

Platinum Group Metal Hydrides

THEIR PROPERTIES AND APPLICATIONS CONSIDERED

Conferences on hydrogen energy and metal-hydrogen systems continue to include significant numbers of contributions concerning hydrides of palladium and other platinum group metals. This article reviews some of the relevant papers presented recently at Colorado Springs.

A continuing worldwide interest in hydrogen as an economically important source of energy has been reflected in the series of World Hydrogen Energy Conferences (1). Papers concerning metal-hydrogen systems included in these conference programmes have had particular general reference to the aspects of hydrogen embrittlement and of hydrogen storage in metallic hydrides. Some of the more recent conferences (2, 3, 4), which have been specifically concerned with metal-hydrogen systems, have also been largely centred around one or other of these subject areas. The most recent of these has been an International Symposium on the Properties and Applications of Metal Hydrides, held in Colorado Springs, U.S.A. during April 1980. However, as in the other conferences, a significant proportion of papers dealt with the hydrides of the platinum metals or their alloys.

In the area of thermodynamic and structural studies, further calorimetric measurements of heats of absorption of hydrogen by palladium, combined with pressure-composition (p-c) relationships were reported by T. B. Flanagan, B. S. Bowerman, C. A. Wulff and G. E. Biehl, of the University of Vermont, and p-c relationships determined with thin palladium films in conjunction with measurements of their electrical resistivities by G. A. Frazier and R. Glosser, of the University of Texas at Dallas. Possible effects of local differences of surface hydrogen chemical potential on palladium cathodes were discussed by F. A. Lewis, of the Queen's University of Belfast, with reference to electrolytic hydrogen isotope separation factors and isotope exchange reactions. Measurements

of hydrogen solubilities in some palladium intermetallics were reported by A. J. Maeland and G. G. Libowitz, of Allied Chemical Corp., Morristown, U.S.A. The formation of a hydride of rhodium as part of a programme of studies at pressures up to 70 kilobars and 750 K was reported by E. G. Ponyatovsky, V. E. Antonov and I. T. Belash, U.S.S.R. Academy of Science, Chernoglovsk. Correlations of hydride formation with electronegativities, electronic structure and chemisorption characteristics were outlined by J. W. Ward of the Los Alamos Scientific Laboratory.

E. Wicke of the University of Münster discussed measurements made at low temperatures of magnetic susceptibility, electronic specific heat and Mössbauer spectra in the palladium-ruthenium-hydrogen system, while evidence from Mössbauer spectroscopy of the hydrogen environment around substitutional rhodium, ruthenium, cobalt and iron in β -phase palladium hydride was reported by F. E. Wagner, M. Karger, and F. Pröbst, of the Technical University of Munich. NMR studies of hydrided rhodium intermetallics were reported by T. C. Jones, T. K. Halstead and K. H. J. Buschow, of the Universities of York and Eindhoven. Measurements of the variation of the temperature of the superconducting transition with silicon content in the palladium-silicon-hydrogen (deuterium) system were presented by B. Stritzker and H. L. Luo, KFA Jülich, Germany and University of California; speculations concerning superconductivity in the platinum-hydrogen system were advanced by D. A. Papaconstantopoulos, Naval Research Laboratory, Washington. Studies of elastic

energy dissipation effects related to hydrogen mobilities, which had been measured over a wide range of hydrogen contents in the palladium-hydrogen system, were reported by F. M. Mazzolai, P. G. Bordoni and F. A. Lewis of the Istituto di Acustica, Rome and Belfast.

The permeation of hydrogen through membranes of palladium and palladium alloys continues to be actively investigated. Effects of cold-rolling on the diffusion of tritium through palladium were reported by B. Huber and G. Sicking of the University of Münster. Influences of hydrogen solubilities on permeation through palladium-rare earth alloys were discussed by D. T. Hughes of the U.K. Electricity Council Research Centre, J. Evans and I. R. Harris, of the University of Birmingham, England, and the efficiencies of palladium overlayers in promoting hydrogen uptake into niobium and tantalum by M. A. Pick, M.

Strongin and M. G. Greene, of the Brookhaven National Laboratory, U.S.A. Apparently extensive studies by E. M. Savitsky and other Russian workers were reported in abstract, concerning the use of membranes of palladium alloyed with ruthenium, rhodium, nickel and copper as hydrogenation catalysts. High efficiencies and selectivities were claimed.

Papers presented at the symposium will be published later this year in the *Journal of Less-Common Metals*. F.A.L.

References

- 1 Third World Hydrogen Energy Conference Tokyo 23-26 June 1980
- 2 *Platinum Metals Rev.*, 1976, **20**, (2), 54; 1977, **21**, (4), 134; 1979, **23**, (3), 99
- 3 *Hydrides for Energy Storage*, (Symp. at Geilo), ed. A. F. Andresen and A. J. Maeland, Pergamon Press, 1978
- 4 Proc. Second Japan Inst. Met Symp. Hydrogen in Metals, Suppl. Trans. Jpn. Inst. Met., Vol. 21, 1980

Platinum-Based Bimetallic Catalysts

THE ROLE OF THE SECOND COMPONENT

The operation of petroleum reforming has been revolutionised in the past decade by the introduction of greatly improved catalysts. A general feature of this new generation of catalysts is that while they all contain platinum as the principal active component, they also have one or more further components, for example rhenium, germanium or tin, which may be regarded as promoters and which serve to increase the life of the catalyst. Although this effect has occasioned much research, there are many features still awaiting clarification. In a lecture at Imperial College, U.K. on 14 April 1980, Dr. Paul Biloen of the Royal Dutch-Shell Laboratory, Amsterdam, reviewed the present state of knowledge of how promoters work, with particular reference to recent work carried out in Amsterdam on the platinum-tin system.

In this programme the reactions of n-hexane, that is hydrogenolysis, isomerisation and dehydrocyclisation, were studied using several platinum, platinum-tin and tin combinations supported on **non-acidic** materials (silica and sodium-poisoned alumina): thus the acidic function was eliminated, and effects associated with the metallic components were isolated. Measurements of the decrease in the rates of

benzene formation with various catalysts definitely showed that the presence of tin reduces the amount of carbon on the metal. The question is, how? Temperature-programmed reduction of a reduced platinum-tin catalyst after gentle reoxidation, in comparison with supported platinum and tin separately, provided strong circumstantial evidence that some alloying of the two metals had occurred. However not all the tin was used in this way: a small amount, about 0.6 weight per cent, remained associated with the alumina support in an irreducible form. Dr Biloen believed that the principal role of the tin was to reduce the average size of ensembles of platinum atoms. More than three atoms of platinum together can probably lead to dehydrogenated and strongly bonded species which are precursors to carbon deposition. Single platinum atoms in platinum-tin alloys have been shown to be active centres in dehydrogenation, and tin-promoted platinum catalysts are more highly selective in dehydrogenation than platinum alone. The inhibition or modification of carbon deposition by the second component goes far towards explaining its beneficial effect. G.C.B.