic Carriers

Y. NAKAO and K. KAERIYAMA, *Chem. Lett. Jpn.*, 1983, (7), 949-950

Hydrosols of Pt, Pd and Rh were prepared by the NaBH₄ reduction of the corresponding metal salts in aqueous solution without using protective agents. Colloidal metals in the hydrosols were effectively adsorbed on inorganic carriers, such as Mg(OH)₂, to give highly active catalysts for olefin hydrogenation.

Zeolite-Supported Ru-Pt Catalysts for Selective Fischer-Tropsch Synthesis

O. OKUDA, T. TATSUMI, K. FUJIMOTO and H.-O. TOMINAGA, *Chem. Lett. Jpn.*, 1983, (8), 1153-1156

Ru-Pt catalysts prepared by simultaneous ion exchange on zeolite HY, selectively produced from synthesis gas branched-chain paraffins in the C₄-C₁₀ range. An exception was for a catalyst with 4wt.% Ru and 2wt.% Pt which was highly active for the exclusive formation of CH₄.

Catalytic Combustion of Low Heat Value Gas. 1. Substoichiometric Combustion with Supported Platinum Catalysts. 2. Reduction of Carbon Monoxide Produced under Substoichiometric Combustion

A. M. MADGAVKAR, R. F. VOGEL and H. E. SWIFT, *Ind. Eng. Chem., Prod. Res. Dev.*, 1983, 20, (4), 628-636, 637-644

Studies of substoichiometric (O₂ deficient) catalytic combustion of a typical low heat value (LHV) flue gas over supported Pt catalysts showed that combustion resulted in significant CO generation between air equivalence ratio values of 0.40-0.75. An evaluation of several Pt bimetallic catalysts for substoichiometric combustion of LHV flue gases is also presented. The production of CO was a function of several other variables, such as the catalyst characteristics which included its preparation procedure and Pt concentration.

ESR-Study of Palladium and Platinum Ions in Pd/MgO and Pt/MgO Catalysts

A. S. SASS, V. A. SHVETS, G. A. SAVEL'EVA, N. M. POLOVA and V. B. KAZANSKII, *Kinet. Katal.*, 1983, 24, (5), 1167-1172

The studies showed that reduced and thermovacuumed Pd/MgO catalysts have a large number of Pd⁺ ions. Adsorption of O₂ at 20°C on reduced samples, leads to a several fold increase in the concentration of Pd⁺ ions with simultaneous formation of anion radicals O₂⁻, stabilised on the cation support. During further oxidation at increased temperatures the O₂⁻ disappears and the concentration of Pd⁺ reaches 20-30%. At this stage Pd²⁺ surface ions are formed. The results showed the presence of paramagnetic Pt ions, Pt⁺, in the reduced Pt/MgO catalysts.

Hydroisomerisation of n-Hexane on Palladium Zeolite Catalysts with High Content of Silica

M. A. SHARIKHINA, A. N. LOGINOVA, V. G. DYRIN, M. E. LEVINTER, B. K. NEFEDOV and T. V. ALEKSEEVA, *Neftekhimiya*, 1983, 23, (14), 485-488

Studies of hydroisomerisation of n-hexane on Pd zeolite catalysts containing high SiO₂ content showed that the catalysts had better Pd distribution on the catalyst surface. The most active isomerisation catalysts were prepared by ionic exchange. The studied high SiO₂ content zeolite Pd catalysts gave 95% of the theoretically possible yield of isomers, at temperatures in the range of 320-360°C.

Metalated Benzyl Polystyrenes

D. E. BERGBREITER, B. CHEN, J. R. BLANTON and T. J. LYNCH, *Polymeric Materials Science and Engineering*, Proc. ACS Div. Polym. Sci. Eng., 1983, 49, ACS 186th Natl. Meet., Washington DC, 74-77

A new convenient route to alkali metal derivatives of polystyrene (PS) is reported. Pd/PS catalysts prepared using these alkali metal polystyrenes as catalyst precursors are described and their use in hydrogenation, decarbonylation and allylic substitution reactions is explained. Pd/PS has better selectivity than 1% Pd/C for alkyne versus alkene hydrogenation, and higher overall rates of terminal alkene hydrogenation. THF solvent should, in general be used in heterogeneous Pd hydrogenations.

Toluene Disproportionation and Transalkylation Reaction over Mordenite Zeolite Catalysts

J.-C. WU and K.-J. LEU, *Appl. Catal.*, 1983, 7, (3), 283-294

The catalytic activity of mordenite zeolite for the disproportionation and transalkylation reaction of toluene was studied in a continuous fixed-bed reactor. Pd and/or Cu were used as catalyst promoters. Without Pd, the catalyst showed fast decay. The best catalyst contained 8.7wt.% Cu and 0.69wt.% Pd. Optimal reaction conditions occurred at 480°C and 300psig pressure. The catalyst could be regenerated with air or steam at 600°C.

