

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Oscillations in the Oxidation of Carbon Monoxide on a Platinum Foil

R. T. PLICHTA and R. A. SCHMITZ, *Chem. Eng. Commun.*, 1979, **3**, (4-5), 387-398

The oxidation of CO in a gradientless reactor on a polycrystalline Pt foil was examined for oscillatory states. Measurements of instantaneous CO₂ concentrations in the reactor effluent were undertaken. The catalytic activity of the Pt foil was found to vary between experimental tests with different feed mixtures from 1.08 to 1.82% CO and reactor temperatures 239-299°C.

Reflection of Helium Ions from Polycrystalline Platinum

E. S. MASHKOVA and V. A. MOLCHANOV, *Zh. Eksp. Teor. Fiz.*, 1979, **77**, (6), 2269-2275

Experimental studies of the energy distribution of 10-35 keV He ions reflected from polycrystalline Pt were performed. The results are compared with the multiple scattering theory developed by Firsov. An appreciable discrepancy between the experiments and theory is observed.

Morphology of Pt-Rh Alloy Crystallites on Amorphous SiO₂

M. CHEN, T. WANG and L. D. SCHMIDT, *J. Catal.*, 1979, **60**, (3), 356-368

The structure of 20-200Å diameter Pt-Rh alloy particles on planar amorphous SiO₂ surfaces following pre-treatment in N₂ or air and temperatures up to 1000°C were examined. Heating in N₂ produces only alloy particles, at all temperatures. Above 400°C a Rh₂O₃ layer grows around each particle. Over 600°C the oxide migrates onto the SiO₂ to form a thin Rh₂O₃ layer surrounding the metal core. Pure Rh particles are completely oxidised by 600°C and are stable to at least 1000°C. Continuous 10Å thick Rh or Pt-Rh films cannot be broken into particles below 700°C by heating in air because the film is stable and adheres strongly to the SiO₂.

Surface Composition of Pt/Rh Alloys

F. L. WILLIAMS and G. C. NELSON, *Appl. Surf. Sci.*, 1979, **3**, (3), 409-415

Pt-Rh alloys containing 90, 50 and 10 at.% Pt were examined by ion scattering spectroscopy to determine surface composition as a function of temperature. Between 800-1400K the surfaces of the alloys were enriched in Pt. At 1300K the surfaces contained 97, 77 and 27 at.% Pt, respectively, and was a maximum near 1050K. Since segregation of Rh to the surface was expected, no satisfactory explanation for the disparity has been found. Below

800K Pt surface segregation decreases to zero (bulk composition). Sputter removal of quenched surface layers indicates that surface enrichment only occurs in the outer atomic layer.

Formation of Platinum Silicides under Ultrahigh Vacuum and Controlled Impurity Ambients

C. A. CRIDER, Ph.D. Thesis, Princeton University, 1979, *Diss. Abstr. Int. B*, 1979, **40**, (3), 1289-1290

The first clean, well controlled silicide kinetic study for the Pt-Si system was performed in an UHV analysis chamber at 1×10^{-10} Torr. High purity Pt films were deposited on atomically clean Si substrates. Diffusivities 10^2 higher than previous works were attained. A strong dependence of diffusivity on deposition rate was observed. Various phase growth sequences were observed for uncontaminated O impurities. Small O concentrations decreased diffusivities. Diffusivities for PtSi formation in samples which initially had O contaminated Pt films are observed to be related to the Pt₂Si diffusivities in the same films, even though the Pt₂Si growth front is believed to sweep out the impurities.

Crystallite Size Effects in the Palladium/Hydrogen System: A Simultaneous Sorption and X-Ray Study

D. H. EVERETT and P. A. SERMON, *Z. Phys. Chem. (Frankfurt am Main)*, 1979, **114**, 109-122

X-ray and simultaneous sorption studies of the effect of crystallite size on H₂ sorption by Pd black were performed. The hysteresis loop shrinks with decreasing crystallite size but never vanishes. The lattice parameters of the α - and β -phases are independent of crystallite size. Two additional phases with lattice parameters between those of the α - and β -phases are detected. The apparent decrease, followed by an increase, in the fraction of the system in the α -phase before the $\alpha \rightarrow \beta$ transition commences is explained.

