

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Kinetics of the Reaction between NO and CO on Polycrystalline Platinum at Low Pressure. II. Interpretation of an Elementary Reaction Sequence

W. ADLHOCH and H.-G. LINTZ, *Surface Sci.*, 1978, 78, (1), 69-78

The reaction between NO and CO on polycrystalline Pt is described by elementary steps including molecular adsorption and desorption of the reactants, dissociation of adsorbed NO to N₂ and atomic O, and finally reaction of this atomic O with CO to form CO₂.

Interactions between Cr and Pt Films: New Cr-Pt Phases

J. BAGLIN, F. D'HEURLE and S. ZIRINSKY, *J. Electrochem. Soc.*, 1978, 125, (11), 1854-1859

Diffusion between Cr and Pt thin films revealed two distinct ordered phases, CrPt₃ and CrPt, which had not previously been recorded in phase diagrams. CrPt₃ is ordered f.c.c. and CrPt is slightly tetragonal.

The Surface Composition of Platinum-Iridium Alloys

F. J. KUIJERS and V. PONEC, *Appl. Surf. Sci.*, 1978, 2, (1), 43-54

Pt-Ir alloys were prepared by evaporating the metals onto a quartz substrate and equilibration at 700K. Auger signal intensities of a monolayer of the elements were determined for the relevant peaks. A pronounced surface enrichment in Pt is observed, which agrees with theoretical predictions. Propane adsorption was also examined.

Improved High Temperature Mechanical Properties of Titanium Alloys by Platinum Ion Plating

S. FUJISHIRO and D. EYLON, *Thin Solid Films*, 1978, 54, (3), 309-315

Studies of the effect of Pt ion-plating on the elevated temperature properties of $\alpha + \beta$ Ti alloys showed that a thin ion-plated Pt layer provided effective oxidation protection and retained its adherence to the alloy surface up to 600°C. Both the creep and high cycle fatigue strengths of the coated alloys were greatly improved at both room and elevated temperatures. This is probably due to the thin Pt layer acting as an oxygen diffusion barrier and thus suppressing the transformation of the metastable β_1 , resulting in higher creep resistance. The compressive hardening of the alloy surface by ion plating is a proposed mechanism for the fatigue life improvement.

Very Active Hydrogenation Catalyst Composed of Extremely Dispersed Palladium on Vitreous Supports

G. COCCO and G. FAGHERAZZI, *J. Chem. Soc., Chem. Commun.*, 1978, (22), 979-980

Small-angle X-ray scattering was used to determine the particle size distribution of Pd metal supported on vitreous materials. The metal was found to be highly dispersed and this is linearly related to the catalytic activity in hydrogenation reactions and to the physical and chemical properties of the support.

On the Growth Kinetics and Structure of Pd₂Ge and PdGe

G. MAJANI, G. OTTAVIANI and A. ZANI, *J. Non-Cryst. Solids*, 1978, 29, (3), 301-309

The growth of PdGe and Pd₂Ge compounds was investigated by analysis of annealed samples of 1000-3000Å thick Pd on single-crystal or amorphous Ge substrates. The growth rates for the two are different, but their compound grain sizes are the same thus invalidating the hypothesis that grain boundary diffusion controls the formation. It is concluded that the growth of the compounds is a diffusion-limited process and that the same mechanism is responsible for the growth. The different growth rates may be due to a different stoichiometry.

Magnetostriction and Magnetic Anisotropy of Ni and Ni-Pd Alloys

T. TOKUNAGA and H. FUJIWARA, *J. Phys. Soc. Japan*, 1978, 45, (4), 1232-1238

Magnetostriction constants of Ni-Pd alloys containing 0-99 at.% Pd were measured at above 77K. The lower magnetostriction constants at 0K, found by extrapolation, increase in magnitude with increasing Pd and reach a maximum at ~70 at.% Pd. Magnetostriction, which may occur since the magnetic anisotropy energy depends on the strain in the crystal, may give useful information about the spin-orbit interaction.

Transport Properties of Osmium Single Crystals at High Temperatures

E. M. SAVITSKII, P. V. GELD, V. E. ZINOVEV, N. B. GORINA, V. I. SPERELUP, V. P. POLYAKOVA and A. L. SOKOLOV, *Phys. Status Solidi A*, 1978, 49, (2), K117-K120

The temperature dependence of the electrical resistivity (ρ) between 290 and 1600K, and the thermal diffusivity between 900 and 3300K of Os single crystals were investigated. At temperatures over 1000K the anisotropy of the transport properties steadily decreases, although the crystal

lattice remains hexagonal. The ρ (T) curve has opposite curvatures along and perpendicular to the hexagonal axis, and this has not been noticed for other transition metals.

