

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

On the Chemisorption of Oxygen on Platinum (111) Surfaces

J. A. JOEBSTL, *J. Vacuum Sci. Technol.*, 1975, **12**, (1), 347-350

Chemisorption of O₂ on clean Pt (111) surfaces was studied at room temperature by a (2 × 2)—O LEED pattern with CO content of the residual gas less than 0.5%. The (2 × 2)—O pattern disappears during re-evacuation of the surface system, showing that a critical ratio of p_{O₂}/p_{CO} is required for the formation of an adsorbed layer of O₂. The results show that similar "clean-off" reactions occur in the Pt-O₂ chemisorption system like those recently observed for the Ag-O₂ and Cu-O₂ system.

Magnetic Structure of Ordered FePt and Fe₃Pt Alloys

A. MENSHIKOV, T. TARNÓCZI and E. KRÉN, *Phys. Status Solidi A, Appl. Res.*, 1975, **28**, (1), K85-K87

Neutron diffraction and magnetic studies of the magnetic structure of the FePt and Fe₃Pt phases with tetragonal CuAu-I and cubic Cu₃Au-I crystal structures, respectively, showed both (100) and (110) type super-reflections in Fe₃Pt but in FePt the reflection (100) is absent indicating that the magnetic moments lie along the *c*-axis of the tetragonal unit cell. The temperature hysteresis of the magnetisation measured in a 6kOe field is explained by ferrimagnetic ordering in FePt.

Magnetic Properties of Ordered and Disordered Ni_{1-x}Fe_xPt

N. KAWAMIYA and K. ADACHI, *Trans. Japan. Inst. Met.*, 1975, **16**, (6), 327-332

The magnetic properties of the ordered and disordered phases of NiPt and Fe-doped Ni_{1-x}Fe_xPt (0 < x ≤ 0.15) system were measured with a magnetic balance at 78-1000K and a vibrating sample magnetometer at 4.2-290K, in magnetic fields up to 18kOe. The results show that the disordered NiPt is ferromagnetic with magnetisation σ_g = 10emu/g, moment μ = 0.23μ_B/atom and the Curie temperature T_c = 95K, but becomes paramagnetic down to 4.2K in the ordered phase. The disordered Ni_{1-x}Fe_xPt alloys are ferromagnetic with a magnetic moment increasing proportionately with the FePt content. In both phases moments as large as 12μ_B are observed. The influence of doping is discussed.

On the Constitution of the Mixture Nickel-Platinum-Gallium

A. A. GADALLA and K. SCHUBERT, *Z. Metallkunde*, 1975, **66**, (5), 307-310

The intermediate phases Ni₂PtGa and NiPt₂Ga were found on the section with 25at.% Ga. The phases Pt₅Ga₃ and PtGa had an extended solubility for Ni, while Pt₂Ga₃ and PtGa₂ had a small solubility for Ni, and Ni₂Ga₃ had a small solubility for Pt. Pt₃Ga₇(Ru₃Sn₇ type) formed a continuous mixed crystal with the isotypic phase of the Ni-Ga mixture.

Crystal Structure of Pd₂₅Ge₉

W. WOPERSNOW and K. SCHUBERT, *J. Less-common Metals*, 1975, **41**, (1), 97-103

Studies of the Pd₂₅Ge₉ phase showed that it crystallises in a hexagonal structure with 34 atoms in the elementary cell. The structure is characterised by interaction of the valence-electron spatial correlation and by two vacancies in a cell which produces a system of displacements.

Constitution of the Mixture Pd-Ga-Ge

S. HEINRICH and K. SCHUBERT, *Z. Metallkunde*, 1975, **66**, (6), 353-355

The extension of the marginal phases into the ternary mixture at 700°C was studied. The phase Pd₁₂Ga₂Ge₅ does not occur in one of the marginal mixtures; its homogeneity range is extended at constant Pd-content.

Some Mechanical Properties of Phase Separated Pd_{0.74}Au_{0.08}Si_{0.18} Metallic Glasses

C.-P. P. CHOU and F. SPAEPEN, *Acta Metall.*, 1975, **23**, (5), 609-613

Studies were made of the effect of phase separation and crystallisation of glassy Pd_{0.74}Au_{0.08}Si_{0.18} on its tensile behaviour, fracture strength, hardness and fracture morphology. The results were discussed in terms of the dilatation mechanism for flow. An "intrinsic" normal fracture stress of 165 kg/mm² was found for the fully amorphous specimens.

X-ray Studies of the α/β Miscibility Gaps of Some Palladium Solid Solution-Hydrogen Systems

M. L. H. WISE, J. P. G. FARR and I. R. HARRIS, *J. Less-common Metals*, 1975, **41**, (1), 115-127

X-ray diffraction studies were made of hydrogenated Pd solid-solution alloys at room temperature and the convergence of the lattice spacings

of the α and β phases within the α/β miscibility gaps was determined. The lattice expansion at the β min boundary exhibited a linear variation with the electron concentration, and the lattice expansion at the α max boundary was thought to be influenced by the solid-solution strengthening of the particular alloy system.