Competitive Hydrogenation of Alkyne-Alkene Mixtures on Palladium Catalysts

L. ČERVENÝ, NGUYEN THI THANH and V. RŮŽIČKA, *Chem. Prum.*, 1983, 33, (10), 513-517

Studies of the competitive hydrogenation of 2-octyne and 1-heptene on Pd supported catalysts and on modified Pd black were performed in the presence of methanol at 20°C and under H₂ at atmospheric pressure. The most selective was Pd black, followed by PdSiO₂ gel catalysts. Least active were catalysts supported on charcoal. A relationship between the selectivity of the hydrogenation and that of the competition between the hydrogenation of a double bond and its isomerisation was found.

Rhodium-Catalysed Hydrogenation of Allene as Revealed by [¹⁴C] Propylene and [¹⁴C] Carbon Monoxide Tracer Studies

N. C. KUHNEN, S. J. THOMSON and G. WEBB, *J. Chem. Soc., Faraday Trans.*, 1983, 79, (9), 2195-2210

Studies of the low pressure hydrogenation of allene over Rh/Al₂O₃ catalysts during a series of hydrogenation reactions showed that the activity of the catalyst progressively decreased to a steady-state value and thereafter remained constant. Adsorption of ¹⁴C CO showed that, while this decrease in activity corresponded to the progressive build-up of a surface hydrocarbonaceous layer, the combined effects of allene and H₂ on a CO-precovered surface led to an increase in the capacity for CO adsorption.

Indirect Effect of the Strong Metal-Support Interaction on the Metal-Metal Interaction in Rh-Ag/TiO₂ Catalysts

D. E. RESASCO and G. L. HALLER, *Appl. Catal.*, 1983, 8, (1), 99-107

An indirect support effect on the bimetallic interaction has been observed on Rh-Ag/TiO₂ catalysts, compared to Rh-Ag/SiO₂. This effect occurs at significantly lower temperatures than the SMSI between Rh and TiO₂. There is a pronounced decay in the H₂ chemisorption capability and activity for ethane hydrogenolysis with time, when catalysts are left in flowing H₂ at 523K.

Effect of SMSI (Strong Metal-Support Interaction) Behaviour on CO-H₂ Reaction over Supported Rh Catalysts

H. ORITA, S. NAITO and K. TAMARU, *J. Chem. Soc., Chem. Commun.*, 1983, (18), 993-994

The catalytic activity and selectivity in the CO-H₂ reaction over supported Rh catalysts, such as RhCl₃/TiO₂, were investigated by changing reduction temperatures, supports and doping alkali metal cations; the reduction at 723K of TiO₂-supported catalysts decreased not only the amount of H adsorption but also the CO conversion.

Effects of Loading on Structure of Rh Zeolite Catalysts and Their Activity for Methanol Carbonylation

S. L.-T. ANDERSSON and M. S. SCURRELL, *Zeolites*, 1983, 3, (3), 261-270

Rh/X zeolites, prepared from RhCl₃ and (Rh(NH₃)₅Cl)₂ by ion exchange at room temperature, were studied with ESCA, volumetric CO adsorption and measurements of activities for carbonylation of methanol. The zeolites are predominantly exchanged with RhCl(H₂O)₃⁺ and Rh(NH₃)₅Cl²⁺, respectively. A surface Rh enrichment is seen, particularly at low metal loadings. A more homogeneous distribution at higher loadings occurs with a reduced CO:Rh ratio and a lower carbonylation activity. The highest unit Rh activity occurs for ~2Rh atoms per unit cell in the surface layer, and CO:Rh < 2.0. Lower unit activity (higher Rh loading) occurs at ~5-10Rh atoms per unit cell in the surface layer and lower CO:Rh.

Effects of Various Pretreatments of the Rh-Y Zeolite on the Catalytic Activity for Ethylene Hydroformylation under Atmospheric Pressure

N. TAKAHASHI, S. HASEGAWA, N. HANADA and M. KOBAYASHI, *Chem. Lett. Jpn.*, 1983, (7), 945-948

The active species for ethylene hydroformylation formed in the Y zeolite are extremely stable under reaction conditions and the steady activity lasts more than one month. The catalytic activity of the Rh/Y zeolite is remarkably affected by catalyst pretreatment; the He-H₂ pretreatment at 338-453K enhances the activity while the He-CO or He-CO-C₂H₄ pretreatment at 400K reduces it.