CHEMICAL COMPOUNDS

Inorganic Optical Activity

R. D. GILLARD and F. L. WIMMER, *J. Chem. Soc., Chem. Commun.*, 1978, (21), 936-937

Optically active crystals of $(\text{NH}_4)_2[\text{Pt}(\text{S}_6)_3]$ were synthesised, and found to contain an excess of one enantiomer. The maximum optical rotation in aqueous solution observed at 546 nm was 1910° , and this is thought to be the first inorganic example of a spontaneous second-order asymmetric transformation. Decomposition to $[\text{PtS}_{10}]^{2-}$ takes place over several days. Optical activity disappears upon dissolution in an ammonium polysulphide solution.

Anionic Complexes of Pt(II) Containing Urea, and Their Antitumoral Properties

A. I. STETSENKO, L. S. TIKHONOVA, M. A. PRESNOV and A. L. KONOVALOVA, *Dokl. Akad. Nauk S.S.S.R.*, 1978, **243**, (2), 381-384

Spectroscopic studies of the reaction of $[\text{PtUr}_2\text{Cl}_2]$ with urea (Ur) in alkaline media K_2CO_3 or $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (pH 9.5), which also optionally contained AgNO_3 or TiNO_3 , showed the formation of complexes $M[\text{Pt}_2\text{Ur}_2(\text{Ur-H})_2(\text{OH})_3]$ where $M = \text{Na}^+$, K^+ , Ag^+ or TI^+ . The complexes are stable in the aqueous solution and their toxicity is not very high; their lethal dose being > 500 mg/kg. The possibility of their use as anti-tumour agents is discussed.

On Some New Co-ordination Compounds of Platinum(II) and Palladium(II) with Multidentate Thioethers

M. SCHMIDT and G. G. HOFFMAN, *Z. Anorg. Allgem. Chem.*, 1978, **445**, (8), 167-174

Reactions of seven synthesised trithioethers with K_2PtCl_4 and K_2PdCl_4 lead to a formation of new co-ordination compounds. In eight cases soluble ring shaped molecules with two metal-S bonds were obtained, whereas in two other cases metal-N co-ordination formed soluble polymeric products.

Palladium(II) Complexes of Diphenylphosphineacetic Acid

J. RČIČKOVÁ and J. PODLANOVÁ, *Coll. Czech. Chem. Commun.*, 1978, **43**, (11), 2853-2861

Reaction of Pd(II) with diphenylphosphineacetic acid (HA) resulted in the formation of trans-square planar $\text{PdX}_2(\text{HA})_2$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{S}$ -bonded SCN) and trans-planar halide (thiocyanate) bridged dimers $\text{Pd}_2\text{X}_4(\text{HA})_2$ complexes, both containing HA as a monodentate P-donor. The extremely stable square planar complex $\text{PdA}_2(\beta_2 > 10^{89})$ with bidentate A-ligands was formed in neutral solutions.

On Polyphosphides of Chromium, Manganese, Ruthenium and Osmium. Synthesis and Crystal Structure of RuP_4 and OsP_4

D. J. BRAUN and W. JEITSCHKO, *Z. Anorg. Allgem. Chem.*, 1978, **445**, (8), 157-166

The new compounds RuP_4 and OsP_4 were prepared by annealing the components in the presence of iodine. Well developed crystals were obtained by reaction of the components in liquid Sn. RuP_4 was found to be triclinic, space group $\text{P}\bar{1}$, with $a = 7.519(8)$, $b = 7.145(7)$, $c = 4.713(5)\text{Å}$, $\alpha = 100.48(10)$, $\beta = 90.35(10)$, $\gamma = 111.08(11)^\circ$, $Z = 3$. Ru is octahedrally surrounded by P. All near neighbour interactions are interpreted as two-electron bonds.

Arene-Transition Metal Complexes. I. Site Exchange and Chemical Characteristics of $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$

M. Y. DARENSBOURG and E. L. MUETTERTIES, *J. Am. Chem. Soc.*, 1978, **100**, (23), 7425-7428

Spectroscopic and chemical studies for the Ru complex have established a unique alane catalysis of a new fluxional process. The addition of trimethylaluminium to this catalytic system raises the rate of arene hydrogenation by a factor of 4 to 5. Cyclohexene production was suppressed by the alane, and the alane stabilises the Ru complex in the reaction. Thus alane qualitatively alters the character of the hydrogenation.

