

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Heat Capacity of Platinum from 350 to 1200K: Experimental Data and an Analysis of Contributions

C.-C. YEH and C. R. BROOKS, *High Temperature Sci.*, 1973, 5, (6), 403-413

The heat capacity of Pt was measured at 350-1200K using dynamic adiabatic calorimetry. Results showed that the 161 data points were all within $\pm 1\%$ of a polynomial fitted to the data, and this polynomial curve was within 1% of the previous measurement.

Study of Crystallisation in Glasses by Means of Electron Microscopy

I. GUTZOW and M. MARINOW, *Silikattechnik*, 1974, 25, (1), 18-23

The morphology of nucleating condensation cores in the glass as well as forms of growth and equilibrium of small Pt, Ir, Rh, Pd, Au metal crystals in the glass melt volume were studied. Experimental details are described.

On the Stoichiometric Chemisorption of Hydrogen on Platinum

V. S. BORONIN, O. M. POLTORAK and A. O. TURAKULOVA, *Zh. Fiz. Khim.*, 1974, 48, (2), 258-264

A review of the present position in this area (50 refs.).

X-ray Photoemission Spectra of Palladium

S. HUFNER, G. K. WERTHEIM and D. N. E. BUCHANAN, *Chem. Phys. Lett.*, 1974, 24, (4), 527-530

The X-ray photoemission spectra of Pd prepared by vacuum evaporation and by argon ion sputtering were compared; the former shows a close correlation with calculated band structure, while the latter exhibits much less detail, strongly suggesting that the sputtered surface is amorphous. Narrow core lines of the evaporated samples show the asymmetry predicted to arise from the hole-conduction electron interaction.

Adsorption of Hydrogen on Palladium Single Crystal Surfaces

H. CONRAD, G. ERTL and E. E. LATTA, *Surface Sci.*, 1974, 41, (2), 435-446

The adsorption of H₂ on clean Pd(110) and Pd(111) surfaces as well as on a Pd(111) surface with regular step arrays was studied by means of LEED, thermal desorption spectroscopy and contact potential measurements. Maximum work function increases of 0.36, 0.18 and 0.23 eV

were determined for Pd(110), Pd(111) and the stepped surface, respectively, being influenced only by absorbed H₂ under the chosen conditions.

Fe₂P-type Phases in the Ternary Alloys of the Rare Earths with Thallium and Palladium

F. FERRO, R. MARAZZA and G. RAMBALDI, *Z. Metallkunde*, 1974, 65, (1), 40-41

The ternary phases of the alloys of the rare earths with Tl and Pd in the stoichiometric ratio 1:1:1 were studied. They are of the Fe₂P-type. The results obtained, compared with those of the isostructural compounds previously known, are briefly discussed.

Equiatomic Ternary Phases in the Alloys of the Rare Earths with Iridium and Nickel or Palladium

R. FERRO, R. MARAZZA and G. RAMBALDI, *Z. Metallkunde*, 1974, 65, (1), 37-39.

The R.E.-NiIn and R.E.-PdIn compounds were prepared and examined by using the methods of chemical analysis, density measurement, and metallographic and X-ray examinations. These phases are of the Fe₂P structural type and their crystallographic constants were determined.

High Field Magnetostriction in a Metamagnetic FeRh Alloy

J. A. RICODEAU and D. MELVILLE, *J. Physique*, 1974, 35, (2), 149-152

The parallel and perpendicular magnetostriction of polycrystalline equiatomic FeRh was measured in pulsed magnetic fields up to 15T in the anti-ferromagnetic phase and at the anti-ferro-ferromagnetic transition induced by the field. The perpendicular anti-ferromagnetic magnetostriction is $\approx 3 \times 10^{-4}$ at 10T and is temperature dependent. The parallel magnetostriction at 10T is -5×10^{-5} and is temperature independent. The lattice parameter change at the transition agrees with that established by thermal expansion measurements.