Supported Transition Metal Compounds. I. A New Method for the Preparation of Alumina-Supported Iridium and Osmium Carbonyls

J. E. CRAWFORD, G. A. MELSON, L. E. MAKOVSKY and F. R. BROWN, *J. Catal.*, 1983, 83, (2), 454-463

An extraction technique for the preparation of Al₂O₃-supported Ir and Os carbonyls, from Ir₄(CO)₁₂ and Os₃(CO)₁₂ is reported. The metal carbonyl species produced are highly dispersed and less than 50Å in diameter. Partial decarbonylation of the metal carbonyls can be effected by varying the preparation conditions and by heating in air. Metal carbonyl species-support interactions are reported.

Ruthenium Tetroxide Catalysed Oxidation of Illinois No. 6 Coal and Some Representative Hydrocarbons

L. M. STOCK and K.-T. TSE, *Fuel*, 1983, 62, (8), 974-976

The use of RuO₄ for the catalytic oxidation of coal molecules under mild conditions has been examined. The selectivity of the reagent for aromatic nuclei has been assessed by a study of the oxidation of selected benzene, naphthalene and phenanthrene derivatives. The catalysed oxidation of Illinois No. 6 coal was studied and preliminary results suggest that this oxidant is effective for the selective oxidation of the aromatic structures in this coal.

Support and Cluster Effects on Synthesis Gas Conversion with Supported Ruthenium Clusters

R. PIERANTOZZI, E. G. VALAGENE, A. F. NORDQUIST and P. N. DYER, *J. Mol. Catal.*, 1983, 21, 189-202

Studies of [Ru₃(CO)₁₂] and [H₄Ru₄(CO)₁₂] supported on Al₂O₃ and MgO showed a significant CH₃OH production for synthesis over [Ru₃(CO)₁₂]/MgO catalyst. After catalysis the anionic cluster [Ru₆C(CO)₁₆]²⁻ was identified on the catalyst, which resulted from the reaction of [HRu₃(CCO)₁₁]⁻ and [Ru₆(CO)₁₈]⁻, originally present on the support, with CO + H₂. [H₄Ru₄(CO)₁₂] supported on Al₂O₃ and MgO also resulted in significant oxygenate yields from CO + H₂. The oxygenate selectivity resulted in the presence of intact metal clusters on the surface.

On the State of Ru and Co in Mono- and Bimetallic Supported Catalysts

G. V. ANTOSHIN, E. S. SHPIRO, V. N. BELYATSKII, O. P. TKACHENKO and KH. M. MINACHEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (8), 1913-1917

Studies of the state of Ru and Co on deposited catalysts in dependence on the nature and treatment of the catalysts showed that Ru and Co reacted more strongly with Al₂O₃ than with SiO₂. This is explained by the higher degree of Ru and Co reduction on SiO₂ and also by the difference in energy state of Ru in the initial monometallic samples. The interchangeable behaviour was observed in trimetallic catalysts which resulted in easier reduction of metals compared to the mono systems.

New Catalysts for the Indirect Liquefaction of Coal

G. A. MELSON, *Q. Tech. Rep.*, Nov. 1, 1982–January 31, 1983; February 1, 1983–April 30, 1983; *NTIS Chem.*, 18 Oct. 1983, 965

Ru/ZSM-5 catalysts were prepared and characterised. The metal species was determined as RuO₂, though Ru was also detected by ESCA during the catalytic evaluation. The catalysts were examined for their ability to catalyse synthesis gas conversion. Liquid hydrocarbons were produced. The aromatic products from the 0.98% catalyst were consistently higher than the 2.88% and 7.32% samples. Thus, if gasoline high in aromatics is required the 0.98% Ru/ZSM-5 would warrant further study. Peak oil production occurred at 260 to 280°C.

Some Observations on the RuCl₃/PR₃ Catalyzed Conversion of Primary Amines to Secondary Amines

C. W. JUNG, J. D. FELLMANN and P. E. GARROU, *Organometallics*, 1983, **2**, (8), 1042–1044

Close examination of the RuCl₂(PPh₃)₃ catalysed synthesis of secondary amines from primary amines revealed benzene formed via PPh₃ decomposition during the reaction. RuCl₃/PBu₃ generates a much more active and stable system. Ratio studies show imine hydrogenation occurs ~200 times faster than the overall reaction, indicating that amine dehydrogenation is probably the rate determining step. Reactions under D₂ reveal deuteration of the α-C of the alkyl amines. A mechanism is proposed.

