

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Kinetic Oscillations during the Isothermal Oxidation of Hydrogen on Platinum Wires

J. E. ZUNIGA and D. LUSS, *J. Catalysis*, 1978, **53**, (3), 312-320

During the oxidation of H₂ on a Pt wire held at constant temperature, thermal oscillations observed in the reaction rate had more than one peak per cycle and were sensitive to surface temperature changes and to the wire pretreatment. The different oscillations existed during the same operating conditions. When Ar or He replaced N₂ as diluent the oscillations decayed and a constant rate resulted.

Silicide Formation with Nickel and Platinum Double Layers on Silicon

T. G. FINSTAD, *Thin Solid Films*, 1978, **51**, (3), 411-424

Diffusion effects and silicide formation in double layers of electron-gun evaporated thin films of Pt and Ni on <100> and <111> Si substrates were studied at 200-900°C. Pt₂Si started growing fast in the Si/Pt/Ni system. When all the Pt was consumed, Ni diffused through the Pt₂Si layer and accumulated at the Si/Pt₂Si interface. In the silicide for the <100> Si/Pt/Ni system the distribution of Ni and Pt was the reverse of the as-deposited distribution (~450°C, 20 min). The existence of a ternary of the type SiNi_{1-x}Pt_x is suggested.

Nitric Oxide Chemisorption on Platinum Contaminated with Lead

G. PRALINE, N. PACIA, J.-J. EHRHARDT and A. PENTENERO, *Compt. Rend., Sér. C*, 1978, **287**, (4), 81-84

Thermal desorption studies of NO_x chemisorption on Pt contaminated with Pb showed a reduction in the amount of chemisorbed NO_x by a factor of two, compared to that observed for clean Pt, when Pb deposits on polycrystalline Pt were greater than a monolayer. The results indicate that NO_x adsorption on the Pb covered Pt is molecular while it is dissociatively adsorbed on clean Pt above 400 K.

Phase Investigations of the Pu-Pt, Pu-Rh, and Pu-Pt-Rh Systems

C. C. LAND, D. E. PETERSON and R. B. ROOF, *J. Nucl. Mater.*, 1978, **75**, (2), 262-273

Phase and crystal structure studies were performed on Pu-Pt, Pu-Rh and Pu-Pt-Rh using metallography, X-ray diffraction and electron microscopy. Previously unreported PuPt_{3-κ} and PuPt_{3-κ'}

polymorphs and a new PuPt₄ phase were identified. Eutectic points in the Pu-Pt and Pu-Rh systems were found for 89.9 at.% Pt and 84.5 at.% Rh, respectively. PuPt₅ is hexagonal, PuPt₄ orthorhombic and PuPt_{3-κ'} b.c. tetragonal.

Elastic Properties of Dilute Palladium-Hydrogen Solid Solutions

R. J. FARRARO and R. B. MCLELLAN, *J. Phys. Chem. Solids*, 1978, **39**, (7), 781-785

A thin-line pulse-echo technique was used to measure the variation of Young's modulus in thin wires of super-pure Pd as a function of temperature and hydrogen concentration. The elastic modulus had a linear decrease with increasing H content.

A New Substrate Holder for Liquid Phase Epitaxy

G. BARTELS and G. PASSIG, *J. Crystal Growth*, 1978, **44**, (3), 363-364

A new substrate holder for growing single crystal garnet layers by LPE in either horizontal or vertical growth position is made from a 95% Pt-5% Au alloy, which has better rigidity than pure Pt. The new holder combines the advantages of horizontal and vertical dipping techniques. Until now vertical growth produced inhomogeneities in thickness and chemical composition. During growth the substrates, clamped in three Pt-Au wires, rotate about the vertical axis.

Hydrogen Diffusion in Palladium by Galvanostatic Charging

J. G. EARLY, *Acta Metall.*, 1978, **26**, (8), 1215-1223

The diffusion of H in α-Pd at ambient temperature was studied by a galvanostatic technique. Single transient and multiple transient charging experiments were conducted over a range of charging currents and specimen thicknesses, and an equation to describe multiple transient charging was developed. The diffusion coefficient at 23°C was determined as $(3.4 \pm 0.2) \times 10^{-7}$ cm²/s, in agreement with earlier results. Bulk H diffusion is the rate controlling process.

Spreading of Pd Layers on W(110) and Vicinal Planes by Surface Diffusion

R. BUTZ and H. WAGNER, *Vakuum-Tech.*, 1978, **27**, (6), 175-178

Studies of Pd surface diffusion on W(110) and vicinal surfaces were carried out using circular Pd films (diameter ~100 μm) and Pd strips (width ~100 μm) evaporated on to the crystal surface. Auger microscopy studies after the diffusion showed the formation of Pd layers of distinct

concentrations. The spreading of the initial circular Pd spots shows an anisotropy on the $W(110)$ plane determined by the structure of this plane.