Deformation of Single-crystal Ruthenium

D. B. SNOW and J. F. BREEDIS, *Acta Metall.*, 1974, 22, (4), 419-427

Studies of Ru crystals oriented for single slip on (1100) deformed by compression at room temperature showed that the dislocation distribution formed during stage 1 consisted of bundles containing primary edge dipoles while the stage 2 dislocation structure consisted of primary-secondary prism dislocation tangles lying between

tight edge multipoles. Cross-slip activity on (0001) was detected during stages 1 and 2.

Thermodynamic Investigations in the Thorium-Ruthenium System

H. KLEYKAMP and M. MURABAYASHI, *J. Less-common Metals*, 1974, **35**, (2), 227-233

The Gibbs free energy of formation of the intermetallic phases ThRu₂, ThRu, Th₃Ru₂ and Th₇Ru₃ existing in the Th-Ru system was determined by e.m.f. measurements using electrolytic cells with solid CaF₂ electrolyte. The measurements of the Gibbs free energies of formation are given for the intermetallic phases at 1020-1170 K.

Dependence of Electrical Resistance of Rhodium, Iridium and Platinum on Enthalpy

M. M. MARTYNYUK and V. I. TSAPKOV, *Fiz. Metal. Metalloved.*, 1974, **37**, (1), 49-54

Temperature coefficients of resistance for Rh and Ir at 298-1550K are initially proportional to specific heat C_p. α varies linearly with temperature which cannot be explained by the s-d theory of scattering. For these metals from 1550K to their melting points and for Pt from 298K up to its melting point the size of C_p predominates over the increase of α .

CHEMICAL COMPOUNDS

Formation of Platinum(III) Chloride during Thermolysis of Hexachloroplatinic Acid

L. K. SHUBOCHKIN, V. I. GUSHCHIN, G. M. LARIN and V. A. KOLOSOV, *Zh. Neorg. Khim.*, 1974, **19**, (2), 460-463

Studies of the thermal decomposition of H₂PtCl₆ at 20-800°C indicated a range of intermediate products. EPR studies on the decomposition of PtCl₄ at 300-330°C showed that PtCl₃ was formed.

Observations on the Formation of Platinum Silicide

M. J. RAND and J. F. ROBERTS, *Appl. Phys. Lett.*, 1974, **24**, (2), 49-51

When thin-film Pt and single-crystal Si are interdiffused, ~100 Å of SiO₂ is evident at the PtSi surface. The SiO₂ can serve to protect the silicide from attack by aqua regia commonly used to remove unreacted Pt. If, however, the SiO₂ is removed, the PtSi on Si will dissolve in aqua regia even faster than Pt. These findings are particularly applicable to contact technology for Si devices and integrated circuits.

Anisotropy of the Electrical Conductivity of the One-dimensional Conductor K₂[Pt(CN)₄]Br_{0.30}·3(H₂O)

H. R. ZELLER and A. BECK, *J. Phys. Chem. Solids*, 1974, **35**, (1), 77-80

The conductivities $\sigma_{||}$ and σ_{\perp} parallel and per-

pendicular to the c-axis in single crystals of K₂Pt(CN)₄Br_{0.3}·3(H₂O) were measured simultaneously by Montgomery's method. The anisotropy $\sigma_{||}/\sigma_{\perp}$ is of the order 10⁵ at room temperature but decreases to 3·10⁵ at 35K.

Ultraviolet to Far Infrared Optical Properties of the One-dimensional Conductor K₂Pt(CN)₄Br_{0.3}·3H₂O

J. BERNASCONI, P. BRÜESCH, D. KUSE and H. R. ZELLER, *J. Phys. Chem. Solids*, 1974, **35**, (2), 145-157

The optical properties of crystals of the quasi-one-dimensional conductor K₂Pt(CN)₄Br_{0.3}·3H₂O were studied at the special range of 45000 to 10 cm⁻¹. For light polarised perpendicular to the highly conducting direction it behaves as a transparent dielectric, as shown by reflection and transmission spectra.