Activation and Activity of Ruthenium on Silica Hydrogenation Catalysts

P. G. J. KOOPMAN, A. P. G. KIEBOOM and H. VAN BEKKUM, *Recl. Trav. Chim. Pays-Bas*, 1983, **102**, (10), 429–432

Studies of the activation of RuCl₃-impregnated SiO₂ by H₂ treatment at high temperature of up to 700°C were made by H₂ desorption. Upon direct reduction, sintering hardly occurred, whereas the Ru metal surfaces increased at higher activation temperature due to the removal of Cl⁻ impurities from the Ru surface. Activity measurements of Ru catalysts for the liquid-phase hydrogenation of benzene and cyclohexene showed the favourable effect of the high-temperature reduction of RuCl₃/SiO₂.

HOMOGENEOUS CATALYSIS

The Platinum Catalyzed Reduction of Nitroarenes to Aminoarenes with Carbon Monoxide and Water

Y. WATANABE, Y. TSUJI, T. OHSUMI and R. TAKEUCHI, *Tetrahedron Lett.*, 1983, **24**, (38), 4121–4122

Nitroarenes were easily transformed to aminoarenes in excellent yields with CO and H₂O over PtCl₂(PPh₃)₂-SnCl₄-Et₃N catalyst under mild conditions. Triethylamine, SnCl₄ and PPh₃ are essential for the high catalytic activity. Nitroarenes are reduced chemoselectively by this procedure.

Transition Metal Nitrosyls in Organic Synthesis and in Pollution Control

K. K. PANDEY, *Coord. Chem. Rev.*, 1983, **51**, (1), 69–98

A review is given of platinum group metal nitrosyls in organic synthesis including oligomerisation, polymerisation of olefins, homogeneous hydrogenation of unsaturated compounds and of their potential in pollution control. (143 Refs.)

The Electrolytic Maintenance of Homogeneous Catalytic Activity

J. B. DAVISON, P. J. PEERCE-LANDERS and R. J. JASINSKI, *J. Electrochem. Soc.*, 1983, **130**, (9), 1862–1865

The lifetimes of homogeneous Pd and Ni catalysts used in the cyanation of aryl chlorides were increased several fold by the application of a reducing potential. Catalytically inactive metal species formed in deleterious side reactions with cyanide were electrochemically intercepted and restored to a catalytically active state. The low number of electrons consumed per mol was 0.06–0.25 for Pd, suggesting that the charge consumed was only used to maintain catalyst activity. The low power consumption makes electrolytic maintenance attractive for prolonging catalyst lifetimes.

Role of Palladium Catalyst in the Synthesis of N-Heterocycles

Y. OHSHIRO and T. HIRAO, *J. Synth. Org. Chem., Jpn.*, 1983, **41**, (7), 605–618

Pd catalysed or promoted reactions, providing a versatile and selective method for the synthesis of heterocyclic compounds are discussed, and the role of Pd complexes in the synthesis of N-heterocycles is surveyed. (82 Refs.)

The Ruthenium Complex Catalyzed N-Heterocyclization of Aminoarenes to Quinoline Derivatives Using Allylic Alcohols and Aliphatic Aldehydes

Y. WATANABE, Y. TSUJI, Y. OHSUGI and J. SHIDA, *Bull. Chem. Soc. Jpn.*, 1983, **56**, (8), 2452–2457

Aminoarenes reacted with 2-propen-1-ol and 2-buten-1-ol at 180°C to give quinoline derivatives in fairly good yields over Ru complex catalysts. Dichlorotris(triphenylphosphine)Ru was found to be the most effective catalyst. The aldehydes reacted with aminoarenes to give Schiff-base dimers which were then cyclised in the presence of the Ru complex catalyst to the quinolines. The ortho-metallated species were proposed, as key intermediates.

The Water Gas Shift Reaction Catalyzed by Ruthenium Carbonyl Complexes

K. TANAKA, M. MORIMOTO and T. TANAKA, *Chem. Lett. Jpn.*, 1983, (6), 901–904

A new method for preparing [Ru(bpy)₂(CO)Cl]⁺ (bpy = 2,2'-bipyridine) and its use in the water gas shift reaction is reported. A cyclic mechanism is proposed to proceed via [Ru(bpy)₂(CO)₂]²⁺, [Ru(bpy)₂(CO)(COOH)]⁺ and [Ru(bpy)₂(CO)H]⁺ as intermediates. The former two were isolated.

Bimetallic Phase Transfer Catalysis

H. ALPER and J.-F. PETRIGNANI, *J. Chem. Soc., Chem. Commun.*, 1983, (20), 1154-1155

γ -Keto acids are obtained by the phase transfer catalysed reaction of alkynes with CO and CH_3I in the presence of catalytic amounts of Ru and Co carbonyl complexes. This is the first example of bimetallic phase transfer catalysis where the reaction does not occur with either metal complex alone.