The Surface Composition of Platinum-Palladium Alloys Determined by Auger Electron Spectroscopy

F. J. KUIJERS, B. M. TIEMAN and V. PONEC, *Surface Sci.*, 1978, **75**, (4), 657-680

Pt-Pd alloys were prepared as powders and films, and their surface compositions determined by AES. The results were then compared with theoretical models. Experimental results indicate surface enrichment in Pd, which agrees with theoretical calculations. Interactions of alloys with CO and propane are discussed and an explanation is suggested.

Effect of High Pressure on the Crystallisation of an Amorphous $Pd_{80}Si_{20}$ Alloy

H. IWASAKI and T. MASUMOTO, *J. Mater. Sci.*, 1978, **13**, (10), 2171-2176

X-ray diffraction studies of an amorphous $Pd_{80}Si_{20}$ alloy annealed at 200-400°C and subjected to a pressure of 100 kbar, showed that pressurisation results in a retardation of the crystallisation of the alloy. It was found that the crystalline phases which form under high pressure have simpler structures than the ones formed under atmospheric pressure.

Effect of Annealing on the Structure of Thin Rhodium Films

J. KOSHY, *Thin Solid Films*, 1978, **51**, (2), L17-L20

Oxidation of evaporated Rh films were studied on single-crystal and polycrystalline film samples heated in a vacuum of 10^{-6} torr, in air and in N_2 for different periods, by transmission electron microscopy. Rh in thin films oxidised at the relatively low temperature of 350°C when heated in air, but did not react with N_2 even at ~600°C. The oxide films formed on single-crystal Rh films were oriented, so providing epitaxial oxides when direct growth was difficult.

The Effect of Phosphorus Segregation to Grain Boundaries in Ir+0.3 wt.% W Alloys on High Temperature Ductility

C. L. WHITE and C. T. LIU, *Scripta Metall.*, 1978, **12**, (8), 727-733

When Ir-0.3 W, used for cladding radioisotopic heat sources in space power systems, is doped with Al, Th, Fe, Ni and Rh its high temperature impact (H.T.I.) ductility is superior to that of undoped alloys. Studies made of a batch of material having H.T.I. considerably poorer than usual revealed a significant level of P segregated at the grain boundaries and specimens fractured in a mostly intergranular manner, similar to undoped alloy and in contrast with other batches of doped alloy which failed in a ductile way. Bulk

concentrations of P as low as 1 ppm can result in this brittleness although it does not affect the segregation of Th to the boundaries, a feature which is advantageous to H.T.I. ductility.

CHEMICAL COMPOUNDS

Hydroxo-Bridged Platinum(II) Complexes. 3. Bis[cyclo-tri- μ -hydroxo-tris(*cis*-diammineplatinum(II)) Trisulfate Hexahydrate. Crystallographic Characterization and Vibrational Spectra

R. FAGGIANI, B. LIPPERT, C. J. L. LOCK and B. ROSENBERG, *Inorg. Chem.*, 1978, **17**, (7), 1941-1945
cis-Pt(NH₂)₂Cl₂, which is the starting material of a new class of antitumour agents and possibly also the species to which *cis*-dichlorodiammineplatinum(II) is transformed before its cancerostatic activity, was reacted with Ag₂SO₄ in water. It yielded the title compound whose structure was determined.

Specific Heat of $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$

I. MATTA, T. MATSUDA, H. DOI, H. NAGASAWA, T. ISHIGURO and S. KAGOSHIMA, *Solid State Commun.*, 1978, **27**, (4), 479-481

Anomalous behaviour of the specific heat of the electrically one-dimensional compound $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ appears at 35 and 65K. This was studied on normal and dehydrated samples. The 65K anomaly appears to be related to ferroelastic softening of shear elastic constants c_{66} . At 120K no anomaly occurs in either type of sample.

Metallacycloalkane Chemistry: Synthesis of the First Palladacyclopentane Derivative and Its Transformation into a η^3 -Butenyl Cationic Complex

P. DIVERSI, G. INGROSSO and A. LUCHERINI, *J. Chem. Soc., Chem. Commun.*, 1978, (17), 735-736

The first palladacyclopentane derivative was synthesised, and some of its reactions, including that with Ph_3C^+ , are reported.