Organoplatinum(IV) Compounds. I. Trimethylplatinum(IV) Azide, Me₃PtN₃

K.-H. VON DAHLEN and J. LORBERTH, *J. Organometal. Chem.*, 1974, **65**, (2), 267-273

The preparation of trimethylplatinum azide via trimethylplatinum sulphate is reported. The compound is characterised by ¹H N.M.R., mass and vibrational spectroscopy and its probable structure is suggested.

Dimethylplatinum(IV) Compounds. III. Acetylacetonate Complexes

J. R. HALL and G. A. SWILE, *J. Organometal. Chem.*, 1974, **67**, (3), 455-466

The preparation of a number of acetylacetonate complexes of dimethylplatinum(IV) is described and their possible structures are proposed.

Some Cationic Carbonyl Complexes of Rhodium(I)

G. K. N. REDDY and B. R. RAMESH, *J. Organometal. Chem.*, 1974, **67**, (3), 443-447

The preparation of a number of cationic Rh(I) complexes of the type [Rh(CO)₂(N-N)]ClO₄, [Rh(CO)₂L₃]ClO₄ and [Rh(CO)(N-N)L₂]ClO₄, where (N-N) = 2,2-bipyridine or 1,10-phenanthroline and L is a tertiary phosphine or arsine, is described and their structure and assigned. The configuration of the complex ion [Rh(CO)₂L₃]⁺ is dependent on the size of the ligand L.

Some Adducts of RhCl[P(C₆H₁₁)₃]₂, a Rhodium Compound Spontaneously Coordinating Dinitrogen

H. L. M. VAN GAAL, F. G. MOERS and J. J. STEGGERDA, *J. Organometal. Chem.*, 1974, **65**, (2), C43-C45

Solutions of RhCl(PCy₃)₂ react with O₂, N₂, C₂H₄, CO and H₂ to give trans-RhClA(PCy₃)₂, where A = O₂, N₂, C₂H₄ and CO and Cy = cyclohexyl, and to give RhClH₂(PCy₃)₂. The spontaneous formation of the fairly air-stable

RhCl(PCy₃)₂N₂ is ascribed to a combination of the steric requirements and electronic properties of the phosphine ligand.

Phase Relations in the Systems Na₂O-IrO₂ and Na₂O-PtO₂ in Air

C. L. MCDANIEL, *J. Solid State Chem.*, 1974, 9, (2), 139-146

The equilibrium phase relations for the Na₂O-IrO₂ and Na₂O-PtO₂ systems were determined in air using the quenching technique. The Na₂O-IrO₂ system contains two stable compounds, Na₂O-IrO₂ and 2Na₂O.3IrO₂, which dissociate at 1235 and 1040°C, respectively. The Na₂O-PtO₂ system contains Na₂O.PtO₂, metastable 2Na₂O.3PtO₂ and Na_xPt₃O₄ (0 ≤ x ≤ 1). They dissociate at 890, 710 and 810°C, respectively. Indexed X-ray diffraction powder patterns for Na₂O.IrO₂ and 3Na₂O.3IrO₂ are given.

Mass Spectrometric Observation and Stability of Gaseous RuC₂, PtC₂, and IrC₂

K. A. GINGERICH, *J. Chem. Soc., Chem. Commun.*, 1974, (6), 199-200

The gaseous molecules RuC₂, PtC₂ and IrC₂ were detected in a high temperature mass spectrometer and their atomisation energies were determined as 1119.0 ± 38, 1084.1 ± 38, ≤ 1088.3 ± 42 kJ/mol.

ELECTROCHEMISTRY

Radiometric and Electrochemical Study of Methanol Adsorption and Oxidation on Platinum

A. WIECKOWSKI, J. SOBKOWSKI and I. SZAMREJ, *Roczniki Chem.*, 1974, 48, 77-85

The adsorption and oxidation of MeOH on a platinised electrode was studied both by electrochemical and radiochemical methods, used simultaneously, in order to establish the mechanism of this reaction.