"Capped" Tri-ruthenium Carbonyl Cluster. X-Ray Crystal Structure of $[\text{Ru}_3(\text{CO})_9\{\text{MeSi}(\text{PBu}_2)_3\}]$

J. B. DE BOER, J. A. VAN DOORN and C. MASTERS, *J. Chem. Soc., Chem. Commun.*, 1978, (22), 1005-1006

A relatively stable tri-metallic cluster compound, $[\text{Ru}_3(\text{CO})_9\{\text{MeSi}(\text{PBu}_2)_3\}]$ was prepared from $\text{MeSi}(\text{PBu}_2)_3$ and $\text{Ru}_3(\text{CO})_{12}$. When compared with $\text{Ru}(\text{CO})_{12}$ this cluster is more resistant to dissociation into monomeric species when treated with mixtures of H_2 and CO at 100 bar pressure and 300°C . Transition metal clusters are potential homogeneous catalysts.

Mixed Phosphine 2,2'-Bipyridine Complexes of Ruthenium

B. P. SULLIVAN, D. J. SALMON and T. J. MEYER, *Inorg. Chem.*, 1978, **17**, (12), 3334-3341

Two types of mixed complex, $[(\text{bpy})_2\text{Ru}(\text{PPh}_3)\text{Cl}]^+$ and $[(\text{bpy})_2\text{Ru}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)]^{2+}$ were prepared from the appropriate ligand and $(\text{bpy})_2\text{RuCl}_2$ (bpy = 2,2'-bipyridine). Electronic spectral and redox properties indicate that the P ligands stabilise the Ru(II) forms of these ions more than pyridine-type ligands, which agrees with the π -acid nature of the phosphine ligands. The chemical stability and high reduction potentials for the Ru(III) type ions make them ideal as stoichiometric oxidants in chemical syntheses.

ELECTROCHEMISTRY

On the Normal Oxygen Potential at a Platinum-Oxygen Alloy Diaphragm Electrode

J. P. HOARE, *J. Electrochem. Soc.*, 1978, **125**, (11), 1768-1771

Pt foil electrodes clamped between the compartments of a dual Teflon cell enabled the rest potential on the frontside of the Pt diaphragm in contact with O₂-saturated 2N H₂SO₄ to be observed, while the back was in contact with aerated concentrated HNO₃. A potential of 1.227V was observed on a 0.00127cm thick Pt foil after 54 h in contact with HNO₃ and 1.221 V on a 0.00762cm thick foil after 358 h. This is the first time that the reversible potential has been reported on a prerduced Pt surface.

Oxidation of Formaldehyde during Heterogeneous Catalytic Decomposition of Hydrogen Peroxide on Pt/Pt Catalyst

I. V. MASHNIKOV, G. I. ELFIMOVA and G. A. BOGDANOVSKII, *Zh. Fiz. Khim.*, 1978, **52**, (11), 2976-2978

Studies of the heterogeneous catalytic decomposition of H₂O₂ on platinised Pt electrode catalysts were performed in H₂SO₄ containing formaldehyde at 35°C. Oxidation of formaldehyde was very intensive resulting mainly in the formation of formic acid (60-70%) with a total conversion of 90%. Data obtained on influence of pH and Hg on the reaction are given.

Effect of Platinum Group Metals on Electro-catalytic Characteristics of Nickel Catalysts

D. V. SOKOL'SKII, P. I. ZABOTIN and C. V. DRUZ', *Zh. Fiz. Khim.*, 1978, **52**, (11), 2950-2951

The effect of the addition of Pt, Pd or Rh on the electrolytic characteristics of Ni catalysts was studied during oxidation in 2N KOH at 30°C. A significant increase in the activity of Ni catalysts covered with micro amounts of Pt group metals was observed, Pt being the best promoter. The maximum specific activities obtained were 150×10^{-7} for Pt, 30×10^{-7} for Rh and 14×10^{-7} A/cm² for Pd.

Electrolytic Hydrogen Isotope Separation Factors and Efficiency of Exchange between D₂O and Hydrogen (Protium) at Palladium Electrodes

F. A. LEWIS, W. F. N. LEITCH and A. MURRAY, *Surface Technol.*, 1978, **7**, (5), 385-399

The electrolytic hydrogen isotope separation factor $S_{D(ads)}$ (H/D absorbed by Pd) was measured at 25°C using Pd wire electrodes in the α -phase region of the Pd/H system. Values for $S_{D(ads)}$ of ~ 9.5 were obtained in 1N 50:50 H₂SO₄:D₂SO₄ solutions with pre-oxidised surfaces which exhibited a high catalytic activity for H isotope exchange with the surrounding solution.

Investigations of the Electrochemical Reduction of Hydrogen Ions on Palladium Electrodes

E. G. DAFPT, K. BOHNENKAMP and H.-J. ENGELL, *Z. Phys. Chem. (Frankfurt)*, 1978, **108**, (1), 33-44

The kinetics of the electrochemical reduction of H ions on α - and β -Pd electrodes were studied in H₂SO₄. The H activity with α -Pd was calculated from the H-permeation current through the Pd foils. Additions of As₂O₃ to the electrolyte strongly inhibit the Volmer reaction. The stationary H concentration and the diffusion coefficient were determined by separate experiments.