The Elastic Modulus and Diffusion Coefficients of Silver-Palladium Composition Modulated Foils

G. E. HÉNEIN, Ph.D. Thesis, Northwestern University, 1979, *Diss. Abstr. Int. B*, 1979, **40**, (6), 279

Measurements of elastic properties were made on Ag-Pd and Cu-Au foils and compared. Values of elastic modulus $Y_{[111]}$ enhancement were a maximum for a 2.3 nm wavelength. This was a 235% increase over the homogeneous value of $Y_{[111]}$. An increase by 220% in the tensile strength also occurred. The increase in $Y_{[111]}$ was proportional to the square of the composition amplitude. Modulated films had non-hookean, but elastic behaviour under stress in the bulge-test experiment.

Electrical Resistivity Studies of $(\text{Pd}_{95}\text{Rh}_5)_x\text{H}_x$

D. J. GILLESPIE and A. C. EHRLICH, *Z. Phys. Chem. (Frankfurt am Main)*, 1979, **114**, 175-183

Temperature dependent electrical resistivity studies were made on the $(\text{Pd}_{95}\text{Rh}_5)_x\text{H}_x$ system. The superconducting transition temperature was determined as a function of H concentration. A series of electrical resistivity measurements was made on a $\text{Pd}_{95}\text{Rh}_5$ sample at 2-3000K using four probe techniques. Both the temperature dependent part of the resistance and residual resistance of the sample decreased with the number of times the sample had been cycled. Each fell approximately 33% in eleven cycles.

The Alloys of Ruthenium with Palladium and Chromium as Well as Some Other Transition Metals

W. WOPERSNOW and C. J. RAUB, *Metall (Berlin)*, 1979, **33**, (12), 1261-1265

In ternary Ru-Pd-Cr alloys, and other Ru or Pd containing samples, deformation characteristics, corrosion resistance in aggressive media and contact behaviour in different conditions were examined. Ru-Pd-Cr alloys combine the most favourable corrosion resistance behaviour of binary Ru-Cr alloys with the good deformation characteristics of Pd-Cr alloys. The isothermal section of the ternary systems of Ru-Pd-Cr at 930°C was established and the binary system Ru-Cr system was re-examined.

Silicide Formation by High-Dose Si^{+} - Ion Implantation of Pd

G. E. CHAPMAN, S. S. LAU, S. MATTESON and J. W. MAYER, *J. Appl. Phys.*, 1979, **50**, (10), 6321-6327

The formation of Pd silicide phases by Si implantation into evaporated Pd films on two different substrates, Si and SiO_2 , was studied. The amount and phase of silicide formed depended on the implantation temperature, substrate type and the penetration of the ions relative to the substrate depth. Pd_2Si formed on both types of surface, even at 150°C. Amorphous Pd_4Si formed at low temperature on SiO_2 substrate, whereas with the Si substrate, Pd_2Si formed under all conditions, and there was a large incorporation of Si from the substrate into the Pd; the extent depending on temperature. This is explained in terms of radiation-enhanced diffusion, assisted by dynamic cascade mixing.

Structural Changes of Amorphous $\text{Pd}_{80}\text{Si}_{20}$ with Neutron Irradiation, with an Interpretation in Terms of the Imperfections in the Structure of Amorphous Solids

K. DOI, T. AYANO and K. KAWAMURA, *J. Non-Cryst. Solids*, 1979, **34**, (3), 405-418

Amorphous $\text{Pd}_{80}\text{Si}_{20}$ was irradiated with neutrons and the structural changes produced were examined by X-ray scattering and differential scanning calorimetry. Before irradiation $\text{Pd}_{80}\text{Si}_{20}$ had dense random packing with the coherence between

neighbouring Pd atoms extending further than expected, and the coherent length being about 8Å. After irradiation the coherent lengths are separated by about 20Å, producing structural inhomogeneities, and the glass transition temperature increases by about 10K.