Effect of Hydrogen Concentration on Superconductivity and Clustering in Palladium Hydride

J. M. E. HARPER, *Phys. Lett. A*, 1974, 47A, (1), 69-70

A method of preparing superconducting PdH by electrolysis is described. The relationship of the superconducting transition temperature to H-concentration and the behaviour of the H-clustering temperature at high concentrations are reported.

Dissolution of Palladium in Aminochloride Electrolytes by Asymmetric Alternating Current of Industrial Frequency

M. N. FOKIN, N. G. MAKAROVA and I. I. MAZURINA, *Zashchita*, 1974, 10, (1), 82-83

Oscillographic and gravimetric studies of anodic

dissolution of Pd in aminochloride electrolytes (20 g/l Pd, pH=8.5) by asymmetric alternating current of industrial frequency showed that the dissolution rate and the power yield are maximum for anodic current density of 400mA/cm². Maximum dissolution rate of Pd is -0.55 μm/min which compares with practical deposition rate 1-3 μm/min.

ELECTRODEPOSITION AND SURFACE COATINGS

Role of Rinsing during the Activation of ABS Plastics Using Mixed SnCl₂/PdCl₂ Catalysts

A. RANTELL and A. HOLTZMAN, *Electroplating Metal Finish.*, 1974, 27, (2), 15-20

In the plating of plastics involving a mixed SnCl₂/PdCl₂ catalyst system the function and importance of the post-catalyst and the post-accelerator rinse is discussed.

LABORATORY APPARATUS AND TECHNIQUE

Protein Coated Electrodes

E. E. UZGIRIS and J. H. KAPLAN, *Rev. Sci. Instrum.*, 1974, 45, (1), 120-121

A simple method for coating platinised Pt electrodes with bovine serum albumin is described. The coating does not alter the electrical properties of the electrodes in dilute salt solutions and prevents a specific type of surface reaction from occurring between the Pt surface and sucrose buffer.

HETEROGENEOUS CATALYSIS

Aromatisation of Isoheptanes in the Presence of Platinum/Alumina Catalysts

YU. N. USOV and V. F. IL'IN, *Neftekhimiya*, 1974, 14, (1), 49-55

Conversions of five isoheptanes and three alkylcyclopentanes were studied over acidic and basic samples of Pt/Al₂O₃ at 1 atm in flowing H₂ at 370-520°C using pulsed microcatalytic conditions. Aromatisation of the isoheptanes occurred by C₅- and C₆-dehydrocyclisation. The composition of the initial isoheptane affects the relative amounts of C₅- and C₆-dehydrocyclisation.

Relation of the Directions of Catalytic Demethylation of 2-Methylhexane to Its Electronic Structure

I. I. LEVITSKII, KH. M. MINACHEV, I. V. STANKEVICH, E. A. UDAL'TSOVA and A. M. GYUL'MALIEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (1), 39-41

The pressure of H₂ alters the direction of de-

methylation of 2-methylhexane over 20%Pt/C at 375°C by promoting the splitting off of the methyl group bonded to the third atom. Studies of the electronic structure of 2-methylhexane showed that C atom of the CH₃ groups carry maximum negative charge but minimum electron density is centred on the third atom.

Investigation of the Efficiency of Platinum/Zeolite Catalysts in the Decomposition of H₂O₂. IV. Activity of Platinum/Zeolite Catalysts Produced by the Ion Exchange Method on CaY Zeolite

T. G. MARTYNYUK, T. A. POSPELOVA, V. I. SHEKHOBALOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1974, **48**, (3), 602-604

The activity of Pt was related to its content in CaY zeolite (SiO₂:Al₂O₃=4.8) for the decomposition of H₂O₂. Results for CaY and NaY zeolites are analogous but catalysts supported on CaY zeolite have 4-12 times greater activity. Activation energy is 10.8 kcal/mole.