The Physical Properties of Some Palladium Alloy Hydrogen Diffusion Membrane Materials

D. FORT and I. R. HARRIS, *J. Less-common Metals*, 1975, **41**, (2), 313-327

The hydrogen solubility as well as magnetic, dilatometric and electrical-resistivity of solid-solution alloys 25% Ag-Pd, 8% Y-Pd and 9% Y-Pd have been measured as a function of temperature in both hydrogenated and non-hydrogenated conditions. The results show an increased solubility of hydrogen in 9% Y-Pd alloy compared with 25% Ag-Pd alloy, and a large increase in the room temperature resistivity shown by this alloy upon hydrogenation.

Magnetic Properties of Ni-Rh Alloys near the Critical Composition for Ferromagnetism

W. C. MUELLNER and J. S. KOUVEL, *Phys. Rev. B.*, 1975, **11**, (11), 4552-4559

The magnetisation of 65-51 at.% Ni-Rh alloys on either side of the critical composition for ferromagnetism ($c_{\text{crit}} \approx 63$ at.% Ni) were measured at 4.2-250 K in the fields up to 56 KOe. The average moment a cluster is deduced to be $\sim(20-24) \mu_B$ and the concentration of magnetic clusters increases rapidly as c_{crit} is approached from the paramagnetic side. Pertinent aspects of the weakly ferromagnetic alloy $\text{Ni}_{65}\text{Rh}_{35}$ is also discussed.

Some Anomalies of the Thermodynamics of Antiferromagnetism to Ferromagnetism Transition in Iron-Rhodium Alloys

V. M. POLOVOV, B. K. PONOMAREV and V. E. ANTONOV, *Fiz. Metal. Metalloved.*, 1975, **39**, (5), 977-986

The heat capacity, critical magnetic field and critical pressure of $\text{Fe}_{0.48}\text{Rh}_{0.52}$ were measured at temperatures close to the antiferromagnetic to ferromagnetic transition. It was found that the thermodynamic characteristics of the transition were different for quenched and slowly cooled samples. The entropy changes on transition as measured in calorimetric, magnetic and high pressure experiments show considerable discrepancies, apparently due to the metastable character of the antiferromagnetic phase.

The Approach to Magnetic Order in Rhodium-Cobalt Alloys

H. C. JAMIESON, *J. Phys. F: Metal Phys.*, 1975, **5**, (5), 1021-1036

Magnetic data are presented for Rh-28 to 44 at.%

Co at 1.6-300 K. At low concentrations the system has been previously described as an enhanced band paramagnet, however it is found that local moments are stabilised in alloys with Co-concentrations below the critical level for long-range ferromagnetism, and it is the local moments which are the dominating influence in the initial stages of magnetic order. Two stages of order are distinguished in those samples which contain local moments. Alloys with concentrations up to 42% have magnetic characteristics commonly associated with spin glasses. There are indications that samples with concentrations in excess of $\sim 36\%$ are ferromagnetic at low temperatures. The magnetic properties are distinctly different at 44%.

Structural Transformation of Near-equiatomic V-Ru Compounds at High Pressure

C. W. CHU, S. HUANG, T. F. SMITH and E. CORENZWIT, *Phys. Rev. B.*, 1975, **11**, (5), 1866-1869

The structural transformation of near-equiatomic V-Ru compounds was studied resistively under hydrostatic pressure up to ~ 21 kbar. The rate of suppression increases the critical concentration for the occurrence of the transformation.

Displacive Transformations in Near-equiatomic Niobium-Ruthenium Alloys—I. Morphology and Crystallography

B. K. DAS and D. S. LIEBERMAN, *Acta Metall.*, 1975, **23**, (5), 579-585

Displacive phase transformations in near-equiatomic Nb-Ru alloys were studied using electrical resistivity measurements, optical metallography and X-ray diffraction. Alloys containing 41-45 at.% Ru undergo a $\text{CsCl}(\beta)$ to tetragonal (β') transformation on cooling from 1500°C to room temperature. Alloys with more than 46 at.% Ru exhibit a two step $\text{CsCl}(\beta)$ to tetragonal (β') to orthorhombic (β'') transformation on cooling to room temperature.

