ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
Structure of Platinum Aggregates Encaged in Y-Type Zeolite. Effect of CO Adsorption and of CO-H₂ Co-adsorption
P. GALLEZOT, Zeolites, 1982, 2, (2), 103–108
The structure of 10 Å Pt particles encaged in Y-type zeolite was determined from the radial electron distribution method from X-ray diffraction data. CO adsorption at 300K on bare Pt leads to an average f.c.c. lattice with normal bond lengths, but with a displacement disorder of the Pt atoms around the nodes. Thus Pt-Pt distances are contracted or elongated compared to their average lattice. Similar observations in molecular Pt carbonyl clusters could provide good modes for these defects appearing in response to CO bonding.

Strength and Plasticity of Palladium-Platinum-Hydrogen Alloys
Studies of the changes in mechanical characteristics of 5–60at.% Pt-Pd alloys under H₂ saturation showed an increase in strength and plasticity for 50at.% Pt-Pd alloys with an occurrence of phase conversion by H₂ saturation. Alloys containing ≥15at.% Pt showed increased strength and some increase in relative pressure during elongation tests of H₂ saturated material.

Overview 19: Hydrogen in Amorphous Metals—I
The solubility and diffusivity of H₂ in amorphous Pd₃₋₅Cu₅Si₆₅ and Ni₄₉Pd₃₁P₁₈.₃ were measured electrochemically. The pressure-concentration isotherms had significant deviations from Sievert's Law, while the amount of H₂ dissolved lies between the solubility of the alloy components. H₂ diffusivity is high (10⁻⁵cm²/s) and depends on temperature and concentration, even at very low H₂.

Wear Characteristic of the Sandwich System Nickel-Palladium-Gold
Microscopic, microanalysis and X-ray diffraction studies of friction-wear of sandwiched Ni-Pd-Au electrodeposits on connectors with thin Au layers between 0.05–0.5 µm were performed. Hard gold alloy (Au-Co) on Pd with a Ni underlayer shows more favourable friction and wear conditions even as a thin layer, than pure Au. With hard gold the insertion forces are nearly independent of thickness of the Au deposit, whereas with fine Au the insertion forces become more pronounced with increasing thickness of the pure Au layer.

Growth Mechanisms and Thermal Stability of Ion-Beam-Induced Epitaxial Pd₅Si Films
Growth mechanisms and thermal stability of ion-beam-induced epitaxial Pd₅Si films were studied by Rutherford backscattering and channelling techniques. Epitaxial growth of Pd₅Si films was observed at room temperature by Ar ion implantation into as-deposited Pd₅Si(III) structures and furnace-annealed Pd₅Si(polycrystalline) / Pd₅Si(epitaxial) / Si(III) structures. The stability of the ion-beam-induced epitaxial Pd₅Si films on subsequent furnace annealing is studied.

The Diffusion of Hydrogen through Palladium-Titaniu and Palladium-Vanadium Solid Solutions
An electrolytic method was used to measure the diffusivity of H₂ through substitutional Pd-Ti and Pd-V alloys containing up to 10at.% Ti or V in the temperature range 273–350K. The diffusivity obeyed the Arrhenius relation. Both Ti and V atoms create trapping sites for H and the mobility of H decreases as the Ti or V increases.

Paramagnetism in High-Nuclearity Osmium Clusters
The cluster H₄O₇₁₇₁₉(CO)₁₄ exhibits intrinsic paramagnetism at temperatures below 70K; such behaviour is characteristic of a particulate metal in the quantum size effect regime.

ELECTROCHEMISTRY
Platinum Corrosion in Alkaline Solution in the Presence of Ba²⁺ and Cl⁻ Ions
Studies of the corrosion behaviour of Pt black in alkaline solutions were made at 0.85–1.37V. The dependence of the rate of corrosion of Pt on the potentials, and the effect of preliminary treatment
and electrochemical reduction of Pt on the rate of corrosion were studied. O₂ adsorption and desorption data on Pt in alkaline solution showed that the process of Pt dissolution proceeds through the formation of intermediate surface oxides.

Reduction of Surface Oxide of Platinum and Gold Electrodes in Aqueous Sulfuric Acid. Local Cell Mechanism and Reactive Species
The surface oxides of Pt and Au electrodes, formed anodically, were gradually reduced at open circuit in aqueous H₂SO₄. The reaction proceeds by the galvanic cell mechanism when the bare surface of the metal acts as an anode which oxidises certain contaminants, and the oxide covered surface acts as a cathode. The formaldehyde used as a contaminant was effective for Pt oxide, but not for Au oxide.