Ultrasonic Attenuation and Velocity Studies of Amorphous PdSiCu

H. ARAKI, G. PARK, A. HIKATA and C. ELBAUM, *Solid State Commun.*, 1979, **32**, (8), 625-629

Ultrasonic attenuation and velocity changes were measured in metallic glass $\text{Pd}_{0.775}\text{Si}_{0.665}\text{Cu}_{0.06}$ as a function of amplitude, in the frequency range 10 to 90 MHz for $0.3 \leq T \leq 10\text{K}$. The amplitude dependent attenuation changes observed were larger by a factor of 100-1000 than values obtained from current two-level system tunnelling theory. The attenuation changes have a linear (rather than quadratic) dependence on frequency and a weak T dependence (rather than 1/T).

Adsorption Properties of Mixed Catalysts Applied on Carbon

G. D. ZAKUMBAEVA, L. A. BEKETAEVA and R. M. LEVIT, *Elektrokhimiya*, 1979, **15**, (8), 1138-1143

Potentiodynamic and X-ray diffraction studies of the adsorption of H_2 on binary Rh-Pd, Rh-Pt and Ru-Pt catalysts supported on C with a wide range of metal ratios and a reduction temperature of 100-300°C were performed. The results showed that the variation in the content of active phase and chemical composition of the catalysts can lead to large changes in the amount and formation of sorbed H_2 at various temperatures.

CHEMICAL COMPOUNDS

A Novel Di-Platinum(II) Octaphosphite Complex Showing Metal-Metal Bonding and Intense Luminescence; a Potential Probe for Basic Protein. X-Ray Crystal and Molecular Structure

M. A. F. D. R. PINTO, P. J. SADLER, S. NEIDLE, M. R. SANDERSON, A. SUBBIAH and R. KURODA, *J. Chem. Soc., Chem. Commun.*, 1980, (1), 13-15

X-ray crystallography and ^{195}Pt and ^{31}P NMR spectroscopy show that an intensely luminescent product from $\text{K}_2\text{PtCl}_4 - \text{H}_3\text{PO}_3$ reactions is a dimer with close Pt atoms bridged by four P-O-P linkages from diphosphorous acid ligands. This may also be required for luminescence in other Pt complexes.

Photosensitive Complexes of Palladium and Platinum with Organo-Tellurium Ligands

Res. Discl., 1979, (187), 624-625

The preparation of various photosensitive Pd and Pt complexes, such as $[(\text{C}_6\text{H}_5)_2\text{Te}]_2\text{Pd}(\text{SCN})_2$ and $[(\text{C}_6\text{H}_5)_2\text{Te}]_2\text{PdC}_2\text{O}_4$ is described. These complexes are sensitive to u.v. or visible radiation and a

photographic element containing a layer of these complexes can be exposed to produce an image containing physically developable Pd or Pt nuclei. The elements can be developed via usual routes with heavy metal developers and non metal developers.

ELECTROCHEMISTRY

Proflavine-Sensitized Photoproduction of H₂ from Water with Electron-Donors and a Colloidal Redox Catalyst

K. KALYANASUNDARAM and M. GRÄTZEL, *J. Chem. Soc., Chem. Commun.*, 1979, (24), 1137-1138

The efficient photoproduction of H₂ from water in the presence of electron donors, such as EDTA or TEOA, and a colloidal Pt-redox catalyst, sensitised by proflavine is reported. This is a two-component redox system for H₂ production, as against the common three-component systems with an electron acceptor.

Electrochemical Glucose Oxidation on a Platinized Platinum Electrode in Krels-Ringer Solution. III. Effect of Urea

L. MARINČIĆ, J. S. SOELDNER, J. GINER and C. K. COLTON, *J. Electrochem. Soc.*, 1979, **126**, (10), 1687-1692

The anodic oxidation of glucose and urea on a platinized Pt rotating disc electrode was studied by linear and triangular sweep voltammetry in a modified Krels-Ringer solution. When glucose was the only reactant, three distinct potential regions of glucose oxidation existed in the current/potential curve. When urea was the only reactant, a small steady-state oxidation current was observed at high potentials and there were absorption effects. When both glucose and urea were present, glucose oxidation was strongly inhibited. For some conditions the relationship between glucose concentration and measured current is hardly affected by changes in urea concentration, suggesting possible development of an implanted electrochemical glucose sensor.