CHEMICAL COMPOUNDS

Hydrogen-Deuterium Exchange at a Saturated Carbon Atom in Tertiary Phosphine Complexes of Platinum(II)

A. A. KIFFEN, C. MASTERS and L. RAYNAND, *J. Chem. Soc., Dalton Trans.*, 1975, (10), 853-857

Chloro-bridged di-Pt(II) complexes of the type $[\text{Pt}_2\text{Cl}_4\text{L}_2]$ ($\text{L} = \text{PPr}_3, \text{PBu}_3, \text{PBuPr}_2, \text{PBu}_2\text{Pr}, \text{PPrPh}_2, \text{PPr}_2\text{Ph}, \text{or PBuPh}_2$), undergo a regio-specific H-D exchange in acetic acid ($\text{CH}_3\text{CO}_2\text{D}$) medium to give complexes containing D in the alkyl groups of the tertiary phosphine moiety. The results show that in internal-metallation reactions of Pt, the ease of ring formation decreases in the order five membered > six membered > four membered rings.

The Crystal and Molecular Structures of *cis*-Dichloroethylenediamineplatinum(II) and Palladium(II)

J. IBALL, M. MACDOUGALL and S. SCRIMGEOUR, *Acta Cryst. B.*, 1975, **31**, (6), 1672-1674

The structures of *cis*-M(en)Cl₂ (M=Pt, Pd) were studied using diffractometer data and refined by least-squares calculations; $R=0.073$ for Pt(en)Cl₂ and 0.057 for Pd(en)Cl₂. The compounds are isomorphous, space groups *C*222, with $Z=4$. The metal atoms have a square-planar configuration and the ethylenediamine rings are puckered, intermolecular Pt-Pt and Pd-Pd distances being 3.381 and 3.369 Å, respectively.

Possible Mode of Action of Anti-Tumour Platinum Drugs: X-ray Evidence for *cis* Binding by Platinum of Two Inosine 5'-Monophosphate Molecules via the N(7) Positions

D. M. L. GOODGAME, I. JEEVES, F. L. PHILLIPS and A. C. SKAPSKI, *Biochim. Biophys. Acta*, 1975, **378**, (1), 153-157

The ion [Pt(NH₃)₂(5'-IMP)₂]²⁺ was obtained by the reaction of *cis*-[Pt(NH₃)₂(H₂O)₂]²⁺ on the disodium salt of inosine 5'-monophosphate. X-ray diffraction studies showed that Pt was bonded to the N(7) atoms of two 5'-IMP moieties. Possible modes of anti-tumour action of platinum compounds are discussed.

Organometallic Compounds with Metal-Metal Bonds. V. New Heteronuclear Tetrametallic Clusters of Platinum with Cobalt or Molybdenum and a New Homotrimetallic Platinum Cluster

P. BRAUNSTEIN, J. DEHAND and J. F. NENNIG, *J. Organometal. Chem.*, 1975, **92**, (1), 117-123

Two new heteronuclear tetrametallic complexes (CO)₅Co₂(CO)₂Pt₂(CO)(PPh₃)₂, (η-C₅H₅)₂(CO)₂Mo₂(CO)₄Pt₂(PPh₃)₂ and a new homonuclear trimetallic complex Pt₃(CO)₉(PPh₃)₄ were synthesised by reaction between Na[Co(CO)₄] or Na[(η-C₅H₅)Mo(CO)₃] and *cis*- or *trans*-PtCl₂(PPh₃)₂. They appear to have a tetrahedral arrangement of the metallic atoms in a butterfly-type structure.

Diolenic Complexes of Rhodium(I) and Iridium(I) with Nitrogen-containing Ligands

G. ZASSINOVICH, G. MESTRONI and A. CAMUS, *J. Organometal. Chem.*, 1975, **91**, (3), 379-388

The synthesis and the substitution and oxidation reactions of the series of Rh(I) and Ir(I) complexes M(L-L)(B)Cl, [M(L-L)(B)₂]X and [M(L-L)(chel)]X, where L-L = *cis*-, *cis*-cycloocta-1, 5-diene, cycloocta-1, 3, 5, 7-tetraene, bicyclo [2.2.1] hepta-2, 5-diene; chel = 8-aminoquinoline, phenylenediamine, dipyriddyketone, substituted phenanthrolines, and X = Cl⁻, PF₆⁻, ClO₄⁻ are described. The use of these complexes as anti-tumour agents is considered.

Hydroxoplatinates(IV) of Calcium, Strontium and Barium

M. TRÖMEL and E. LUPPRICH, *Z. Anorg. Allgem. Chem.*, 1975, **414**, (2), 169-175

CaPt(OH)₆, CaPtO₂(OH)₂, SrPt(OH)₆·2H₂O and BaPt(OH)₆ were prepared by precipitation from alkali hydroxoplatinate(IV) solution with alkali earth salt solutions. These salts are characterised by X-ray diffraction and chemical analysis. The crystal structure of CaPt(OH)₆ was determined. Probable H positions are calculated and H-bonding is discussed.