Acidity and Catalytic Activity of Pt-containing Zeolites

K. V. TOPCHIEVA, V. A. DOROGOCHINSKAYA and KHO SHU TKHOANG, *Zh. Fiz. Khim.*, 1974, **48**, (1), 182-184

The acidity of Pt/zeolite, determined by high temperature NH₃ adsorption, was compared with catalytic activity for *n*-C₆H₁₄ isomerisation. Acidities of samples after reduction of Pt by H₂ are almost equal and are much less than acid than initial Ca-decationised samples. Strong acid centres are unnecessary for *n*-C₆H₁₄ isomerisation.

Investigation of the Stepwise Mechanism and Selectivity of Hydrogenation of Stable Iminoxyl Radicals on Pt Catalyst

E. F. LITVIN, L. M. KOZLOVA, A. B. SHAPIRO, L. KH. FREIDLIN and E. G. ROZANTSEV, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (1), 48-52

Studies of the liquid phase hydrogenation of iminoxyl radicals on Pt black showed that biradicals are reduced selectively through the formation of hydroxylamine radicals. The selectivity is due to more stable adsorption of biradicals on Pt compared to the intermediate formation of nonradicals. Noncatalytic reduction of the biradicals by phenylhydrazine is non-selective, with simultaneous formation of hydroxylamine radicals and of dihydroxylamine.

Exhaustion of Absorption Platinum Catalysts in the Decomposition of H₂O₂

T. G. MARTYNYUK, Z. V. LUK'YANOVA, V. I. SHEKHOBALOVA, T. A. POSPELOVA and N. I. KOBOZEV, *Zh. Fiz. Khim.*, 1974, **48**, (2), 327-330

The activity of Pt/SiO₂, Pt/zeolite, Pt/C, Pt/ZnO, and Pt/WO₃ for H₂O₂ decomposition is stable after reduction by aqueous NaBH₄ solution but when reduced by electrolytic H₂ at 300-380°C

or when treated before use with H₂O the activity falls, first sharply and then gradually. Pt black reduced by these methods shows no loss of activity. Activation energy remains constant at 11 kcal/mole. The loss of activity is suggested as being caused by the action of the solvent on the surface of the catalyst support.

Hydrogenation of Dimethylethynylcarbinol on Palladium/Polymer Catalysts in the Presence of Some Cations

O. A. TYURENKOVA and N. A. TERPUGOVA, *Zh. Fiz. Khim.*, 1974, **48**, (1), 67-69

Potentiometric studies of the hydrogenation of dimethylethynylcarbinol on Pd/polymer catalysts in the presence of Zn, Pb and Cd ions showed that ZnSO₄ reduces the rate of hydrogenation on polyacrylonitrile and anide catalysts, and increases the rate of H₂ addition on colloidal catalysts by protection by polyvinyl alcohol. The rate of double bond hydrogenation is greatly reduced. Pb acetate and Cd sulphate solutions almost completely suppress the reaction.

Hydrogenation of Dimethylethynylcarbinols on Mechanical Mixtures Containing Pd/CaA Zeolite Catalysts

D. V. SOKOL'SKII, N. A. GOGOL' and N. L. SHLIOMENZON, *Zh. Fiz. Khim.*, 1974, **48**, (1), 131-133

Studies of the activity of mechanical mixtures containing Pd/zeolite with 0.1-5.0 wt.% active component for hydrogenation of dimethylethynylcarbinol showed that their activities are generally similar, variation only occurring for selectivity of hydrogenation of triple bonds.

Activity of Pd Catalysts Produced in an Ultrasonic Field in the Original State

I. V. SOLOV'eva and A. N. MAL'TSEV, *Zh. Fiz. Khim.*, 1974, **48**, (1), 194-195

The activity of newly formed Pd catalysts during hydrogenation of acrylic acid was compared for those formed from PdCl₂ using H₂ in an ultrasonic field and those formed with vibration. Pd catalysts in the crystalline state have higher activity when produced in the ultrasonic field, thus indicating the specific action of an ultrasonic field during catalyst generation.