Activation of RuO₂ and PtO Electrode Surface for Immobilization Reactions Using Thionyl Chloride
RuO₂ and supercritically oxidised Pt electrodes are reacted with thionyl chloride in an attempt to produce activated chlorinated surfaces which bind and immobilise appropriately substituted reagents. The activated surfaces stably bind reagents such as amonophenylferrocene, tetra(p-amino)phenylporphyrin and [Ru(bpy)₄][4,4'-bipyridine]⁺, which then display electrochemical reactions similar to those of the surfaces. (43 Refs.)

PHOTOCONVERSION

Photocatalytic Hydrogen Evolution from Alcohols Using Dodecawolframosilicic Acid and Colloidal Platinum
Photocatalytic H₂ evolution from alcohols using SiW₁₂ and colloidal Pt, prepared by boiling aqueous Na citrate and H₂PtCl₄ for 4h, and illuminated with a 900W xenon lamp was studied. Illumination of SiW₁₂ and colloidal Pt leads to photocatalytic H₂ evolution with a quantum yield for H₂ of 0.1 mol/einstein.

A Rechargeable Photo-Electrochemical Solar Cell
A rechargeable photoelectrochemical solar cell based on the n-type BaTiO₃/Co₀.₆%Ce³⁺/Fe²⁺/Pt system has been made. The cell has 0.6V open circuit voltage and 0.12mA/cm² short-circuit current when fully charged. The power conversion efficiency of the cell is 0.01% under AM2-sunlight irradiation (75mW/cm²). The fill factor of the cell is 0.26. Charging and discharging were characterised; flat-band potential and carrier concentrations of the BaTiO₃ were calculated and effects of pH and different electrolytes were studied.

Visible Light Induced Water Cleavage in Colloidal Solution of Chromium-Doped Titanium Dioxide Particles
Surface doping of colloidal TiO₂ particles with Cr ions precipitated from aqueous H₂SO₄ solution produces very small (<0.1 μm) mixed-oxide particles which absorb light in the 400-500nm region in addition to the band-gap adsorption of anatase. Ultrafine deposits of Pt or RuO₂ are necessary to promote H₂O decomposition. A pronounced synergistic effect in catalytic activity is noted when both RuO₂ and Pt are co-deposited onto the particles.

HETEROGENEOUS CATALYSIS

Study of the Effect of Hydrogen on C₅ Hydrocarbon Transformations in the Presence of Platinum-Alumina Catalysts
Studies of the effect of H₂ on the conversion of C₅ hydrocarbons in the presence of 0.6%Pt/Al₂O₃ and 0.55%Pt-0.002%Re-0.3%F/Al₂O₃ catalysts showed that activity, selectivity and conversion mechanism depend on partial H₂ pressure in the gaseous phase. Skeletal isomerisation of alkanes proceeds through a predominantly C₅-cyclic mechanism at high H₂ concentration and through a bifunctional mechanism at low H₂ concentrations.

n-Heptane Transformations on Modified Reforming Catalysts
Studies of the effects of additions of small amounts of metal containing Si organic compounds on the catalytic activity of Pt/Al₂O₃ reforming catalysts were made during n-heptane transformation. Modification of the catalysts by Si-organic compounds was found to increase their activity, selectivity and stability.

Ceria-Promoted Three-Way Catalysts for Auto Exhaust Emission Control
Studies were made of the effects of Ba, Mg, Cr, Mn, Co, Ni and Ce promoters on the performance of a typical three-way catalyst (TWC) Pt-Pd-Rh/Al₂O₃.
Heterogeneous Water Gas Shift Reaction Catalyzed by Titanium Dioxide Supported Noble Metals


Various transition metal catalysts supported on SiO₂, PVA, TiO₂, and zeolite were studied for the water gas shift reaction in the liquid and gas phases at 100 to 285°C and CO pressures ≤1 atm. Parameters such as pH, temperature and preparation method have a drastic effect on catalytic activity. The catalyst Pt₃KₓCOₓ/YTiO₂ was the most efficient catalyst for the reaction, its turnover frequency varied from 360/h at 200°C to 3600/h at 268°C.