Characterization of Hg-Pt Optically Transparent Electrodes. Transmission Spectroelectrochemical Study of Anion Adsorption at a Hg-Pt Optically Transparent Electrode

J. F. GOELZ and W. R. HEINEMAN, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **103**, (2), 147-154, 155-163

A Hg-coated Pt film optically transparent electrode (Hg-Pt OTE) has been studied with respect to its surface. The method for preparing Hg-Pt OTEs by electrochemically depositing Hg on a vapour-deposited Pt OTE was developed. The specific adsorption of anions on Hg-Pt OTEs was studied by transmission spectroelectrochemistry. Double potential step studies performed while passing 525 nm light through a Hg-Pt OTE in contact with aqueous solutions of NaF, NaBr, NaNO₃, Na₂CO₃, etc. produce optical signals. The optical response for NaBr is wavelength-dependent from 400-600 nm.

Sintering of Dispersed Platinum and Rhodium in Aqueous Solutions of Electrolytes

B. I. PODLOVCHENKO and T. D. GLADYSHEVA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **103**, (3), 375-381

The sintering of electrolytic deposits of Pt and Rh and Pt black in 0.5M H₂SO₄ and in aqueous solutions of acidified sulphate, chloride, bromide and alkali sulphate was studied under potentiostatic conditions. The effect of the anions on the degree of Pt sintering was largely determined by the effect of the specific adsorption of the anion on the values of σ . It is suggested that the changes in the surface of the Pt are due to the migration of vacancies and the surface self-diffusion of Pt atoms which leads to a decrease in the microporosity. (38 Refs.)

Cyclic Cleavage of Water into H₂ and O₂ by Visible Light with Coupled Redox Catalysts

K. KALYANASUNDARAM and M. GRÄTZEL, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, (9), 701-702

A complete system of cleaving water by the light from a 250W lamp, comprises the catalysts Pt and RuO₂ and the sensitizer Ru(bpy)₃²⁺ as well as acceptor methylviologen. 150 ml of solution gave 0.6 ml of H₂ and 0.3 ml of O₂ in 3 hours.

The Chemisorption of CO and CO₂ on Rh(III) Studied by High Resolution Electron Energy Loss Spectroscopy

L. H. DUBOIS and G. A. SOMORJAI, *Surf. Sci.*, 1980, **91**, (2/3), 514-532

ELS, TDS and LEED were used to study CO and CO₂ chemisorption on Rh(III). The vibrational spectra of CO indicate two distinct binding sites, atop and bridged, whose relative populations and vibrational frequencies are determined by both substrate temperature and background pressure. Bridge bonded CO have ~4 kcal/mol less binding energy to the surface than the species located in the atop site. Surface pretreatment affected CO adsorption; O₂ and C inhibited CO chemisorption and weakened the metal-adsorbate bond strength. CO₂ adsorption had identical spectra to chemisorbed CO.

Nitric Oxide Adsorption and Decomposition on the (111) and (110) Surfaces of Iridium

P. A. ZHDAN, G. K. BORESKOV, A. I. BORONIN, A. P. SCHEPELIN, W. F. EGGLEHOF and W. H. WEINBERG, *J. Catal.*, 1979, **60**, (1), 93-99

UPS and XPS were used to study adsorption states of NO on Ir(111) and Ir(110) surfaces. On Ir(110) one state predominates and this decomposes at a higher temperature than the two states of equal population on Ir(111). NO decomposition studies show that Ir is a better decomposition than reduction catalyst, and CO is needed to prevent poisoning by a surface oxide. Surface oxide formation begins at a lower temperature with NO as oxidising agent than with O₂.