Novel Three Co-ordinate Rhodium(I) Hydrido-Compounds, $[RhH(PBu_3)_2]$ and $[RhH\{P(cyclohexyl)_3\}_2]$

T. YOSHIDA, T. OKANO and S. OTSUKA, *J. Chem. Soc., Chem. Commun.*, 1978, (19), 855-856

The Rh(I) hydride dinitrogen complexes *trans*- $[RhH(N_2)(PBu_3)_2]$ and $[(trans-Rh\{P(cyclohexyl)_3\}_2)(\mu-N_2)]$, prepared by reducing $RhCl_3 \cdot 3H_2O$ with Na-Hg in the presence of the appropriate phosphine, dissociate the co-ordinated dinitrogen to give novel three co-ordinate complexes $RhHL_2$. These complexes are extremely versatile being efficient catalysts for hydrogenation of unsaturated organic compounds and for the H-D exchange reaction of aromatic compounds with D₂O which occurs through the activation of water.

Nitrosyl Complexes of Ruthenium

F. BOTTOMLEY, *Coord. Chem. Rev.*, 1978, **26**, (1), 7-32

A review is given of nitrosyl Ru complexes {RuNO}³⁺, {RuNO}²⁺, {RuNO}⁺ and {RuNO}⁰. Their structures and bondings, bridging complexes and the reactions of NO_x over Ru metal catalysts are discussed. (154 Refs.)

ELECTROCHEMISTRY

Adsorption of Hydrogen Peroxide on Platinised Platinum Studied by Impulse Methods

T. M. SEMENKINA, G. I. ELFIMOVA and G. A. BOGDANOVSKII, *Zh. Fiz. Khim.*, 1978, **52**, (7), 1713-1716

The adsorption of H₂O₂ on platinised Pt electrodes was studied in 1N H₂SO₄ by an impulse method. The results showed that the adsorbed H₂O₂ is distributed evenly on the Pt surface and occupies oxygen as well as oxygen free sites.

Thermal Decomposition of Hexachloroplatinic Acid

A. E. SCHWEIZER and G. T. KERR, *Inorg. Chem.*, 1978, **17**, (8), 2326-2327

Thermographs of chloroplatinic acid [H₂O]₇-[PtCl₆].xH₂O, where x is variable, were obtained. Intermediate compounds were analysed via hydrogen reduction to Pt. The volatility of Pt₆Cl₁₂ in the thermal decomposition to metallic Pt explains the ease of dispersing Pt as small crystallites on high surface area catalysts and catalyst supports.

Effect of Laser Radiation on the Catalytic Decomposition of Formic Acid on Platinum

M. E. UMSTEAD and M. C. LIN, *J. Phys. Chem.*, 1978, **82**, (18), 2047-2048

Laser excitation was used in the decomposition of formic acid on Pt, into CO₂+H₂ and CO+H₂O. The laser excitation influenced both the rates of reaction of surface species and the relative amounts of the products. This is the first observation of this effect and indicates the possibility of combining the unique properties of both catalysts and lasers to drive chemical reactions in selected synthetic routes.

The Palladium and Platinum Precipitation from Aqueous Solutions by Ozone

A. F. CHUDNOV, *Izv. V.U.Z., Tsvetnaya Metall.*, 1978, **20**, (5), 80-83

Spectrophotometric studies of the Pd and Pt precipitation from aqueous solution by ozone were carried out by bubbling an ozone-air mixture (8 mgO₃/l) through aqueous solutions of K₂[PdCl₄] and K₂[PtCl₄] at room temperature. The Pt(II) (K₂[PtCl₄] concentration 2.10⁻⁴-2.10⁻³ mg/l) was oxidised to water soluble products of Pt(IV) in HCl, H₂SO₄ and HNO₃. In

alkaline and neutral media, the formation of colloid solutions of hydrated dioxides of Pt with K₂[PtCl₆] additions was observed. The results showed better precipitation of Pt than Pd, probably due to a higher stability of Pt(IV) in solution.

Methanol-Air Fuel Cell

L. ONICIU, E. RUS, E. SCHMIDT and V. TOPAN, *Rev. Chim.*, 1978, **29**, (8), 739-741

A methanol-air fuel cell with nickel sintered anodes activated with Pt-Pd and active coal doped with Ag as cathodes is presented. The stack use bipolar collectors.

Reasons for Loss of Activity of RuO₂ and TiO₂ Coated Titanium Anodes

T. LOUČKA and Z. TERNBACH, *Chem. Průmysl*, 1978, **28**, (7), 335-337

The effect of pH, ionic strength and the composition of anodic gas on the lifetime of RuO₂ and TiO₂ coated Ti anodes was studied. The life of the anode decreased with the increase of O₂ content in anodic gas. Lowering the pH value and decreasing the ionic strength of the solution also had a negative effect on the life of the anodes.