Kinetics of the Selective Hydrogenation of Dimethylethynylcarbinol on Palladium in the Vapour Phase. II. Reaction of Dimethylethynylcarbinol with Deuterium and the Kinetic Isotope Effect

D. Z. LEVIN, E. P. PROKOFIEV, B. S. GUDKOV, S. L. KIPERMAN and M. A. BESPROZVANNYI, *Kinet. Kataliz*, 1974, **15**, (1), 98-103

Studies at 153 and 203°C of the reaction of dimethylethynylcarbinol with D₂ in the vapour phase over Pd in a steady system showed that the

kinetic isotope effect for H_2 - D_2 exchange during the hydrogenation was 1.8-1.9. Theoretical and experimental values were close. The distribution of D_2 in the reaction products was measured by infra-red spectroscopy, proton magnetic resonance and mass spectroscopy.

On the Mechanism of Reaction of Butyn-2-diol-1,4 with Degasified Rhodium-Zirconium and Zirconium Electrode Catalysts

M. V. AVRAMENKO, V. M. TSINTSEVICH, G. P. KHOMCHENKO and M. B. KATS, *Zh. Fiz. Khim.*, 1974, **48**, (3), 749-750

Studies of the mechanism of adsorption of butyn-2-diol-1,4 on Rh-Zr and Zr skeleton electrodes showed that the electrooxidation current is hardly affected by the pH of the media (0.1N H_2SO_4 and 0.1 N KOH), or by the potentials at which the double layer is formed. The dehydrogenation current is proportional to the initial diol concentration. Adsorption of the diol occurs by a chemical mechanism.

Carbon Dioxide Methanation on a Ruthenium Catalyst

P. J. LUNDE and F. L. KESTER, *Ind. Engng. Chem., Process Des. Dev.*, 1974, **13**, (1), 27-33

The rate of methanation of CO with H_2 was empirically determined at 200-350°F on a 0.5% Ru/ Al_2O_3 catalyst according to $4H_2(g) + CO_2(g) \rightleftharpoons 2H_2O(g) + CH_4(g) + 43$ kcal. Various feed ratios of $H_2:CO_2$ were investigated. Theoretical equilibrium compositions for the feed mixture from 200-800°F are given.

Hydrogenolysis of gem-Dimethylcyclobutane on Group VIII Noble Metals

O. V. BRAGIN, E. G. KHELKOVSKAYA-SERGEVA, S. V. ZOTOVA, E. I. VOSTOKOVA and A. L. LIBERMAN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (2), 363-365

Hydrogenolysis of gem-dimethylcyclobutane on 20wt.% Pt/C, Pd/C, Rh/C, Ir/C and Ru/C occurs selectively at the unshielded bonds and produces 2, 2-dimethylbutane.

HOMOGENEOUS CATALYSIS

Homogeneous Hydrogenation of Sulpholene-3 into Sulpholane in the Presence of the Reduced Complex of $PtCl_2(H_2O)[P(C_6F_5)_3]$

V. F. ODYAKOV, K. I. MATVEEV, N. N. SUSHILOVA and A. V. MASHKINA, *Kinet. Kataliz*, 1974, **15**, (1), 76-81

Sulpholene-3 in the presence of $PtCl_2(H_2O)[P(C_6F_5)_3]$ reduced by H_2 is converted to sulpholane at 25°C with only partial intermediate isomerisation to sulpholene-2. Rate of hydrogenation is proportional to total Pt concentration, tending to a maximum at increased concentration

of sulpholene-3 and increased p_{H_2} . Activation energy is 10.9 ± 1.3 kcal/mole. Butadiene activates the catalyst and SO_2 in low concentration poisons it.