Oxidative Control of Organosulfur Pollutants

D. C. AYRES and C. M. SCOTT, *Environ. Sci. Technol.*, 1979, **13**, (11), 1383-1387

RuO₄ was studied to find its effectiveness in pollution control against a group of thiophenes and related odorants. Rates of oxidation of these substances in saturated K permanganate were determined at pH 12 and 22°C. A considerable residue would survive scrubbing with permanganate since half-life times were in the range 12.5-1215 min. However, with aqueous RuO₄, a powerful primary oxidant, the oxidation rates were at least 100 times those found for permanganate.

Production of H₂ and CO from Liquid Water Using Solar Energy

T. KAWAI and T. SAKATA, *J. Chem. Soc., Chem. Commun.*, 1979, (23), 1047-1048

Gaseous H₂, CO and CO₂ were produced from water and C by photocatalytic processes using TiO₂-RuO₂ as a catalyst. TiO₂, RuO₂, C and water vapour were heated from 60-80°C to assist the oxidation of C, after which the reaction rate increased by five times and CO₂ was also formed.

ELECTRODEPOSITION AND SURFACE COATINGS

Creep Property Improvement of $\alpha + \beta$ Titanium Alloys by Platinum Ion Plating

S. FUJISHIRO, D. EYLON and R. W. GEHRING, *Thin Solid Films*, 1979, **63**, (1), 55-60

The effect of Pt ion plating on the creep property improvement of $\alpha + \beta$ Ti alloys was studied on specimens with high surface to volume ratios, and with and without coating, which were compression tested in air. The coated specimens sustained long exposures at 593°C without failure whereas uncoated ones buckled in compression after short exposure at 538°C. The creep improvement of the coated alloys was achieved only at the secondary creep stage. The results showed that the Pt diffusion barrier increases the creep resistance only in alloys containing both the β and α phases. A mechanism explaining the enhanced creep rates in $\alpha + \beta$ alloys in the presence of O₂ is suggested.

LABORATORY APPARATUS AND TECHNIQUE

Phase Diagrams of Thin Films of the Palladium Hydrogen System Using a Quartz Crystal Thickness Monitor

G. A. FRAZIER and R. GLOSSER, *J. Phys. D.*, 1979, **12**, (10), L113-115

A technique for obtaining pressure-concentration isotherms of the Pd-H system is given. A quartz crystal monitor is used to determine directly the quantity of H absorbed by an evaporated Pd film. The method is applicable to metal film-gas systems.

HETEROGENEOUS CATALYSIS

The Efficiency of Supported Platinum Catalysts for the Destructive Oxidation of Odorous Compounds in Air

J. G. IRWIN, T. A. DORLING and R. L. MOSS, *Atmos. Environ.*, 1979, **13**, (11), 1569-1579

The efficiency of catalysts of Pt/honeycomb, promoted Pt metals on crimped ribbon and 0.3% Pt/Al₂O₃ spheres were tested for the destructive oxidation of malodorous compounds in air. Dimethyl sulphide (4-24 vpm) and n-butanol (15-100 vpm) were used to study effects of temperature, inlet concentration, space velocity, bed depth and catalyst structure. For near complete removal of dimethyl sulphide gradual catalyst deactivation determines the lowest useful temperature. At high temperatures removal is limited by mass transfer and varying bed depth and catalyst support geometry.

The Oxidation of Ethylene over a Supported Platinum Catalyst

J. R. HAWKINS and S. W. WANKE, *Can. J. Chem. Eng.*, 1979, **57**, (5), 621-626

Studies of the complete oxidation of C₂H₄ over a 0.3% Pt/Al₂O₃ catalyst were performed at C₂H₄ concentrations of ≤ 1 mol/m³ and O₂ concentrations of 0.16-8.6 mol/m³ in a recycle reactor at 362-472K. The rate of oxidation was directly proportional to the O₂ concentration and inversely proportional to the C₂H₄ concentration. The activity of Pt/Al₂O₃ catalysts during the C₂H₄ oxidation was a function of prior thermal treatment of the catalysts. Thermal treatment in air at temperatures higher than the temperature of the kinetic runs is required to stabilise the catalyst activity. Prolonged use of this catalyst at below 300K does not cause deactivation.