Charge Separation in Photoinitiated Electron Transfer Reactions Induced by a Polyelectrolyte

D. MEYERSTEIN, J. RABANI, M. S. MATHESON and D. MEISEL, *J. Phys. Chem.*, 1978, **82**, (17), 1879-1885

The effect of a negative polyelectrolyte polyvinyl sulphate (PVS) on the photoinduced electron transfer reaction from Ru(bpy)₃²⁺ to uncharged acceptors was studied. Adding PVS reduces the quenching rate to 60%. The high potential field of the polyelectrolyte repels the negatively charged acceptor product, enhances charge separation and slows the back reaction of the initially separated products. These effects may be useful in solar energy conversion. In photogalvanic cells, photovoltage increases with photoredox product concentration, which increases with enhanced photochemical yield and inhibited back reaction. These two effects may aid conversion of the photoredox products to useful fuels.

X-Ray Photoelectron Spectroscopic Studies of RuO₂-Based Film Electrodes

J. AUGUSTYNSKI, L. BALSENC and J. HINDEN, *J. Electrochem. Soc.*, 1978, **125**, (7), 1093-1097

Different species present in the surface region of RuO₂ and RuO₂-TiO₂ film electrodes before and after anodic polarisation in NaCl solution were determined by XPS. The existence of a surface defect structure of RuO₃, analogous to that found on RuO₂ powder was confirmed for both electrodes. RuO₃ may be responsible for the good stability of RuO₂ anodes. Two different chlorine species, Cl⁻ and adsorbed atomic chlorine, were present on the electrode surfaces used as anodes for chlorine evolution.

A Spectrophotometric Investigation of the Products of the RuO₄ Reduction in HCl Solutions

I. G. TIKHONOV, V. A. BODNYA and I. P. ALIMARIN, *Vest. Moskov. Univ., Ser. II Khim.*, 1978, **19**, (4), 463-466

A spectrophotometric study of the products of RuO₄ reduction in aqueous and aqueous-ethanol HCl solutions was carried out and the conditions for the rapid and complete reduction of RuO₄ in chloride complexes to Ru(III) were determined. The best results were obtained from 0.5-2.0 M HCl solution containing 20 vol. % of ethanol heated at 98°C for 30-60 min.

LABORATORY APPARATUS AND TECHNIQUE

Kinetics of Crystal Nucleation in Lithium Disilicate Glass. A Comparison between Melts Prepared in Platinum and Silica Crucibles and between Melts Prepared from Ordinary and High Purity Starting Materials

P. F. JAMES, B. SCOTT and P. ARMSTRONG, *Phys. Chem. Glasses*, 1978, **19**, (2), 14-17

The effect of Pt on the kinetics of crystal nucleation was studied in four Li disilicate glasses, two had ordinary impurity levels, while the others were of high purity. One of each type was melted in a Pt crucible, and in a SiO₂ crucible under Pt-free conditions. No significant differences in crystal nucleation kinetics on Pt particles were observed between the glasses. The heterogeneous nucleation on Pt particles was negligible. This is important considering the widespread use of Pt containers and stirrers for melting.

The Melt Growth and the Thermal Expansion of Na₂CO₃ Crystals

M. MIDORIKAWA, T. HASHIMOTO, Y. ISHIBASHI and Y. TAKAGI, *J. Crystal Growth*, 1978, **44**, (4), 505-506

Na₂CO₃ crystals were prepared by a modified Bridgman method in a composite ampoule with an inner Pt crucible and outer quartz ampoule. No trace of reaction between Pt and Na₂CO₃ was found when the crucible had a small diameter cylindrical end which limited crystal growth.

Secondary Ion Mass Spectrometry and Auger Electron Spectroscopy Investigations of Vb Metal Foils Prepared for Hydrogen Permeation Measurements

N. BOES and H. ZUCHNER, *Surface Technol.*, 1978, **7**, (5), 401-412

Coating clean outgassed surfaces of V, Nb and Ta with a vapour deposited thin film of Pd, permeable only to H₂, prevents surface corrosion layers building up. These layers almost entirely prevent the H interphase transfer into the metal at normal temperatures.