Reductive Syntheses of Transition Metal Fluoride Compounds. Synthesis of Rhenium, Osmium and Iridium Pentafluorides and Tetrafluorides

R. T. PAINE and L. S. ASPREY, *Inorg. Chem.*, 1975, **14**, (5), 1111-1113

Two simple syntheses of third-row transition series MF₅ and MF₄ (M=Re, Os, Ir) reduced by H₂ or Si metal in anhydrous HF at room temperature are described. The MF₅ and MF₄ are characterised and the data are discussed in terms of known properties of similar compounds.

Alkynyl Compounds of Transition Metals. XXIX. Alkynyl [ethylenebis(diphenylphosphine)] Complexes of Platinum(II)

R. NAST, J. VOSS and R. KRAMOLOWSKY, *Chem. Ber.*, 1975, **108**, (5), 1511-1517

Cis-[PtCl₂(dpe)] reacts with alkali acetylides in liquid NH₃ or liquid methylamine to yield nonionic monomers of the type *cis*-[Pt(C≡CR)₂(dpe)], where dpe = (C₆H₅)₂P[CH₂]₂P(C₆H₅)₂; R = H, CH₃ or C₆H₅. The analogous reaction with the divalent anion of *o*-diethynylbenzene, however, gives the polymeric *cis*-[Pt(C≡C)₂C₆H₄(dpe)]_n. With an excess of acetylide polymeric complexes of the type [K₂Pt(C≡CR)₄(dpe)]_n are precipitated.

Oxidative Addition Reactions of Halogens to Rh(I) Complexes

M. R. GAJENDRAGAD and U. AGARWALA, *J. Inorg. Nucl. Chem.*, 1975, **37**, (7/8), 1834-1835

Studies on oxidative addition reactions of complexes of metal ions of the *d*⁸ system are reported for phosphine complexes of Ir(I) and dihalodicarbonyl complexes of Ir(I). Complexes of Rh(I) are also potential species for such reactions.

Metal-Olefin Complexes: Synthesis and Molecular Structure of *trans*-Chloro(ethylene) bis(triphenylphosphine)iridium(I), IrCl(C₂H₄)(PPh₃)₂

R. J. RESTIVO, G. FERGUSON, T. L. KELLY and C. V. SENOFF, *J. Organometal. Chem.*, 1975, **90**, (1), 101-109

The complex *trans*-IrCl(C₂H₄)(PPh₃)₂ was isolated and its structure determined in the solid state.

The crystals are monoclinic $P2_1/c$, with $a=12.334$, $b=22.957$, $c=14.039\text{\AA}$, $\beta=125.54^\circ$ and $Z=4$. The molecule has a *trans*-square planar configuration. The coordinated C_2H_4 is π -bonded to the Ir atom and is essentially perpendicular to the P_2IrCl plane with a very short C=C distance of 1.375\AA .

ELECTROCHEMISTRY

Interaction of Acetone and Isopropyl Alcohol with Platinum-Black

L. V. RUSALINA, A. D. SEMENOVA and ZH. V. STRELNIKOVA, *Zh. Fiz. Khim.*, 1975, **49**, (6), 1570-1571

Chemisorption behaviour of acetone and isopropyl alcohol on Pt-black in 1N H_2SO_4 was studied using electrochemical and gas chromatography methods. The results show that partial dehydrogenation and breaking down of molecules occurred during chemisorption.

Electrochemical Generation and Reactivity of Organo-Cobalt(IV) and -Rhodium(IV) Chelates

I. LEVITIN, A. L. SIGAN and M. E. VOL'PIN, *Zh. Chem. Soc., Chem. Commun.*, 1975, (12), 469-470

The electro-oxidation of organo-cobalt(III) and -rhodium(III) chelates was investigated. It is found that the reactivity and ease of formation of organometallic cations $[RM^{IV}(\text{chel})]^+$, where R is a primary or secondary alkyl group, depends on the nature of the σ bonded organic ligand which behaves as a carbonium ion and contributes significantly to the structure.

Study of the Hydrogen Adsorption on Ruthenium Catalysts. I. The Effect of Medium Acidity on the Strength of Hydrogen Adsorption on Ruthenium Black Studied by Electrochemical Methods

A. A. VEDENYAPIN, N. D. ZUBAREVA, E. I. KLABUNOVSKII, I. P. GODYASHCHEVA and I. A. RUBTSOV, *Zh. Fiz. Khim.*, 1975, **49**, (6), 1480-1485

Charging curves of H_2 adsorption in 1N H_2SO_4 and 1N KOH on Ru-black showed that the adsorption capacity as well as the strength and heat of adsorption were higher in the alkaline than in the acidic solutions. It is suggested that O_2 atoms present on the surface of Ru in alkaline solutions can act as additional centres for H_2 adsorption.

ELECTRODEPOSITION AND SURFACE COATINGS

Interpolation of Pd and Pt in n-doped BaTiO₃ Ceramics

H. SCHMELZ, *Keram Z.*, 1975, **27**, (4), 198-199

The influence of Pd and Pt containing coatings on the conductivity of n-doped BaTiO₃ ceramics

was studied. Pd or Pt diffusion from the coating into the ceramics during sintering lowers the high permittivity of laminated ceramics to that of the permittivity of the original BaTiO₃, which is smaller by an order of magnitude.