Improved Hydrodechlorination Catalysis: Chloroform over Platinum-Alumina with Special Treatments

C. J. NOELKE and H. F. RASE, *Ind. Eng. Chem., Prod. Res. Dev.*, 1979, **18**, (4), 325-328

Improved activity and activity maintenance occurred during the hydrodechlorination of chloroform to methylene chloride over a commercial Pt/Al₂O₃ reforming catalyst. Continuous H₂O addition more than doubled the reaction rate by removing chloride from the Al₂O₃, thereby preventing excessive acidity and associated rapid coking. The highest sustained activity with the catalysts tested was observed at 195°C on 0.3% Pt/Al₂O₃ when H₂O was used with the feed. Pt-Re/Al₂O₃ was not as active.

Catalytic Combustion in a Tube with Electrical Discharge: Preliminary Measurements of Augmented Reaction Rates

F. A. KULACKI and S. BORIAH, *Nature*, 1980, **283**, (5745), 362-364

The catalytic combustion of H₂ at one atmosphere was studied in an annular Pt coated Al₂O₃ flow reactor, where the catalyst is uniformly accessible,

with a small diameter stainless steel wire through the centre. The reaction rate increases by 20–25% for moderate levels of corona current, which may be an increase of the mass transfer coefficient owing to the uniformly accessible catalyst surface. Thus, with rapid surface reactions, corona wind increase may limit the effects of diffusion and so increase catalyst effectiveness. Improvement in the overall rate constant would be useful in air pollution control, energy conservation and the design of compact, controlled heat flux catalytic combustors.

The Investigation of Heterogeneous Catalytic Reactions by the Thermal Desorption Method. IV. Nonuniformity of Pt/ γ -Al₂O₃ Catalysts.

V. V. ROZANOV, J. GLEND and A. V. SKLYAROV, *Kinet. Katal.*, 1979, **20**, (5), 1249–1255

Studies of n-heptane dehydrocyclisation over Pt/ γ -Al₂O₃ catalysts with various dispersities, and prepared by the impregnation of γ -Al₂O₃ with small amounts of H₂PtCl₆ solution in the presence and absence of HCl, were performed from room temperature to 500°C by a thermal desorption method. The results showed the presence of various types of centres on the Pt/ γ -Al₂O₃ catalyst with different concentrations and activities. The reaction on various centres proceeded under different mechanisms.

Catalyst Decay in the Kinetics of Methylcyclohexane Dehydrogenation over Pt/NaY Zeolite

A. CORMA, R. CID and A. LOPEZ AGUDO, *Can. J. Chem. Eng.*, 1979, **57**, (5), 638–642

The kinetics of the dehydrogenation of methylcyclohexane to toluene over Pt/NaY zeolite catalyst was studied at 390°C and atmospheric pressure. A new technique, based on the "time-on-stream" theory, was used to study the kinetics of reactions with catalytic decay, and the rate constants for both dehydrogenation and catalyst decay were determined. The reaction occurred via a series of consecutive partial dehydrogenations, with the first dehydrogenation as the rate controlling step. The effect of the partially dehydrogenated products and toluene on catalyst deactivation is discussed.

Initial Activation of Platinum-Rhodium Gauzes for the Catalytic Oxidation of Ammonia

J. A. BUSBY and D. L. TRIMM, *J. Catal.*, 1979, **60**, (3), 430–440

The activation of Pt-Rh gauzes used for the catalytic oxidation of NH₃ was studied using optical microscopy, electron probe micro analysis and electron spectroscopy. The initial washing procedure reduced C surface residues, and the catalyst became active at lower temperatures. Activation in a H₂ flame or in O₂ causes surface rearrangements and enriches the surface with Rh, which is partially reversed in the early stages of the NH₃ oxidation. Water vapour deactivates the activated gauze.

n-Hexane and n-Heptane Isomerisation on Polycation Palladium Containing Y-Zeolites