HETEROGENEOUS CATALYSIS

The Formation of Compounds with the C≡N Bond during Reduction of NO over Rhodium and Platinum Catalysts

R. J. H. VOORHOEVE, C. K. N. PATEL, L. E. TRIMBLE and R. J. KERL, *J. Catalysis*, 1978, **54**, (1), 102-105

The formation of HCN by reduction of NO over Pt and Rh catalysts was studied. The concentrations of HCN, NH₃, NO₂ and H₂O in the effluent were simultaneously measured by an optoacoustic cell, and the effect of O₂ on HCN and NH₃ formations was studied at various temperatures. With Pt sponge diluted by α-Al₂O₃, 345 ppm HCN was found in the mixture which decreased to 37 ppm on adding 4.6% H₂O to the inlet gas, while on adding 2% O₂ it decreases to 7 ppm. For Rh sponge diluted with α-Al₂O₃ the results varied depending on the catalyst history but HCN yields were lower than those obtained with Pt.

Cyclotrimerisation of Ethylene over Promoted Platinum-Alumina Catalysts

O. V. BRAGIN, A. V. PREOBRAZHENSKY, T. V. VASINA and K. D. EROKHINA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (9), 2061-2064

Cyclotrimerisation of C₂H₄ was carried out over 0.5-0.6% Pt/γ-Al₂O₃ catalysts modified by compounds of Bi, Pb, Tb, Pr, Nd, Re and Sn-Ce, and over 10% Pt/Al₂O₃ catalysts with NaNO₃ and HNO₃. The best results were obtained over 0.5% Pt/Al₂O₃ activated with Nd₂O₃ and also over 0.6% Pt/Al₂O₃(HNO₃).

Activity of Metal Catalysts. VIII. A Study of Cyclopentane Hydrogenolysis on Platinum-Alumina Catalysts at Various Dispersions

J. BARBIER, P. MARECOT, A. MORALES and R. MAUREL, *Bull. Soc. Chim. Fr.*, 1978, (7/8), 309-310

A kinetic study of the hydrogenolysis of cyclopentane was carried out on three series of Pt/Al₂O₃ catalysts with various dispersions. These were obtained by varying the following parameters: amount of metal deposited, calcination temperature in air and reduction temperature in hydrogen. The results showed a difference in specific rate constants for various samples of the catalyst. The hydrogenolysis reaction of cyclopentane occurred on particular sites but the Pt crystallite size was not as relevant as previously assumed.

Competitive Hydrogenation of Aromatic Hydrocarbons on a Sulphur Resistant Platinum Catalyst in Presence of Organic Sulphur Compounds

J. COSYNS, J.-P. FRANCK and J. M. GIL, *Compt. Rend., Sér. C*, 1978, **287**, (4), 85-88

Competitive hydrogenation of benzene and alkylbenzene feeds containing S was performed

over a S-resistant Pt/Al₂O₃ catalyst. Absence of the S compounds reduced the reaction rate for benzene. Sulphiding the Pt increases the adsorption of the most basic aromatics and thus of the heaviest alkyaromatics.

The Influence of Catalyst Preparation and Thermal Treatment on the Hydrogen Adsorption on Platinum Catalysts

G. D. ZAKUMBAEVA, N. A. ZAKARINA and V. P. KUIDINA, *Zh. Fiz. Khim.*, 1978, **52**, (7), 1699-1703
The adsorption of H₂ on Pt black and Pt/C catalysts was studied in relation to different preparation and thermal treatments. It was shown that the Pt/C catalysts have higher sorptional activity and better thermal stability than Pt black. The heats of adsorption of H₂ on various Pt catalysts were found to depend on the preparation and the content of the active phase in the catalyst.

Preparation of Supported Platinum-Gold, Platinum-Tin, and Rhodium-Copper Catalysts and Some Tests with n-Hexane/Hydrogen Reactant

J. K. A. CLARKE, I. MANNINGER and T. BAIRD, *J. Catalysis*, 1978, **54**, (2), 230-242

The effect of differences in preparation on the dispersion and alloying of the metals in silica-supported Pt-Au, Rh-Cu, and (in part) Pt-Sn catalysts was examined via n-hexane conversion. Pt-Au showed little interaction, 15% Rh-85% Cu was poorly alloyed, and a Rh-rich region remained after heat treatment before and during the reaction. This catalyst shows selectivity of ~25% for C₅ and C₆ products, whereas 100% Cu has only a small selectivity and 100% Rh a negligible cyclisation selectivity.

Conversion of NO to Isocyanic Acid and Ammonium Cyanate over Pd, Ir, and Pt-10% Rh Catalysts

R. J. H. VOORHOEVE and L. E. TRIMBLE, *J. Catalysis*, 1978, **54**, (2), 269-280

The formation of HNCO and NH₄OCN was studied over unsupported Pd, Ir, and Pt-10% Rh catalysts. All reactions, involving NO, CO and H₂, produced yields of over 75%. The reactions may be attractive routes for the production of ammonium cyanate or its isomer urea, and isocyanic acid or its trimer isocyanuric acid.