Interactions of Rhodium and Rh₂O₃ with Hydrogen Chloride

A. I. PYUMIN and YA. I. IVASHENTSEV, *Zh. Priklad. Khim.*, 1978, **51**, (9), 1921-1924

Studies of the interaction of metallic Rh and Rh₂O₃, prepared by calcination of RhCl₃·5H₂O at 900°C, with gaseous HCl were carried out at elevated temperatures. Metallic Rh was practically unreactive with HCl at 20-1000°C while the reaction of Rh₂O₃ with HCl at up to 650°C yielded RhCl₃. Increasing the volume of HCl in the stream from 10 to 40% considerably increased the rate of chlorination of Rh₂O₃. Decomposition of RhCl₃ was observed at 600°C and a similar decomposition was observed in the stream of inert gas (Ar).

Electrochemical Oxidation and Reduction of the RuO₂/Ti Electrode Surface

K. DODLHOFFER, M. METIKOŠ, Z. OGUMI and H. GERISCHER, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, (10), 1046-1050.

Thin homogeneous RuO₂ film electrodes, prepared on highly polished Ti surfaces by thermal decomposition of Ru salts, were studied by electrochemical techniques. The oxidation state of the surface of Ru atoms was found to change in the potential range between H₂ and O₂ evolution from +2 to +6 in 1M H₂SO₄. Hydrogen adsorption is proposed at potentials more cathodic than +0.4V. The associated bulk diffusion processes are discussed.

The Oxygen Electrode Reaction in Alkaline Solutions on Oxide Electrodes Prepared by the Thermal Decomposition Method

M. H. MILES, Y. H. HUANG and S. SRINIVASAN, *J. Electrochem. Soc.*, 1978, **125**, (12), 1931-1934

The effectiveness of various metal oxide electrodes toward O₂ evolution during water electrolysis was studied and found to decrease in the order Ru > Ir ~ Pt ~ Rh ~ Pd ~ Ni ~ Os >> Co >> Fe. When mixed with 70 mol % TiO₂ all metal oxides except RuO₂ were ineffective in catalysing the reaction. RuO₂ films on Ti require $\sim 10^{-6}$ mol RuO₂/cm² to mask the effect of the Ti substrate.

Oxygen Evolution from Water via Redox Catalysis

J. KIWI and M. GRÄTZEL, *Angew. Chem. Internat. Ed. En.*, 1978, **17**, (11), 860-861

The first evidence that O_2 production by the reaction $4D^+ + H_2O \rightarrow 4D + 4H^+ + O_2$ can be mediated by redox catalysts PtO_2 or IrO_2 is reported, the D^+/D system being Ce^{4+}/Ce^{3+} . The Ce^{3+} produced can regenerate Ce^{4+} photochemically with simultaneous production of H_2 . The reduction of $Ru(bpy)_3^{3+}$ by water, promoted by PtO_2 or IrO_2 , to produce O_2 also occurred. $Ru(bpy)_3^{3+}$ can be regenerated by light with the evolution of H_2 .

LABORATORY APPARATUS AND TECHNIQUE

A Metallic Glass Tip—A Promising Field Electron Emission Source

H. HEINRICH, T. HAAG and J. GEIGER, *J. Phys. D, Appl. Phys.*, 1978, **11**, (17), 2439-2442

A method for etching field emission tips from $Pd_{77.5}Si_{16.5}Cu_6$ glass wire welded to a Ta hairpin support is described. The field electron emission from these tips is sufficiently stable at 10^{-9} torr, and is confined to a cone of half-angle 0.15 rad for a total emission current of about 15 A.

JOINING

Ultrasonic Ball/Wedge Bonding of Aluminium Wires

C. J. DAWES, *Weld. Inst. Res. Bull.*, 1979, **20**, (1), 9-14

Ball/wedge ultrasonic bonding, which is at present used to connect microcircuit chips to external circuitry, was examined using 25 μ m diameter Al wire welded to Pd-Ag thick films, Al thin films and Au flashed Kovar. All bonds had good mechanical strength, the shear strength for Pd-Ag, up to 800 mN, being the greatest.

HETEROGENEOUS CATALYSIS

Methylene Chloride from Chloroform by Hydrochlorination

D. A. DODSON and H. F. RASE, *Ind. Engng. Chem. Product Res. Dev.*, 1978, **17**, (3), 236-240

Three reforming catalysts ($Pt-Re/Al_2O_3$, Pt/Al_2O_3 and $Pd/charcoal$) were compared on the basis of activity, activity maintenance, and selectivity in the hydrochlorination of chloroform to yield methylene chloride. The Pd catalyst deactivated rapidly due to coke formation and sintering of the Pd. Both Pt/Al_2O_3 and $Pt-Re/Al_2O_3$ had long life, the former being more active under the studied conditions. A coke deposit which caused a decline in activity was successfully removed by regeneration with O_2 .