Homogeneous Catalysts for Carbon Dioxide/Hydrogen Activation Alkyl Formate Production Using Anionic Ruthenium Carbonyl Clusters as Catalysts

D. J. DARENSBOURG, C. OVALLES and M. PALA, *J. Am. Chem. Soc.*, 1983, **105**, (18), 5937-5939

The catalytic hydrocondensation of CO_2 and H_2 by $\text{HRu}_3(\text{CO})_{11}$ or $\text{HCO}_2\text{Ru}_3(\text{CO})_{10}$ clusters in the presence of methanol to provide methyl formate is reported. At the end of the run the catalyst had changed to $\text{H}_3\text{Ru}_4(\text{CO})_{12}$ which was slightly more effective at catalysing the production of methyl formate, with a turnover rate of 7.3.

ELECTRICAL AND ELECTRONIC ENGINEERING

Gate Controlled Amplifier for Platinum NMR Thermometry

Y. JINZAKI, Y. OKUDA and A. J. IKUSHIMA, *Cryogenics*, 1983, **23**, (6), 321-324

The free induction decay signal of the nuclear spin of Pt was measured for use in thermometry. The maximum value of the spin-spin relaxation time observed in Pt is $\sim 1\text{ms}^2$, which becomes shorter if there is inhomogeneity in the static or transient magnetic field. Circuitry for detecting Pt nuclear susceptibility was developed and is described. The system is used for nuclear thermometry < 30 mK.

NEW PATENTS

METALS AND ALLOYS

Multilayered Amorphous Alloy

TOKYO SHIBAURA DENKI K.K. *European Appl.* 90,973

Multiple layers are produced by feeding a sequence of molten metals or alloys on to the surface of a roll rotating at high speed so that the metal solidifies. In one example one of the layers consists of Pd alloyed with 20% Si. The alloy structures may be used for superconductors, springs and latch relays.

Electrical Contact Alloy

YU. F. SHEVAKIN ET AL *U.S. Patent* 4,380,528

A contact alloy of high strength, elasticity and corrosion resistance contains 5-30% Pd, 0.1-0.5% Mg, 0.01-0.5% Al, remainder Ag.

Stability of Pd/Nb₂O₅/Amorphous Hydrogenation Silicon Solar Cells

V. PREMACHANDRAN and S. GUHA, *Solar Cells*, 1983, **9**, (3), 203-208

The stability of Pd/Nb₂O₅/amorphous hydrogenated Si solar cells was investigated. Heat treatment in vacuum at 70°C increased the saturation current density and reduced the open-circuit voltage to values close to those for Pd Schottky structures. Further deterioration in the characteristics take place on exposure to H₂.

Formation of Nickel and Palladium Silicides by a Short-Pulse Light-Flash and Its Application in the Metallization of Solar Cells

J. T. LUE, *Solid-State Electron.*, 1983, **26**, (8), 787-793

Si-rich compounds not reproducible by conventional furnace annealing can be formed by a short-pulse light flash. Pd is chemically deposited on Si wafers which are then thermally annealed before being Ni plated. A rather stable Pd₂Si is obtained after sintering the sample near 350°C. The Pd silicide acts as a buffer layer to impede the Ni diffusion. This method of manufacture gives comparable characteristics to those obtained by the Ti-Pd-Ag alloy method.

Electron Tunneling and Hopping Possibilities in RuO₂ Thick Films

N. C. HALDER, *Electrocomponent Sci. Technol.*, 1983, **11**, (1), 21-34

A proposal that the TCR in thick film resistors arises from the usual particle-to-particle conduction, electron tunnelling and phonon-assisted hopping is suggested. Equations for activation energies are derived for the temperature minimum of the resistance with and without hopping. New equations for TCR are suggested. RuO₂ thick film resistors have been used to test the TCR and activation energy, and the results agree with the evidence.

ELECTROCHEMISTRY

Electrolytic Cell Electrodes

IMI MARSTON LTD. *British Appl.* 2,113,718A

A cell such as a hypochlorite cell is operated with one anode consisting of a Ti base coated with platinum group metal and two cathodes made of TiO_x. One cathode is used while the other is being cleaned by local acid generation.

Corrosion Protection Anode

ORONZIO DE NORA IMPIANTI ELETTROCHIMICI S.p.A. *European Appl.* 84,875

Platinum group metal-coated valve metal anode elements are used in a new design of linear anode structure for cathodic protection.