Intraparticle Mass Transfer Effects and Selectivity in the Palladium-Catalyzed Hydrogenation of Methyl Linoleate

K. TSUTO, P. HARRIOTT and K. B. BISCHOFF, *Ind. Engng. Chem., Fund.*, 1978, **17**, (3), 199-205

Studies of the hydrogenation of methyl linoleate to methyl oleate were carried out in a stirred batch reactor using several particle size fractions of a 1% Pd/C catalyst. The intraparticle mass transfer of the liquid reactants effected the

product selectivity, and the effective diffusivity of the liquid reactants between the catalyst particles was about 1/100 of that of H. The selectivity was more sensitive to H concentration than to the catalyst particle diameter.

Use of Fixed Palladium π -Allyl Complexes as Heterogeneous Telomerisation Catalysts

YU. I. ERMAKOV, A. M. LAZUTKIN, A. I. LAZUTKINA and V. I. PROZOROVA, *Kinet. Kataliz.*, 1978, **19**, (4), 911-914

The activity of catalysts containing phosphines and π -allyl complexes of Pd on SiO₂ was studied during the telomerisation of butadiene with diethylamine to the tertiary amine C₈H₁₃N(C₂H₅)₂. The catalytic activity of the applied phosphine containing Pd catalysts was nearly two orders higher than the activity of homogeneous catalysts.

Synthesis Gas Conversion over Supported Rhodium and Rhodium-Iron Catalysts

M. M. BHASIN, W. J. BARTLEY, P. C. ELLGEW and T. P. WILSON, *J. Catalysis*, 1978, **54**, (2), 120-128

A supported Rh catalyst used in conversion of synthesis gas above 25 atm pressures produces acetic acid, acetaldehyde, ethanol and methane with a chemical efficiency around 50%. These results are different from previously reported ones. Adding Fe to Rh reduces acetic acid and acetaldehyde yields, and ethanol and methane become the major products.

Carbonylation of Methanol and Ethanol on a Rhodium-Zeolite Catalyst

B. CHRISTENSEN and M. S. SCURRELL, *J. Chem. Soc., Faraday Trans. I*, 1978, **74**, (9), 2313-2319

The effect of the concentration of alkyl iodide "promoter" on the reaction selectivity during carbonylation of methanol and ethanol on a Rh/X-zeolite catalyst was studied. A maximum in selectivity was observed for both alcohols with an increase in the alkyl iodide content in the reactant stream. Near-stoichiometric quantities of methyl iodide were used for methanol carbonylation. The effect of the absence of "promoter" on the catalyst is discussed.

Genesis of a Supported-Metal Catalyst. Aggregation of Polymer-Bound Rhodium Clusters

M. S. JARRELL, B. C. GATES and E. D. NICHOLSON, *J. Am. Chem. Soc.*, 1978, **100**, (18), 5727-5732

A polymer containing small Rh clusters was obtained as a product of the reaction of poly(styrene-divinylbenzene) containing PPh₂ groups with a solution of Rh₆(CO)₁₆ in benzene at 25°C. The polymer was found to be an active, stable catalyst for the hydrogenation of ethylene and cyclohexene at 1 atm and 80°C. In presence of O₂ flowing over the catalyst the phosphine groups were oxidised and the Rh agglomerated into clusters ~20Å in diameter.

Surface Area Stabilization of Ir/Al₂O₃ Catalysts by CaO, SrO, and BaO under Oxygen Atmospheres: Implications on the Mechanism of Catalyst Sintering and Redispersion

G. B. MCVICKER, R. L. GARTEN and R. T. K. BAKER, *J. Catalysis*, 1978, **54**, (2), 129-142

The sintering of dispersed Ir/Al₂O₃ catalysts impregnated with Ba, Ca or Sr oxides, at temperatures up to 650°C in O₂, was completely inhibited when the oxide concentration was greater than that of the acid sites on the support. Studies of presintered Ir/Al₂O₃ catalysts to which BaO was added showed that Ir could be redispersed by treating with O₂ at 600°C. The oxidative stabilisation and redispersion is consistent with the capture of mobile, molecular Ir oxide species; the trapping mechanism may proceed by formation of stable immobile surface iridates.