Reaction Mechanism of Methylcyclopentane Ring Opening over a Bifunctional Pt/Al_2O_3 Catalyst

E. G. CHRISTOFFEL and K.-H. RÖBSCHLÄGER, *Ind. Engng. Chem. Product Res. Dev.*, 1978, **17**, (4), 331-334

Ring opening of methylcyclopentane and 1,2-dimethylcyclopentane over "fresh" and partially aged Pt/Al_2O_3 catalysts was studied in a microcatalytic fixed bed reactor by the pulse method. The reactions over the fresh catalyst yielded ring opening products from nonselective ring cleavage, and over partially aged catalyst yielded n-hexane and n-heptane as main products. At higher temperatures the primary formed ring opening products undergo secondary reactions, such as isomerisation and cracking.

Spurious Limit Cycles and Related Phenomena during CO Oxidation on Supported Platinum

P. VARGHESE, J. J. CARBERRY and E. E. WOLF, *J. Catalysis*, 1978, **55**, (1), 76-87

A study of CO oxidation on $Pt/\alpha-Al_2O_3$ was carried out in O_2 at 370-420K. Spurious limit-cycle phenomena resulting from trace impurities in the O_2 stream were observed. These phenomena could be suppressed by water vapour in the reaction mixture. Even low levels of impurities in the gas appear to provoke spurious behaviour.

On the Reactions of Surface Isocyanates over Platinum Catalyst

F. SOLYMOSI, J. KISS and J. SÁRKÁNY, *Magy. Kem. Foly.*, 1978, **84**, (10), 465-469

Reactions of isocyanates on Pt/Al_2O_3 were investigated by i.r. and mass spectroscopies. Their stabilities were dependent on the formation conditions, and decreased with the surface concentration of chemisorbed O_2 and with Pt content in the catalyst. The number of isocyanate species exceeded the number of Pt surface atoms, showing a significant proportion of isocyanate is located on the carrier. In the presence of water at 200-400°C the hydrolysis of surface isocyanate into NH_3 was almost complete.

The Effect of Alumina Properties on Pt/Al_2O_3 Selectivity in Dehydrogenation of n-Alkanes

G. A. TARASOVA, L. E. STARANNIKOVA and G. V. ISAGULYANTS, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (11), 2615-2618

The effect of Al_2O_3 properties on the selectivity of 0.25% Pt/Al_2O_3 catalysts (prepared by impregnation of three crystalline modified θ , γ and η Al_2O_3 carriers) was studied during n-alkane dehydrogenation in a quartz reactor. Selectivity of the catalysts in the dehydrogenation of n-decane and n-hexane to n-alkenes increased in order: $Pt/\eta-Al_2O_3 < Pt/\gamma-Al_2O_3 \ll Pt/\theta-Al_2O_3$.

Catalysts Obtained by Interaction of Organic Transition Metal Compounds with Support Surfaces. Calorimetric Study of Hydrogen and Oxygen Adsorption on Pt/SiO₂, W/SiO₂ and (W+Pt)/SiO₂ Catalysts

YU. D. PANKRAT'EV, E. M. MALYSHEV, YU. A. RYNDIN, V. M. TURKOV, B. N. KUZNETSOV and YU. I. ERMAKOV, *Kinet. Kataliz*, 1978, **19**, (6), 1543-1548
Calorimetric studies of H₂ and O₂ adsorption on Pt/SiO₂, W/SiO₂ and (W+Pt)/SiO₂ catalysts prepared by interaction of SiO₂ with Pt(π -C₄H₇)₂ and/or W(π -C₄H₇)₄ organic metal compounds, followed by their reduction in H₂ at 400 and 600°C, were performed. A substantial decrease in adsorption temperatures of H₂, and a sharp increase in O₂ adsorption temperature were observed on a catalyst of Pt with W²⁺ chemically fixed to the SiO₂ surface. Reasons behind the changes in adsorption and catalytic properties of Pt+W catalysts are discussed.

The Effect of the Support on the Formation and Stability of Surface Isocyanate on Platinum

F. SOLYMOSI, L. VÖLGYESI and J. SÁRKÁNY, *Ĵ. Catalysis*, 1978, **54**, (3), 336-344

The effects of SiO₂, MgO, Al₂O₃ and TiO₂ carriers on the formation and stability of isocyanate complexes in the NO + CO reaction on a Pt catalyst were investigated. Isocyanate formed most easily on Pt/TiO₂, but on other catalysts, particularly Pt/SiO₂ it was much slower. The stability of the isocyanate depended on the support; it decomposed rapidly on Pt/TiO₂, but was stable on Pt/SiO₂. Isocyanate is assumed to be formed either on Pt acceptor sites or from N atoms formed by dissociation on Pt which then migrate to the support and react with gaseous or adsorbed CO.