Catalytic Combustion of Hydrogen. II. An Experimental Investigation of Fundamental Conditions for Burner Design


The performances of catalysts, consisting of a ceramic honeycomb impregnated with Pt, Ni metal foams coated with Pd powder, and ceramic foam coated with Co-Mn-Ag oxide powder, were studied for the design of a catalytic combustor using H₂ fuel. In the diffusive mode of operation the Pd coated Ni foam with larger pores exhibited the highest combustion efficiency. Combustion efficiency was improved by increasing the amount of premixed air.

Fischer-Tropsch Studies over Well-Characterized Silica-Supported Pt-Ru Bimetallic Clusters


A Fischer-Tropsch (F-T) study over a well-characterised series of SiO₂ supported Pt-Ru bimetallic clusters showed that the increase in surface concentration of Pt has a marked effect on methane selectivity. The F-T reaction was shown to be structure sensitive, occurring predominantly on Ru surface sites. It is concluded that Pt surface sites are inactive in the CO→H₂ reaction under the studied conditions and the role of Pt is, therefore, reduced to that of a surface diluent.

Transformation of 1,3-Pentadiene on Membrane Catalysts Made of Binary Palladium Alloys


Studies of catalytic conversion of 1,3-pentadiene under H₂ pressure through membrane catalysts made of Pd-9.8% Ru and Pd-2.0% Sm alloys showed an increase in rate of H₂ transfer through the catalyst. The effect of α- and β-hydride phases on selectivity of the hydrogenation process is discussed.

AlPO₅-Supported Rhodium Catalysts. I. Effect of the Preparation Variables on Cyclohexene Hydrogenation


The liquid phase catalytic hydrogenation of cyclohexene over Rh/AlPO₅ catalysts in 1 wt.% methanol solvent and initial H₂ pressure of 5.6 bar and 40°C is reported. Catalytic activity was strictly dependent on the conditions of reduction of the precursors. The highest catalytic activity was obtained when the precursor was reduced under mild conditions; at higher temperatures, or if the precursor was calcined, activity was lower.

Hydrogenation of CO and CO₂ over Rhodium Catalysts Supported on Various Metal Oxides


The formation of hydrocarbons in the reaction of CO+H₂ and CO₂+H₂ was studied over Rh catalyst supported on ZrO₂, Al₂O₃, SiO₂ and MgO. In the studied reaction, Rh/ZrO₂ was the most active and Rh/MgO was least active. The activity for the CO+H₂ reaction over the oxidized Rh/ZrO₂ and Rh/Al₂O₃ catalysts was 2-10 times higher than that on the reduced catalyst.

Improvement of the Catalytic Performance of an Osmium Powder in Ammonia Synthesis by the Use of a Cyclic Procedure


The catalytic activity of Os in NH₃ synthesis is greatly impeded by H₂ under the usual reaction conditions. Decreasing the H₂ content of the reactant mixture reduces inhibition and increases the reaction rate. The reaction is also inhibited by NH₃. Decreasing the H₂ shifts the synthesis equilibrium to lower NH₃ contents. Cycling with pure N₂ and H₂ increases Os activity and the best average rate is 5-50 times higher than the best steady rate, depending on temperature in the range 400-250°C.

Mechanistic Study of Carbon Monoxide Hydrogenation over Ruthenium Catalysts


The mechanism of the hydrogenation of CO over 4.5 wt.% Ru/Al₂O₃ catalyst prepared by impregnation of SiO₂ with an aqueous solution of RuCl₃ hydrate was studied. It is concluded that all the hydrocarbon products are produced via dissociatively adsorbed CO with no CO insertion. The rate-determining step comprises the conversion of C₃ intermedates.
**HOMOGENEOUS CATALYSIS**

**Novel Palladium(II) — Catalyzed Copolymerization of Carbon Monoxide with Olefins**


The series of cationic Pd(II) compounds 

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[Pd(CH,CN)_{2}]^{2+} \quad \text{and} \quad [Pd(CH,CN)_{2}]^{2+} \quad \text{in} \quad \text{PPh}_{1}(n=1-3) \quad \text{which catalyse the copolymerisation of CO with a range of olefins under unusually mild conditions is reported. The species prepared by reactions of AgBF}_{6}^{2-} \quad \text{with} \quad \text{Pd(PPh)_{3}Cl} \quad \text{and} \quad \text{similar conditions. Catalysts prepared with a} \\
\text{PPh}_{1}: \text{Pd}^{2+} \quad \text{ratio of 1–3 were active but those with} \\
\text{ratios} \quad 4 \quad \text{and} \quad 6 \quad \text{were found to be inactive, which shows the need for easily accessible co-ordination sites.}
\]