Palladium-catalysed Linear Dimerisation of Conjugated Dienes

A. D. JOSEY, *J. Org. Chem.*, 1974, **39**, (2), 139-145

The dimerisation of isoprene in the presence of bis(triphenylphosphine) maleic anhydride palladium(O) occurs in exclusively tail-tail fashion to give 2,7-dimethyl-1,3,7-octatriene. 2-Ethyl-1,3-butadiene is dimerised similarly to give the corresponding 2,7-diethyl derivative. The isoprene-butadiene codimer is rearranged by catalytic amounts of base to a single conjugated triene or cyclised by stoichiometric base to isomeric dimethylcycloheptadienes.

Study of the Direction and Selectivity of the Hydrogenation of Acetylene Hydrocarbons in the Presence of the Chloro(dimethylsulphoxide)palladium Complex

L. KH. FREIDLIN, YU. A. KOPYTTSEV and N. M. NAZAROVA, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1974, (3), 604-608

Hydrogenation of $C \equiv C$ bonds catalysed by chloro(DMSO) Pd complex is zero order with respect to the substrate; the reaction rate is not related to the length of substituted hydrocarbons. Monosubstituted alkyl acetylenes are reduced at a lower rate than disubstituted acetylenes. Reduction of alkyls occurs by stages with high selectivity and stereospecificity. Diphenylacetylene is reduced by a stageless mechanism to form diphenylethane.

Noble Metal Catalysis. III. Preparation of Dialkyl Oxalates by Oxidative Carbonylation

D. M. FENTON and P. J. STEINWAND, *J. Org. Chem.*, 1974, **39**, (5), 701-704

Dialkyl oxalates were prepared by oxidative carbonylation in the presence of alcohols and dehydrating agents using a Pd redox system and O_2 .

Effect of the Nature of the Oxidiser on the Rate of Oxidation of Ethylene in the Presence of Aquo-complexes of Palladium(II)

N. B. SHITOVA, L. I. KUZNETSOVA and K. I. MATVEEV, *Kinet. Kataliz*, 1974, **15**, (1), 72-75

C_2H_4 was oxidised over aqueous acidic Pd_2SO_4 solutions with *n*-benzoquinone, $Fe_2(SO_4)_3$ and $K_2Cr_2O_7$. *n*- $C_6H_4O_3$ is stable up to $[n-C_6H_4O_2]/[Pd] = 1$. Reaction rate is not related to *n*- $C_6H_4O_2$ concentration at $[n-C_6H_4O_2]/[Pd] = 1.5-8.0$. Pd is precipitated when $[Fe^{3+}]/[Pd] > 200$. *n*- $C_6H_4O_2$ is better able than Fe^{3+} to form Pd(O) complexes. Reaction rate is proportional to the square root of $Cr_2O_7^{2-}$ concentration. The limiting stage of the reaction is a stage in the oxidation of Pd(O) to Pd(II) complexes.

Hydrogenation of Unsaturated Hydrocarbons in the Presence of Platinum Group Metals and Phosphorus-containing Polymers

R. G. MURATOVA, R. Z. KHAIRULLINA, S. V. SHULYNDIN, B. E. IVANOV and R. I. IZMAILOV, *Kinet. Kataliz*, 1974, 15, (1), 137-140

Studies of the liquid-phase hydrogenation of isoprene, phenylacetylene and hexyne-1 in C_2H_5OH solution in the presence of $PdCl_2$ or H_2PtCl_6 with P-containing polymers at 10-40°C showed that the polymer increases the rate of hydrogenation by 1.5 to 10 times. There was a negative temperature coefficient of hydrogenation of isoprene and phenylacetylene. It is suggested that the hydrogenation occurs in stages and that the thermal effect of intermediate complex formation is larger than the activation energy for conversion of intermediates to the final product.