The Influence of Catalyst Preparation on the Structure and Physico-Chemical Properties of Platinum and Palladium Catalysts

A. B. FASMAN, V. YA. KITAIGORODSKAYA and A. P. GOROKHOV, *Kinet. Kataliz*, 1978, **19**, (5), 1243-1247

The phase composition, structure and physical properties of Pt and Pd catalysts prepared by the Frampton method were studied by techniques including chemical and X-ray analyses, and optical and electron microscopies. The influence of the modifying additions on the dispersion was also studied.

Isotopic Equilibration of Nitrogen on Potassium-Promoted Transition Metal Catalysts

K. URABE, A. OH-YA and A. OZAKI, *Ĵ. Catalysis*, 1978, **54**, (3), 436-438

The effect of adding K to Pt, Rh, Ru, Ir, Os, Fe, Ni, Co, Re or Mo supported on C and used for ammonia synthesis was studied. Ru-K/C was found to be outstandingly active, followed by Os-K/C, then Fe-K/C.

Hydrogenation of Dicyanobutene to Adiponitrile with Palladium-on-Charcoal

R. T. STIMEK and H. F. RASE, *Ind. Engng. Chem. Product Res. Dev.*, 1978, **17**, (3), 227-231

The deactivation of Pd/charcoal in the hydrogenation of dicyanobutene (DNB) to adiponitrile was studied in industrial conditions where all the three modes of deactivation occurred simultaneously. The catalyst was reversibly poisoned by H₂S generated from the charcoal, deactivated by a nitrogenous coke from DNB and deactivated by sintering. A means for reactivating the catalyst using H₂O addition was developed.

Ultrastable Zeolites as Catalysts for Hydrocracking n-Decane

M. STEIJNS, G. FROMENTS, P. JACOBS, J. UYTTERHOEVEN and J. WEITKAMP, *Erdöl Kohle*, 1978, **31**, (12), 581

Hydrocracking and hydroisomerisation of n-decane over ultrastable Y (US-Y) zeolite containing 0.5 wt.% Pt were investigated. Differences in reactions were ascribed to different catalysts, reactor types and pressures. The 0.5 Pt/US-Y zeolite is a highly active hydrocracking catalyst with all the features of 0.5 Pt/CaY in respect to the distribution of decane isomers. The catalyst has high activity at low reaction temperatures with the possibility of high isomerisation conversion and pure primary cracking.

Versatile Polymer-Bound Hydrogenation Catalyst. Anthranilic Acid Anchored Palladium(II) Catalysis

N. L. HOLY, *Ĵ. Org. Chem.*, 1978, **43**, (24), 4686-4688

Anchoring the bidentate ligand anthranilic acid to chloromethylated polystyrene beads, followed by refluxing with PdCl₂ results in a catalyst which can hydrogenate alkenes, dienes and benzene. The catalyst is stable in air and has a lifetime of at least 10,000 catalytic cycles per Pd atom.

Ready Hydrogenation of Nitrobenzene and Benzonitrile with a Polymer-Bound Palladium Catalyst

N. L. HOLY, *Ĵ. Chem. Soc., Chem. Commun.*, 1978, (23), 1074-1075

A polymer-bound catalyst has been discovered which provides the first example of hydrogenation of nitro and nitrile functional groups with a Pd^{II} catalyst. This is a significant departure from previous Pd chemistry, and catalyst activity is similar to the most active homogeneous catalysts.

Chemico-Physical Properties and Preparative Variables in Supported Metal Catalysts

G. R. TAUSZIK, *Chim. e Ind.*, 1978, **60**, (9), 737-742
A review is given of supported noble metal catalysts, their chemico-physical properties and variables during preparation. (63 Refs.)

Kinetics of the Ruthenium-Catalyzed Reduction of Nitric Oxide by Hydrogen

S. L. MATSON and P. HARRIOTT, *Ind. Engng. Chem. Product Res. Dev.*, 1978, **17**, (4), 322-328

The kinetics of reduction of NO by H₂ over a supported Ru catalyst were studied in integral and differential reactor tests at 100-350°C with reactant concentrations of 60-3200 ppm NO and 0.15-2.5% H₂. The reduction of NO was half order to H₂. Selectivity of NH₃ formation depended only weakly on NO concentration but increased with temperature in the range 100-200°C, reaching a maximum of ~50% and then declining at higher temperatures.