Hydrogenation of Aromatic Nitro Compounds in the Presence of an Iridium Catalyst

V. I. SAVCHENKO, V. G. DOROKHOV, R. S. TSAREVA, G. M. BALMASHOVA, N. A. CHEKH, E. N. IZAKOVICH, K. A. BRIKENSHTEIN and M. L. KHIDEKEL', *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1978, (10), 2329-2332

The hydrogenation of aromatic nitro compounds was carried out using a 5% Ir/C catalyst. It was found that this catalyst is highly stable and efficient, and can be used to obtain halogen substituted amines by hydrogenation of halogen nitrobenzenes.

Structural and Chemisorption Characteristics of Supported Iridium in Iridium Alumina Catalysts

E. M. MOROZ, S. V. BOGDANOV, N. E. BUYANOVA and O. V. KOVRIZHINA, *Kinet. Kataliz*, 1978, **19**, (4) 1029-1034

X-ray studies of structural and chemisorption characteristics of dispersed particles of Ir supported on various Al₂O₃ substrates were made on catalysts containing 5-31.5 wt.% Ir. Higher H₂ chemisorption was observed on catalysts containing <15 wt.% Ir/Al₂O₃. This is assumed to be due to the supplementary H₂ adsorption on the carrier which allows penetration of Ir particles through the defective structure. The presence of the spinel structure enclosing Ir ions was detected in the catalysts.

Ammonia Synthesis Activity of a Raney Ruthenium Catalyst

K. URABE, T. YOSHIOKA and A. OZAKI, *J. Catalysis*, 1978, **54**, (1), 52-56

A Raney Ru catalyst, prepared from a Ru-Al alloy with ratio Ru : Al of 1 : 3, had a high activity for NH₃ synthesis. The apparent activation energy for NH₃ synthesis is less on the Raney catalyst than on pure Ru by 5 kcal/mol. The specific activity with respect to the number of surface Ru atoms is three times higher on a Raney

catalyst at 300°C, and adding K increases activity a further 12 times, whilst the activation energy remains low. The high activity of Raney Ru is caused first by an increase in surface area which is stable at temperatures as high as 400°C, and second by electronic promotion, both of which occur on alloying with Al.

HOMOGENEOUS CATALYSIS

Homogeneous Catalysis of the Water Gas Shift Reaction Using a Platinum Chloride-Tin Chloride System

C.-H. CHENG and R. EISENBERG, *J. Am. Chem. Soc.*, 1978, **100**, (18), 5968-5970

An efficient catalyst for the water gas shift reaction H₂O + CO ⇌ H₂ + CO₂ was found to consist of 0.1g of K₂PtCl₄ and 2.5g of SnCl₄·5H₂O dissolved in 40ml of glacial acetic acid, 10ml of concentrated HCl and 10 ml of H₂O. This catalyst was several times more active than the previously used rhodium carbonyl iodide catalyst. It is thought that CO₂ forms via aqueous attack on a Pt(II) co-ordinated carbonyl and that H₂ is produced via a platinum hydride species and its reaction with H⁺.

Promoting Action of Oxides of Transition Metals on the Activity of the PdCl₂ Catalyst in the Carbonylation of Nitrocompounds

B. K. NEFEDOV, V. I. MANOV-YUVENSKII, A. L. CHIMISHKYAN and V. M. ENGLIN, *Kinet. Kataliz*, 1978, **19**, (4), 1065-1067

Systematic studies of the effect of transition metal oxides on the activity of the PdCl₂ catalyst were carried out during carbonylation of nitrocompounds (molar ratio PdCl₂ : C₆H₅NO₂ = 1 : 40) in a rotating autoclave under CO pressure of 160 atm at 200°C. The maximum promoting action was achieved by metal oxides of Groups V and VI. The addition of V₂O₅, Nb₂O₅ or MoO₃ to the catalysts in the weight ratio to PdCl₂ of 1 : 1 resulted in nitrobenzene conversion of 80-100%. The increase in weight ratio of MoO₃ (V₂O₅) : PdCl₂ promoted the yield of phenylisocyanates with selectivity of up to 93%.

Chemistry and Catalytic Properties of Oxidised Rhodium Chlorocarbonyl Complexes Rh₄Cl₄(CO)₄(O₂)₂P₂; P = Tertiary Phosphine Ligands

W. R. CULLEN, B. R. JAMES and G. STRUKUL, *Can. J. Chem.*, 1978, **56**, (13), 1965-1969

Studies of the reactions of the title Rh complexes with both H₂ and CO were carried out in solution in the absence and presence of excess P. The reaction stoichiometries, particularly a measured CO₂ evolution, confirm the formulation of the reactant tetramolecular complex. The complexes are effective for catalytic hydrogenation and hydroformylation of olefinic substrates, and the nature of the active catalysts was considered.