Mechanism and Kinetics of the Decarbonylation of Para-substituted Benzoyl and Phenylacetyl Chlorides by Chlorotris(triphenylphosphine) rhodium(I)

J. K. STILLE and M. T. REGAN, *J. Am. Chem. Soc.*, 1974, 94, (5), 1508-1514

Mechanism of Decarbonylation of Acid Chlorides by Chlorotris(triphenylphosphine) rhodium(I). Stereochemistry

J. K. STILLE and R. W. FRIES, *Ibid.*, 1514-1518

Mechanism of Acid Chloride Decarbonylation with Chlorotris(triphenylphosphine) rhodium (I) Stereochemistry and Direction of Elimination

J. K. STILLE, F. HUANG and M. T. REGAN, *Ibid.*, 1518-1522

Studies using $RhCl(Ph_3P)_3$ indicated the mechanism and kinetics for decarbonylation of para-substituted benzoyl and phenylacetyl chlorides, acid chlorides and acid chloride decarbonylation.

Aspects of Catalysis. Part II. Dimethyl Sulphoxide Complexes of Iridium(III) including Hydrides

Y. M. Y. HADDAD, H. B. HENBEST and J. TROCHAGRIMSHAW, *J. Chem. Soc., Perkin Trans. I.*, 1974, (5), 592-595

The preparation of a number of DMSO Complexes of Ir(III) is described, including the catalytically active dichlorotris(DMSO) hydrido-iridium(I). Structures of these complexes are assigned.

Hydrogen Transfer Reactions Promoted by Iridium Complexes

R. ZANELLA, F. CANZIANI, R. ROS and M. GRAZIANI, *J. Organometal. Chem.*, 1974, 67, (3), 449-454

The use of Ir(I) complexes to promote hydrogen transfer from EtOH to diphenylacetylene to give *trans*-stilbene is described and a reaction mechanism is proposed.

Reactions of $RuCl_2(PPh_3)_3$ with Carbinols: Formation of Ethers, Hydrogen-Deuterium Exchange, and Racemisation of Optically Active Alcohols

Y. SASSON and J. BLUM, *J. Chem. Soc., Chem. Commun.*, 1974, (8), 309-310

Studies of $RuCl_2(PPh_3)_3$ catalyst during conversion of tertiary and substituted secondary carbinols into ethers, H-D exchange in primary and secondary alcohols, and racemisation of optically active alcohols showed the intermediacy of Ru alkoxides, and β -H₂ transfer in the formation of Ru hydrides from carbinols.

CHEMICAL TECHNOLOGY

Corrosion Behaviour of Titanium and Its Palladium Alloy during Heat Transfer in Moving Solutions.

I. V. RYSHKIN, M. G. KOLOSOV and N. D. TOMASHOV, *Zashita Met.*, 1974, 10, (1), 28-32

Corrosion studies of Ti and 0.2% Pd/Ti during the heat exchange in moving 5-20% HCl showed that the corrosion resistance depends on the temperature of the media, quantity of heat transferred and the direction of the thermal current. Temperature range of corrosion resistance increased in turbulent flow around the disc electrode in the air absorbed HCl.

ELECTRICAL AND ELECTRONIC ENGINEERING

Structure and D.C. Electrical Properties of a Au-Rh-Glass Thick-Film System

J. W. M. BIESTERBOS, *J. Appl. Phys.*, 1974, 45, (1), 153-160

The structure and d.c. properties of a metal-glass thick-film system were studied and the influence of the firing treatment, and of the film composition are discussed. Different types of conduction observed in this thick-film system are correlated with film structure.

TEMPERATURE MEASUREMENT

Catalytic Effects on Pt-Pt/Rh Thermocouples in Combustion Systems Involving Hydrogen as the Fuel

M. V. D. 'SOUZA, G. A. KARIM and M. RASHIDI, *J. Phys. E, Sci. Instrum.*, 1974, 7, (1), 65-66

Extensive tests were carried out to assess the performance of quartz sheathed Pt:13% Rh-Pt thermocouples in a stirred reaction which was fuelled with H₂. Observation of thermocouples contamination by SiO₂ when heated for 50h at 1200°C showed. 1% increase in the indicated temperature of 0.076 mm diameter Pt:13% Rh-Pt thermocouples.