Electrodeposition of a Palladium-Bismuth Alloy

S. N. VINOGRADOV, L. M. FIRYULINA and L. N. KHURTOVA, *Zashchita Metal.*, 1975, **11**, (3), 380-383

The electrodeposition of a Bi-Pd alloy on electrical contacts, from an electrolyte containing Pd and Bi in a complex form was studied. The deposits are characterised by low internal stresses and ease of soldering, in comparison with pure Pd deposits.

LABORATORY APPARATUS AND TECHNIQUE

Cyclic Voltammetric Studies on Platinum Electrodes in Aqueous Electrolytes

K. A. NATARAJAN and I. IWASAKI, *J. Electrochem. Soc. India*, 1975, **24**, (1), 1-6

The experimental techniques involved in cyclic voltammetry are discussed with respect to the electrochemical behaviour of Pt electrodes in inorganic electrolytes. The behaviour of the electrode is studied with reference to the effect of O_2 , electrode pretreatment, scan rate, solution pH and ionic strength of the electrolytes.

HETEROGENEOUS CATALYSIS

Hydrogen Adsorption by Alumina-supported Platinum

L. T. DIXON, R. BARTH, R. J. KOKES and J. W. GRYDER, *J. Catalysis*, 1975, **37**, (2), 376-382

Isotherms at 295 and 77 K for H_2 adsorbed on wet or dry Pt/Al₂O₃ were used to study five kinds of H_2 adsorption. Type I is reversible at 77 K, type II is irreversibly bound at 77 K and type III is an activated chemisorption with i.r. band at 2060/cm. Type IV has i.r. band at 2120/cm and its binding energy is lower than that for type III. Type V H_2 is irreversibly bound at room temperature and is necessary for the adsorption of type IV at 77 K.

Toluene Dealkylation on Platinum Group Metals in the Presence of Water Vapours

G. L. RABINOVICH and V. N. MOZHAIKO, *Neftekhimiya*, 1975, **15**, (3), 373-378

Studies of toluene dealkylation over catalysts containing Pt group metals on γ -Al₂O₃ in the presence of water vapours at 350-510°C showed that the catalytic activity changed in the following manner: Rh > Ir > Pt > Pd > Ru > Os, whereas the selectivity was highest for Pt and Pd followed by Ir, Os, Rh and Ru.

Study of the Mechanism of Isomerisation of 2,2-Dimethylbutane on Platinum/Alumina Catalyst in a Pulsed Regime

YU. N. USOV, N. I. KUVSHINOVA and E. D. CHEKUROVSKAYA, *Neftekhimiya*, 1975, **15**, (2), 224-230

The isomerisation of 2,2-dimethylbutane was carried out on an industrial (0.5% Pt-Al₂O₃-0.3%F) platinum/fluorated γ -Al₂O₃ catalyst. It was shown that the isomerisation process took place on both the γ -Al₂O₃ and metallic Pt surfaces. The mechanism was explained in terms of intermediate carbonium-ion formation on the γ -Al₂O₃ surface and the electron exchange between Pt atoms and the hydrocarbon resulting in the formation of σ and π complexes.

Infra-red Active Species of Hydrogen Adsorbed by Alumina-supported Platinum

L. T. DIXON, R. BARTH and J. W. GRyder, *J. Catalysis*, 1975, **37**, (2), 368-375

Studies were made of two i.r. active H species adsorbed on Pt/Al₂O₃ with bands at 2120 and 2060/cm. Corresponding bands for D at 1520 and 1480/cm were also observed. The results show that the species with i.r. band at 2060/cm is a stronger form with increased intensity in the presence of H₂O and an activated adsorption occurring only above 130 K. The species with a band at 2120/cm adsorbs irreversibly at 77 K if the sample has been exposed to H₂ at 300 K.

Activity of Metallic Catalysts. IV. Influence of the Nature of the Support and Effect of Sulphur-containing Poisons on Two Examples of "Demanding Reactions"

R. MAUREL, G. LECLERCQ and J. BARBIER, *J. Catalysis*, 1975, **37**, (2), 324-331

The activity of various Pt/Al₂O₃ in crystallised or amorphous form with various amounts of sulphate ions, was studied during the hydrogenolysis of cyclopentane at 300°C and the reactions of benzene with D₂ at 85°C, in addition and exchange. The results show that the nonproportionality of activity to metallic surface area of the support are caused by a selective poisoning, S being a selective poison, whereas SO₂ and H₂S at 300°C are nonselective poisons.