**Activation of Molecular Hydrogen by Transition Metal Complexes. 6. Role of Molecular Oxygen in Formation of Palladium Complexes Active in Hydrogenation of Unsaturated Compounds**


Studies of the interaction of \([\text{Ph,Pd(OAc)}]_{2}\) with \(\text{H}_{2}\) showed the formation of intermediate complexes \((\text{Ph,Pd})_{2}(\text{OAc})_{2}\) and final yields of \((\text{Ph,Pd})_{2}\text{Pd}_{2}\) and \((\text{Ph,Pd})_{2}\text{Pd}_{2}\). The cluster \((\text{Ph,Pd})_{2}\text{Pd}_{2}\) was found to be active in the hydrogenation of unsaturated hydrocarbons.

**Mechanism and Stereoselectivity of Asymmetric Hydrogenation**


Rh complexes containing chiral phosphine ligands catalyse the hydrogenation of olefinic substrates such as \(\alpha\)-aminoacrylic acid derivatives, giving chiral products with very high optical yields. It is concluded that the stereoselection is dictated by the much higher reactivity of the minor diastereomer of the catalyst-substrate adduct, corresponding to the less favoured binding mode.

**Selective Homogeneous Transfer Hydrogenolysis of Trihalomethyl Compounds by Alcohols and Ruthenium-Phosphine Catalysts**


Ru(Ph3P)2Cl2 was shown to catalyse \(\text{H}_{2}\) transfer from halogen-free alcohols to \(\alpha\)-trichloromethyl- and \(\alpha\)-trifluoromethyl carbinols and to give selectively dialkylmethyl derivatives. Benzyl alcohols proved to be very efficient \(\text{H}_{2}\) donors. The catalytic process was affected by the electronic structure of the catalyst and of the \(\text{H}_{2}\) acceptor but not by \(\text{H}_{2}\) donor.

**The Cluster Anion \([\text{HRu}_{3}(\text{CO})_{11}]^{1-}\) as Catalyst in Hydroformylation, Hydrogenation, Silacarbonylation and Hydrosilylation Reductions of Ethylene and Propylene**

G. SASS-FINK and J. REINER, *J. Mol. Catal.*, 1982, 16, The trinuclear cluster anion \([\text{HRu}_{3}(\text{CO})_{11}]^{1-}\) was found to catalyse hydroformylation, hydrogenation, silacarbonylation and hydrosilylation reactions. Ethylene and propylene were hydroformylated with CO and \(\text{H}_{2}\) to give the corresponding aldehydes; in the case of propylene a high yield of the unbranched butyaldehyde was obtained. The catalytic turnover of these reactions was observed to be 50–400.

**ELECTRICAL AND ELECTRONIC ENGINEERING**

**Dynamics of Interfacial Electron-Transfer Processes in Colloidal Semiconductor Systems**


The dynamics of interfacial electron-transfer reactions were studied with colloidal TiO2 and CdS particles, which form transparent aqueous dispersions. Experiments with Pt-loaded CdS established catalytic \(\text{H}_{2}\) production by conduction-band electron with electron transfer to adsorbed \(\text{MV}^{2+}\). \(\text{RuO}_{2}\) deposits enhance hole transfer from the valence band to solution species.

**Hydrogen Detection by Schottky Diodes**


A Schottky diode was made from a 20 nm evaporated Pd film, a very thin SiO2 film and n-type Si substrate. Two diodes were obtained on the Si substrate, one was used for \(\text{H}_{2}\) detection and the other as a reference diode. The detector, operating at room temperature was able to detect 2000 ppm \(\text{H}_{2}\) in air within 10 s. There was no degradation found over an 8 month operating period.

**TEMPERATURE MEASUREMENT**

**Measuring Low Temperature in the 13 through 80K Range Using ZPA, MT-100 Platinum Temperature Sensors**


The basic thermometric properties of the ZPA Pt temperature sensors of the MT-100 type are described for the temperature range 13–80K. The dependence of electrical resistance, sensitivity and temperature resistance coefficients on temperature are described. The dynamic stability of the electrical resistance is tested by the cycling method.