B. A. DADASHEV, S. E. MAMEDOV, A. A. SARYDZHANOV and B. A. GASIMOV, *Kinet. Katal.*, 1979, **20**, (6), 1601–1602

Isomerisation of n-hexane and n-heptane was performed at 320 and 310°C, respectively, on polycation 0.5 wt.%Pd/Y-zeolite catalysts, prepared by ion exchange of zeolite Na(SiO₂/Al₂O₃ = 5) with CaCl₂, Ni(NO₃)₂ and R.E.(NO₃)₃ solutions, with the degree of the ion exchange being 81%. Pd was deposited on the polycation form of the zeolite by saturation from [Pd(NH₃)₄]Cl₃ solution. The result of the isomerisation is given and its selectivity is compared.

Rhodium: A Powerful Methanation Catalyst

O. KULELI, *Fuel*, 1979, **58**, (11), 837–838

A light paraffinic naphtha fraction was hydrogenolysed on a Rh catalyst in a flow system. The powdered Rh was mixed in the ratio 1:4 with ground pyrex glass, heated to 800°C in N₂ and activated by H₂. Reactions occurring included C₅→C₄ + C₁ (70%) and C₅→C₃ + C₂ (30%). At higher temperatures full hydro-methanisation occurred C₅→5C₁ (>90% conversion). The high ethane and methane selectivities enabled the production of a synthetic fuel gas with heating values >33.5 MJ/m³. Compared with substitute natural gas it operates at low temperatures, needs no downstream separation, and produces high quality fuel gas.

Selective Fischer-Tropsch Synthesis of Hydrocarbons: Particle Size Effect of Ruthenium Metal in Faujasite-Type Zeolites

H. H. NIJS, P. A. JACOBS and J. B. UYTTERHOEVEN, *J. Chem. Soc., Chem. Commun.*, 1979, (23), 1095–1096

Selective synthesis of hydrocarbons from CO and H₂ over RuY zeolites had a drastic decline in chain growth probability after C₅ or C₁₀, depending upon the particle size of the Ru metal. The larger the Ru metal particles, the longer the C chain desorbing out.

HOMOGENEOUS CATALYSIS

Quantum Chemical Study of Reactions Catalysed with Metal Complexes.

1. Electronic Structure of *trans*-XHPd(PH₃)₂ and *trans*-XYPd(PH₃)₂

O. V. GRITSENKO, V. A. KORSUNOV, A. A. BAGATUR'YANTS, I. I. MOISEEV, I. V. KALECHITS and V. B. KAZANSKII, *Kinet. Katal.*, 1979, **20**, (5), 1146–1151

Electronic structure and mechanism of the activation of H₂ by Pd complexes was studied on a number of hydride complexes of the type *trans*-XPd(PH₃)₂. The structures of the initial pseudo-tetragonal plane complexes *trans*-X₂Pd(PH₃)₂ and *trans*-XYPd(PH₃)₂, where X = OH, OCOCH₃, Cl, Y = Cl, were found.

Hydrogenolysis in Hydrazo-Benzene Interaction with Propan-2-ol in the Presence of Rhodium and Ruthenium Triphenylphosphine Complexes

B. M. SAVCHENKO, V. Z. SHARF, V. N. KRUTII and K. KH. FREIDLIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, (11), 2632-2634

Complexes $\text{RhCl}(\text{PPh}_3)_3(\text{I})$ and $\text{RuCl}_2(\text{PPh}_3)_3(\text{II})$ catalyse the H transfer reaction from propan-2-ol to hydrazo-benzene forming aniline. The addition of KOH to the complex solution (I) promotes the hydrogenolysis of N-N bond of hydrazo-benzene. However, the reaction of hydrogenolysis of hydrazo-benzene catalysed only by alkalis is slower than the reactions catalysed by Rh complexes (I) and (II).