Activation of Nitrogen by Alkali Metal-Promoted Transition Metal. VIII. Reactivity of Sorbed Nitrogen on Ru-K/Al₂O₃ Catalyst

K. URABE, K. SHIRATORI and A. OZAKI, *J. Catalysis*, 1978, **55**, (1), 71-75

N₂ is absorbed by Ru-K/Al₂O₃, but hardly at all by Ru or K on Al₂O₃. Although the absorbed N₂ can be converted to NH₃ by H₂ treatment above ~270°C, the rate of hydrogenation is much slower than the rate of NH₃ synthesis on the catalyst. Isotopic mixing between the sorbed and gaseous N₂ also becomes detectable above ~270°C.

An Infrared Spectroscopic Study of the Formation of Isocyanate Species on Ru/Al₂O₃

F. SOLYMOSI and J. RASKÓ, *Magy. Kem. Foly.*, 1978, **84**, (9), 430-432

The formation of isocyanate surface complexes on reduced and oxidised Ru/Al₂O₃ was studied by i.r. spectroscopy. Bands indicative of the formation of surface isocyanate complexes appeared at 2265 and 2244 cm⁻¹. The optimum temperature of isocyanate formation is 250°C. The composition of the reacting gas mixture greatly influences isocyanate formation. At 250°C a maximum intensity was obtained at a NO:CO ratio of 1:5. The unique behaviour of Ru in the catalytic reduction of NO and the characteristics of the isocyanate formation on reduced and oxidised Ru have been correlated.

Steady-State Oxidation of Carbon Monoxide over Supported Noble Metals with Particular Reference to Platinum

N. W. CANT, P. C. HICKS and B. S. LENNON, *J. Catalysis*, 1978, **54**, (3), 372-383

Activation energies, kinetic orders and relative activities were determined for the oxidation of CO by O₂ over five supported noble metal catalysts. For Ru, drifts in reaction rate occurred for many hours following pressure and temperature changes, but the initial responses were qualitatively similar to the behaviour for Ir, Rh and Pd. Pt had the lowest activation energy.

Deuterium Exchange with Hydrogen on the Surface of Zeolite Catalysts. V. Palladium Containing Zeolites

KH. M. MINACHEV, A. N. DETYUK, R. V. DMITRIEV and P. I. SLYUNYAEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (12), 2678-2682

Studies of D₂ exchange with H₂ over 0.1, 1.0 or 3.0 wt.% Pd/zeolite catalysts prepared by saturation of CaY (x=4.8), 0.7 OHNaY and NaY (x=4.4) with [Pd(NH₃)₄]²⁺ or [Pd(NH₃)₄]Cl₂ solutions, heated in vacuum at 450°C for 2 h followed by calcination in O₂ at 450°C and 760 torr for 3 h, were made. D₂ exchange greatly increased on mechanical contact with the OH radical of the 0.7 OHNaY surface of the Pd catalyst. The surface migration coefficient of D₂ activation was at least 3 orders higher than the diffusion coefficient of the nucleus of the OH radical.

Selective Hydrogenation of Benzene over Platinum or Palladium Supported on Organic Polymer Catalysts. I. Preparation and Catalytic Properties of Palladium Deposited on Polyamide-66

C. MICHEL, C. HOANG-VAN and S. J. TEICHER, *J. Chim. Phys.*, 1978, **75**, (9), 819-825

The activity and selectivity of polyamide-66 supported Pd catalysts were studied during hydrogenation of benzene as a function of impregnation conditions, nature and concentration of Pd salt, and morphology of the polyamide carrier. The catalysts were prepared by impregnation of polyamide with an aqueous solution of Pd salt at 100°C for ≤30 min. The catalytic properties depended on the nature of ionic precursors in the impregnation solution, which were determined by the nature and concentration of the metallic salt and the pH of the solution. The catalyst with the larger carrier surface area was more effective.

Electrochemical Study of Carbon-Supported Palladium-Copper Catalysts

T. MALLAT, J. PETRÓ and M. SCHÄFFER, *Acta Chim. Acad. Sci. Hung.*, 1978, **98**, (2), 175-185

Potentiodynamic polarisation studies of H₂ adsorption over 0-40 at.% Cu-Pd/C catalysts (Pd content is 5 wt.% for Cu=0) prepared by consecutive reductions were performed. The activities of the catalysts were measured in the liquid-phase hydrogenation of cyclohexene. Apart from the Cu content of the samples, the examined characteristics depended mainly on the age of the catalyst.

Synthesis of Isocyanic Acid from Nitric Oxide over Palladium and Iridium Catalysts

R. J. H. VOORHOEVE and L. E. TRIMBLE, *Science*, 1978, **202**, (4367), 525-526

A novel convenient synthesis of isocyanic acid and its trimer isocyanuric acid was obtained by the conversion of NO. NO, CO and H₂ mixed in He to a concentration of 0.3-5% reacted over Ir

and Pd catalysts at 280–450°C to form HNCO in yields of 60–75%. Major products are ammonium cyanate at low temperatures and NH₃ or N₂ at high temperatures. The total conversion NO→N₂→NCO is 73% for Pd and 86% for Ir.