On the Differences in the Mechanisms of C₅- and C₆-Dehydrocyclisation of Alkanes in the Presence of Pt/C

O. V. BRAGIN, A. V. PREOBRAZHENSII, A. L. LIBERMAN and B. A. KAZANSKII, *Kinet. Kataliz*, 1975, **16**, (2), 472-475

Studies of rates of C₅- dehydrocyclisation of 2- and 3- methylpentanes alone and with ~20% of the corresponding olefins on 20% Pt/C at 300°C showed that the olefins retard the reaction and cannot, therefore, be reaction intermediates. Similarly the yield of C₆H₆ from hexene-1 is higher than from *n*-hexene.

Hydrogenation of Acetone and Isopropyl Alcohol on Platinum Black in Hydrogen Adsorbed Bed

A. D. SEMENOVA, ZH. V. STRELNIKOVA and L. V. RUSALINA, *Zh. Fiz. Khim.*, 1975, **49**, (6), 1572-1573

The hydrogenation of acetone and isopropyl alcohol on a Pt-black electrode in 1N H₂SO₄ at 25°C was studied. The presence of propane and ethane in the reaction products suggest that the hydrogenation is accompanied by chemisorption followed by dehydrogenation and the subsequent breakdown of the reactants molecules.

Interaction of Acetone with the Surface of Skeleton Platinum-Iridium Catalysts Free from Chemisorption Products

N. V. KROPOTOVA, A. D. SEMENOVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1975, **49**, (6), 1430-1433

The rate of dehydrogenation of acetone on Ir-0-100% Pt skeleton catalysts was studied. For a Ir-75% Pt catalyst the rate of dehydrogenation at 20°C was higher than for pure Pt and Ir catalysts. This is attributed to the presence of an increased number of unpaired d-electrons on its surface. The activation energy of dehydrogenation for the Ir-75% Pt catalyst is 2 ± 1 kcal/mol, whereas for all the other compositions it is 9 ± 1 kcal/mol.

Reactions of Hexanes, Unlabelled and Labelled with ¹³C, on Alumina-supported Palladium-Gold and Platinum-Gold Alloys

A. O'CONNOR and F. G. GAULT, *J. Catalysis*, 1975, **37**, (2), 311-323

Studies of isomerisation and hydrocracking of unlabelled and labelled hexanes over Au-Pd and Au-Pt alloys (10% of metal/Al₂O₃) showed the "cyclic mechanism" on Au-15% Pt alloys but mostly "bond-shift" mechanism on Pt catalyst. A nonselective ring opening of methylcyclopentane also occurred on Au-Pt alloy, but on Pt, only the CH₂-CH₂ secondary-secondary bonds were broken. The Au-15% Pt alloy was active only after pretreatment by air and was deactivated in the presence of H₂.

On the Stability of Palladium/Zeolite Catalysts during Storage

D. V. SOKOL'SKII, N. A. GOGOL', N. L. SHLIOMENZON and L. D. ZHUBANOVA, *Zh. Fiz. Khim.*, 1975, **49**, (4), 896-899

The activities of freshly prepared Pd/zeolite CaA, CaX, NaY(SiO₂/Al₂O₃=1.3; 1.5 and 8.9) catalysts were compared with those stored for up to 4 years. The CaA and CaX catalysts containing 0.2% Pd showed high initial activities as measured in the hydrogenation of dimethylethynylcarbinol. After storage the CaX catalyst decreased in activity while the CaA remained unchanged.

Reduction of Nitric Oxide by Monolithic Supported Palladium-Nickel and Palladium-Ruthenium Alloys

C. H. BARTHOLOMEW, *Ind. Engng. Chem. Prod. Res. Dev.*, 1975, **14**, (1), 29-33

The effect of reaction parameters such as temperature, space velocity and pollutant concentration was studied in a laboratory reactor. Freshly prepared Pd-Ni and Pd-Ru catalysts convert 100% NO (1000 p.p.m.) with less than 5% NH₃ formation in a 0.4% O₂ (1% CO and 250 p.p.m. C₃H₆) mixture at 600 and 480°C, respectively. Conversions of NO, CO and C₃H₆ decrease slightly with increasing space velocity. The effect of dynamic exposure to 100 p.p.m. of SO₂ is to lower slightly but reversibly the NO and C₃H₆ conversions while significantly and irreversibly lowering conversion of CO.

Catalytic Reduction of Nitric Oxide on Ruthenium

R. L. KLIMISCH and K. C. TAYLOR, *Ind. Engng. Chem. Prod. Res. Dev.*, 1975, **14**, (1), 26-29

The details of NO catalytic reduction by CO and H₂ over a supported Ru catalyst were investigated. The feed stream used in these studies resembled automotive exhaust. The effect of space velocity and various reactant concentrations on the NH₃/N₂ product distribution were studied along with the effect of these various parameters on the rate of NO removal.