A Convenient Synthesis of Cyclopentanones via Rhodium(I)-Catalysed Intramolecular Hydroacylation of Unsaturated Aldehydes

R. C. LAROCK, K. OERTLE and G. F. POTTER, *J. Am. Chem. Soc.*, 1980, **102**, (1), 190-197

The Rh(I) catalysed intramolecular hydroacylation of unsaturated aldehydes was investigated and three new catalyst systems were developed. The catalysts were prepared from chlorobis(cyclooctene)Rh(I) dimer and 2 equivalents of tri-*p*-tolylphosphine, tri-*p*-anisylphosphine or tris(*p*-dimethylamino-phenyl)phosphine in methylene chloride saturated with ethylene. With these, 4-5-unsaturated aldehydes are catalytically cyclised to cyclopentanones. Substitution in the 2 and 5 positions reduces the yield of cyclic ketone and corresponding ethyl ketones appear as side products. This procedure is applicable to the synthesis of spirocyclic and fused bicyclic ketones.

NEW PATENTS

METALS AND ALLOYS

Dispersion Hardened Platinum Metals

COMPTOIR-LYON-ALEMAND-LOUYOT

British Appl. 2,023,667 A

Dispersion hardened Pt, Pt-Rh, Pt-Ir and other platinum group metal alloys are produced by spraying the molten alloy and the refractory oxide additions such as 0.2-1% Y oxide onto a target, at high pressure.

Jewellery Alloys

JOHNSON MATTHEY & CO. LTD. *U.S. Patent* 4,165,983

Jewellery alloys having improved castability compared with known Pt alloys contain at least 95% Pt, 1.5-3% Ga, the balance being In, Au, Pd, Ag, Cu, Co, Ni, Ru, Ir and/or Rh. A Ga-Au-Pt alloy is preferred for ornamental applications and a Ga-In-Pt alloy, optionally including Au, Ag or Pt, for the manufacture of springs and clasps.

Homogeneous Catalysis of the Water Gas Shift Reaction by Ruthenium and Other Metal Carbonyls. Studies in Alkaline Solutions

C. UNGERMANN, V. LANDIS, S. A. MOYA, H. COHEN, H. WALKER, R. G. PEARSON, R. G. RINKER and P. C. FORD, *J. Am. Chem. Soc.*, 1979, **101**, (20), 5922-5929

Homogeneous catalysis of the water gas shift reaction $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$, has been demonstrated for a number of metal carbonyl complexes under alkaline conditions. For Ru carbonyl in aqueous ethoxyethanol solution the principal species present were $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ and $\text{HRu}_3(\text{CO})_{11}^-$. The catalysis rate is first order in CO partial pressure and the total Ru concentration. Catalysts prepared by adding both Ru and Fe carbonyls to the same solution are more active than either catalyst alone.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ru and RuO₂ as Electrical Contact Materials: Preparation and Environmental Interactions

R. G. VADIMSKY, R. P. FRANKENTHAL and D. E. THOMPSON, *J. Electrochem. Soc.*, 1979, **126**, (11), 2017-2023

Ru and RuO₂ were evaluated as electrical contact materials for use at low voltages. The contact resistance of RuO₂ was 1mΩ, only slightly higher than that of Ru and Au. Ti coated with RuO₂ has contact resistance of <15mΩ. Ru and RuO₂ are stable at temperatures up to at least 90°C and at all relative humidities, even in the presence of 1 ppm H₂S or flowers of S vapour.

CHEMICAL COMPOUNDS

Rhodium Complexes

CALIFORNIA INSTITUTE OF TECHNOLOGY

U.S. Patent 4,169,030

Deep blue "Rh bridge" complex ions, dirhodium tetrakis(1,3-diisocyanopropane), in water when irradiated between 500 and 600 nm cause direct reduction of the protons in water to H₂, converting the Rh bridge to a yellow form. This H₂ producing visible photo-reaction can be used in a solar-driven water splitting cycle.

ELECTROCHEMISTRY

Electrodes for Membrane Cells

SOLVAY & CIE.

British Patent 1,556,253

Vertical electrodes in gas-producing electrolytic cells, such as water electrolytic cells, have vertical slots with angled vanes along their edges to prevent gas