Study of Palladium State in Pd/SiO₂ Supported Catalysts in Ethylene Carbonylation

A. L. LAPIDUS, S. D. PIROZHKOVA, A. R. SHARIPOVA, A. N. DETYUK, R. V. DMITRIEV and KH. M. MINACHEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (11), 2627–2629

A study of the Pd state in 0.1–3.0% Pd/SiO₂ was carried out during carbonylation of C₂H₄ in the presence of C₂H₅COOH in a rotating autoclave. Carbonylation conversion of C₂H₄ over 0.5% Pd/SiO₂ was 82.4 and the yield of propynoic acid was 73.5%. Pd(o) was the catalytically active form.

HOMOGENEOUS CATALYSIS

Activation of Molecular Hydrogen by Transition Metal Complexes. I. Autocatalysis in Hydrogenation of [(PPh₃)Pd(OAc)₂]₂

A. S. BERENBLYUM, A. G. KNIZHNIK, S. L. MUND and I. I. MOISEEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (12), 2711–2714

Activation of H₂ with [LPd(OAc)₂]₂ (L = PPh₃) prepared in solutions of 2.21g of 10⁻² mol Pd(OAc)₂, 2.62g of 10⁻² mol PPh₃ and 10 ml toluene was found to have autocatalytic character. The induction period of the reaction depended on the nature of the solvent and on component concentrations; increasing with the decrease of the Pd complex and H concentrations and with the increase of the PPh₃ concentration.

Lewis Acid Influenced Ethylene Hydrogenation by Rhodium(I) Complexes

S. H. STRAUSS and D. F. SHRIVER, *Inorg. Chem.*, 1978, 17, (11), 3069–3074

The hydrogenation of ethylene at subatmospheric pressures in benzene was catalysed by RhCl(PPh₃)₃, RhH(PPh₃)₃ and RhH(PPh₃)₄ with and without

added Lewis acids. RhH(PPh₃)₃ is produced from the system RhCl(PPh₃)₃ and AlEt₃. RhH(PPh₃)₃ is 39 times more active than RhCl(PPh₃)₃. A mechanism for hydrogenation by RhH(PPh₃)₃ is proposed. It appears that there are sites on Rh(I) hydrides which are more basic than triphenylphosphine towards common Lewis acids.

Hydrogen Evolution from Water by Visible Light, a Homogeneous Three Component Test System for Redox Catalysis

K. KALYANASUNDARAM, J. KIWI and M. GRÄTZEL, *Helv. Chim. Acta*, 1978, 61, (7), 2720–2730

Irradiation by visible light of a neutral aqueous solution containing Ru(bipy)₃²⁺ as a sensitizer, methylviologen (MV²⁺) as an electron acceptor, and triethanolamine or cysteine as an electron donor, leads to the formation of the stable methylviologen radical cation (MV^{•+}). In the presence of PtO₂ as catalyst, MV^{•+} was oxidised by H₂O with simultaneous H₂ evolution.

ELECTRICAL AND ELECTRONIC ENGINEERING

Deep Levels of Platinum in Silicon

P. M. SANDOW, M. B. DAS and J. STACH, *J. Electron. Materials*, 1978, 7, (5), 687–703

Pt was introduced into n- and p-type Si and its energy levels and distribution examined. Pt concentration follows the B concentration near the junction in p-type Si. Pt may be useful as a means of lifetime-control in Si.

Recent Progress in Thin-Film Solar Cells

J. I. B. WILSON, J. MCGILL and D. WEAIRE, *Adv. Phys.*, 1978, 27, (3), 365–385

Recent work on thin-film solar cells based on doped amorphous silicon, including the development of a large area Si cell using a Pd M-I-S structure (50 cm² cells giving 600 mV in open-circuit and 2 mA/cm in short-circuit) is reviewed in detail. (80 Refs.)

NEW PATENTS

METALS AND ALLOYS

Skin-Melted Metal Articles

UNITED TECHNOLOGIES CORP.

British Patent 1,530,776

The use of Pd-Cu-Si alloys is described with reference to metallic articles having surface layers with metallurgical structures and properties which differ from those of the substrate.

ELECTROCHEMISTRY

Fungicides

HOECHST A.G.

British Patent 1,528,838

Alkoxyacyl cyclic amines, useful as agricultural fungicides, are obtained by electrolysis of the acylamines in alcohol. The electrodes are nets or plates of Pt or Pd, or the cathode is a base metal coated with a platinum group metal.