Kinetic Study and Catalyst Structural Analysis for the Dehydrogenation—Hydrogenolysis of *n*-Pentane over Ru-Al₂O₃ Catalysts

V. RAGAINI, L. FORNI and L. V. MAO, *J. Catalysis*, 1975, **37**, (2), 339-347

Studies were made of the reaction of *n*-pentane over 0.034-1.492% Ru/γ-Al₂O₃ at 1 atm, 450-490°C and molar feed ratio of 5-20. The catalyst activity was strongly dependent on surface topography and a maximum specific activity was at 0.085 wt.% Ru. The results also show that the number of Ru atoms constituting the active centre for dehydrogenation is 2-3.

HOMOGENEOUS CATALYSIS

Fixation of Molecular Nitrogen in Aqueous Solution. Catalysis by Platinum Group Metal Ions

M. M. T. KHAN and A. E. MARTELL, *Inorg. Chem.*, 1975, **14**, (4), 938-939

Isotopic studies of the fixation of N₂ in aqueous solution catalysed by Ru(II)-, Ru(III)-, Rh(III)-, Ir(III)-, Os(II)-, and Os(III)- chloro complexes at 1 atm showed prominent peaks of N₂O at mass numbers 44 and 45 which established N₂ fixation in catalyst systems Ru(II)+TiCl₃ and Rh(III)+SnCl₂. These were the systems which gave the highest yields of NH₃.

A Palladium-Catalysed Conjugated Diene Synthesis from Vinylic Halides and Olefinic Compounds

H. A. DIECK and R. F. HECK, *J. Org. Chem.*, 1975, **40**, (8), 1083-1090

The reaction of vinylic bromides or iodides with olefin compounds at 100-150°C in the presence of a trialkylamine and a catalytic amount of Pd[P(C₆H₅)₃]₂(OAc)₂ produced conjugated dienes. These showed appreciable stereospecificity when (*Z*)- or (*E*)- vinylic halides were treated.

Group VIII Metal Complexes as Catalysts for Halogen Exchange between Alkyl Halides

J. E. LYONS, *J. Chem. Soc., Chem. Commun.*, 1975, (11), 418-419

Chromatographic studies were made of alkyl halide exchange reactions catalysed by coordinatively unsaturated group VIII metal complexes [MX(CO)(Ph₃P)₂] (M=Rh, Ir; X=Cl, Br, I) at 100°C and under 150 lb/in² of either Ar or CO. The results showed formation of acyl Rh complexes under CO pressure.

Selective Hydrogenation of Mesityl Oxide to Methylisobutylketone with the Catalyst RhCl(PPh₃)₃

W. STROHMEIER and E. HITZEL, *J. Organometal. Chem.*, 1975, **91**, (3), 373-377

Mesityl oxide dissolved in toluene is selectively hydrogenated to methylisobutylketone in the presence of RhCl(PPh₃)₃. After 70% conversion the catalyst is deactivated. Without solvent, distilled but not degassed mesityl oxide is completely and selectively hydrogenated to methylisobutylketone. Turnover numbers are 4400. Under these hydrogenation conditions the catalyst is active for >100h.

Homogeneous Catalytic Hydrogenolysis of the C-O Bond: the Selective Reduction of Cyclic Carboxylic Acid Anhydrides to γ-Lactones Catalysed by [RuCl₂(Ph₃P)₃]

J. E. LYONS, *J. Chem. Soc., Chem. Commun.*, 1975, (11), 412-413

[RuCl₂(Ph₃P)₃] efficiently catalyses the selective homogeneous hydrogenolysis of carboxylic acid anhydrides at 100°C and 150 lb/in² H₂. The results show that when the C-O bond of the anhydride is cleared, γ-lactone is formed.

Ruthenium Promoted Oxidation of Amines

S. E. DIAMOND, G. M. TOM and H. TAUBE, *J. Am. Chem. Soc.*, 1975, **97**, (10), 2661-2664

Studies of the oxidation of benzylaminepentaammineruthenium(III) showed a high yield of the nitrite bound to the ion with the imine as a recognisable intermediate stage. The formal reduction potentials for the pentaammineruthenium(III)-(II) couples are given.

Reactions of (η -Allyl)tricarbonylchlororuthenium(II) with Hydrogen and Unsaturated Substrates: Catalytic Hydrogenation and Isomerisation of Alkenes