Homogeneous Catalysis of the Water Gas Shift Reaction by Mixed-Metal(Iron/Ruthenium) Catalysts

P. C. FORD, R. G. RINKER, C. UNGERMANN, R. M. LAINE, V. LANDIS and S. A. MOYA, *J. Am. Chem. Soc.*, 1978, **100**, (14), 4595-4597

Ru catalysts for the water gas shift reaction were studied. Ru carbonyl was found to form active catalysts in many reaction media and a mixed Ru and Fe carbonyl catalyst of $\text{Ru}(\text{CO})_{12}$ and $\text{Fe}(\text{CO})_5$ was more active in basic solutions than metal carbonyl. The water gas shift reaction is an important way of making dihydrogen from water, since it derives a larger energy fraction from coal reserves.

An Arene Hydrido-Complex of Ruthenium(II) as Catalyst for the Homogeneous Hydrogenation of Benzene and Olefins

M. A. BENNETT, T.-N. HUANG, A. K. SMITH and T. W. TURNER, *J. Chem. Soc., Chem. Commun.*, 1978, (14), 582-583

Under mild conditions, the complex $[\text{RuHCl}(\eta\text{-C}_6\text{Me}_6)(\text{PPh}_3)]$ is an active homogeneous catalyst for the hydrogenation of benzene giving cyclohexane, and for the hydrogenation of olefins using either molecular hydrogen or secondary alcohols. The catalyst is stable, long-lived and can be easily prepared.

Homogeneous Hydrogenation Catalysed by Tris(diphenyl-p-tolylphosphine)dichlororuthenium(II)

S. VANCHEESAN, S. PRABHA SETHI, J. RAJARAM and J. C. KURIAKOSE, *Indian J. Chem.*, 1978, **16A**, (5), 399-402

Tris(diphenyl-p-tolylphosphine)dichlororuthenium(II) was found to be an efficient catalyst for the homogeneous hydrogenation of selected olefins, such as heptene-1 and 4-methylpentene-1. The rate of hydrogenation increased in the

presence of a basic co-solvent like ethanol but the excess of (diphenyl-p-tolylphosphine) slowed down the rate. The catalyst was found to selectively hydrogenate terminal olefins. However, the hydrogenation slowed down or even stopped in the presence of internal and cyclic olefins.

CHEMICAL TECHNOLOGY

Catalytic Decomposition of Finish Residues

Res. Discl., 1978, (171), 19

During texturing and drawtexturing of continuous filament man-made fibres, deposits form on the heaters and must be removed. A Pt co-ordination complex, such as diamine dinitro Pt(II) is reacted with a neutral mono or bidentate ligand, such as NH_3 ethylenediamine, to form a soluble Pt complex such as tetraamine dinitro Pt(II) or diamine ethylene diamine dinitro Pt(II). This salt is then reacted with hydrazine hydrate on the heater surface to form Pt metal which catalyses the oxidative degradation of the finish residues. Pd may also be used.

Reactions of the Platinum Group Metals at High Temperatures

C. J. RAUB, *Metall.*, 1978, **32**, (8), 802-804

Various uses of platinum group metals for laser technology, the glass industry, catalysis and high temperature electrical technologies are discussed. For high temperature use all need stable form, no reaction between the working material and surrounding atmosphere, good physical reproducibility and constant chemical and physical properties over a wide operational range. The behaviour of platinum group metals, alloys and compounds at high temperatures are examined from these points of view. Their reaction with air, oxygen, other gases, corrosion with liquid metals, alloy formation and optimum properties are discussed.

NEW PATENTS

METALS AND ALLOYS

P.G.M.-Containing Ni and/or Co-Based Alloys

JOHNSON MATTHEY & CO. LTD.

British Patent 1,520,630

The high temperature strength, creep resistance and oxidation and sulphidation resistance of superalloys is increased by incorporation of a platinum group metal. The alloys contain, in wt.%, Ni and/or Co 40-78, Cr trace-23.5, Al and/or Ti trace-7, and trace-6, respectively, and platinum group metal(s) trace-15. Certain other metals and nonmetals may be present in minor proportions.

Noble Metal Ordered Alloys

SONY CORP.

U.S. Patent 4,093,453

Ordered alloys, which can contain Pt, Pd, Au, Ag, Ir and Rh, are produced by providing a solid imperforate metal base of one metal, depositing on it a thin layer of another metal not greater than 10 μm thick, the second metal can form an ordered alloy with the first and heating them.

Ferromagnetic Palladium Alloys

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 4,098,605

The alloys, for use in magnetic devices and having improved corrosion resistance, contain 20-65 at.% Pd, up to 80 at.% Fe and 0-55 at.% Ni.