G. SBRANA, G. BRACA and E. BENEDETTI, *J. Chem. Soc., Dalton Trans.*, 1975, (9), 754-761

Studies were made of the reactions of $[\text{RuCl}(\text{C}_3\text{H}_5)_2(\text{CO})_3]$, with unsaturated substrates such as acrylonitrile (acn), alkynes, butadiene, and acetylenic esters using i.r. and n.m.r. techniques. The solids $[\{\text{RuCl}(\sigma\text{-C}_3\text{H}_5)(\text{CO})_2(\text{acn})\}_2]$, $[\{\text{RuCl}(\text{OC.CR}:\text{C}_3\text{H}_5)(\text{CO})_2\}_2]$ ($\text{R}=\text{R}'=\text{H}$; $\text{R}=\text{H}$, $\text{R}'=\text{Ph}$; and $\text{R}=\text{R}'=\text{Rh}$), and $[\text{RuCl}\{(\text{C}_4\text{H}_9)_2\text{C}_3\text{H}_5\}(\text{CO})_3]$ were isolated. In the case of diethyl acetylenedicarboxylate an alkenyl complex of formula $[\text{RuCl}\{\text{C}(\text{CO}_2\text{Et})\text{CH}.\text{C}(\text{OEt})\text{O}\}(\text{CO})_3]$ was obtained.

Asymmetric Synthesis by Chiral Ruthenium Complexes. I: Enantioselective Hydrogenation of Ketones and Ketoximes Catalysed by $\text{H}_4\text{Ru}_4(\text{CO})_8$ [(-)-DIOP] $_2$

C. BOTTEGHI, M. BIANCHI, E. BENEDETTI and U. MATTEOLI, *Chimia*, 1975, 29, (6), 256-258

$\text{H}_4\text{Ru}_4(\text{CO})_8$ [(-)-DIOP] $_2$ catalyses asymmetric hydrogenation of C-O and C-N double bonds at high temperature and pressure. In the case of *z*-butylphenylketoxim the degree of asymmetric induction reaches 14.5%.

Acid-dependent Selectivity in the Homogeneous Hydrogenation of Mono- and Dienes by Acetatotriphenylphosphine Complexes of Ruthenium and Rhodium

A. SPENCER, *J. Organometal. Chem.*, 1975, 93, (3), 389-395

The hydrogenation of mono- and di-enes by catalysts derived from protonation of $\text{Ru}(\text{CO}_2\text{Me})_2(\text{PPh}_3)_2$ and $\text{Rh}(\text{CO}_2\text{Me})(\text{PPh}_3)_3$ in methanolic solution with *p*-toluenesulphonic acid was studied. The rate of hydrogenation is highly dependent on the acidity. Rapid highly selective reduction of cyclic dienes to monoenes occurs. This selectivity is attributed principally to the superior coordinating power of the dienes.

NEW PATENTS

CHEMICAL COMPOUNDS

New Rhodium Carbonyl Salts

UNION CARBIDE CORP. *U.S. Patent* 3,878,290
New salts have the formula $\text{M Rh}_{12}(\text{CO})_{30}$ where M is divalent Be, Mg, Ca, Sr, Ra, Sc, Y, Mn, Fe, Ru, Re, Co, Ni, Pd, Pt, Zn, Cd, Hg, Ce and Eu.

CHEMICAL TECHNOLOGY

Interaction of Os (IV) Halogen Complexes with Trialkylphosphine Oxides in Extraction Processes

K. A. BOLSHAKOV, N. M. SINITSYN, N. M. BODNAR and M. N. SHAKHOVA, *Zh. Neorg. Khim.*, 1975, 20, (6), 1641-1646

Extraction of Os in the form of $[\text{OsCl}_6]^{2-}$ and $[\text{OsBr}_6]^{2-}$ complexes in HCl medium was carried out using tri-*n*-butylphosphine oxide and tri-*n*-octylphosphine oxide. The extent of Os recovery measured in terms of coefficient of distribution D increases with increasing HCl concentration and attains a maximum at ~ 4 mol HCl. The influence of different extracting reagents, ligands and diluents on the recovery process as well as on the structure and properties of the complexes obtained was also investigated.

ELECTRICAL AND ELECTRONIC ENGINEERING

I-V Characteristics of PtSi-Si Contacts Made from CVD Platinum

M. J. RAND, *J. Electrochem. Soc.*, 1975, 122, (6), 811-815

The use of CVD Pt to make PtSi contacts was studied. With heavily doped Si and sintering at 450-700°C no electrical anomalies appear. With light doping there is still no problem provided a relatively low ($\sim 450^\circ\text{C}$) is used. CVD Pt reliably forms PtSi at this temperature. The effects of higher contact formation temperatures are discussed.

TEMPERATURE MEASUREMENT

Rh-Ir Thermocouples Operate at 2100°C

L. R. THOMAS, *Metal Prog.*, 1975, 107, (6), 55

The new Feussner thermocouples, Ir:40% Ir-Rh, are recommended for applications where continuous temperatures exceed 1700°C up to 2100°C. Accuracy is $\pm 10^\circ\text{C}$. Below 1500°C, Pt is preferred.

ELECTROCHEMISTRY

Electrolytic Electrodes

ELECTRONOR CORP. *British Patent* 1,398,211
Electrolytic electrodes are provided with more stable coatings by depositing a mixture of a Pt-Ir alloy and 2.5-20% of a valve metal oxide on their