

The Platinum Metals in Catalysis

PAPERS AT THE SECOND CANADIAN SYMPOSIUM

The second Symposium on Catalysis organised by the Canadian Institute of Chemistry was held in June at McMaster University, Hamilton, Ontario, and was well attended by workers mainly from Canadian industries and universities. Of the twenty-eight papers presented, covering a very wide range of subjects, some eight or nine had relevance to the use of platinum metals in heterogeneous and homogeneous catalysis, including two on electrocatalytic phenomena.

The electrochemical behaviour of gold-palladium alloys was described in a paper by T. J. Gray, R. Rozelle, A. Schneider and M. L. Soeder (Alfred University, New York State); by studying alloys containing about 12, 26, 44, 62 and 68 per cent gold, the authors established that the maximum rate of hydrogen occlusion occurred with the 26 per cent gold alloy, for which the H/Pd ratio at the rest potential (32 mV) was 0.042. Alloys containing 12 and 44 per cent gold did not achieve rest potentials (indicating lower rates of occlusion), while the alloy having 68 per cent gold behaved similarly to pure gold. The observations reported by D. J. G. Ives, F. R. Smith, P. D. Marsden and J. B. Senior, of Birkbeck College, on the cathodic activation of mercury-poisoned platinum and of gold strongly suggested that the desorption of hydrogen atoms is retarded on these inactive surfaces.

The mechanism of the exchange of liquid saturated hydrocarbons with deuterium catalysed by supported platinum metals differs substantially from the corresponding gas phase processes. J. G. Atkinson, M. O. Luke and R. S. Stuart, of Merck, Sharp and Dohme, Montreal, disclosed that in the liquid phase systems the exchange is predominantly stepwise, and by continually passing pure deuterium through the liquid

hydrocarbon in which the catalyst was suspended they were able to achieve complete substitution of all the hydrogen atoms.

R. J. Harper and C. Kemball, of Queen's University, Belfast, compared the behaviours of palladium and platinum with those of nickel and tungsten in the exchange of a series of mono-halogenated benzenes with deuterium. The exchange rates, which decreased in the sequence of increasing atomic number of the halogen (iodobenzene could not however be studied), were all slower than for benzene itself. The noble metals were less poisoned by the small amount of halogen cleaved from the ring than were the base metals.

The development of a new platinum-on-alumina catalyst having high activity and selectivity for the isomerisation of *n*-hexane was described by W. J. M. Pieters and G. C. A. Schuit, of the Technical University, Eindhoven. It is well established that treatment of platinum on alumina with carbon tetrachloride at elevated temperatures forms a surface layer of aluminium chloride which greatly increases the activity of the catalyst for isomerisation. However, Pieters and Schuit were able to show that selectivity could also be improved by controlled poisoning of the platinum by thiophene.

G. C. Bond (Johnson Matthey) reviewed the hydrogenation of acetylene catalysed by the platinum group metals. The ability of palladium to hydrogenate acetylene selectively to ethylene in the presence of a large excess of ethylene was attributed to its ability to become rapidly and selectively poisoned for ethylene hydrogenation. The addition of deuterium to acetylene over palladium and platinum catalysts gives about 80 per cent of *cis*-C₂H₂D₂, rhodium and iridium giving a broader distribution of deuterated ethylenes.

Two of the contributions dealt with homogeneous catalysis by platinum metal compounds. P. R. Rony, of Monsanto, St Louis, gave a theoretical treatment of supported catalytic solutions, and showed that there should exist an optimum liquid loading for efficient catalysis. The system had been discovered independently by workers in both the Monsanto Company and the Johnson Matthey Research Laboratories (G. J. K. Acres, G. C. Bond, B. J. Cooper and J. A. Dawson, *J. Catalysis*, 1966, 6, 139).

The various products obtained from the reaction of disubstituted acetylenes with palladous chloride were listed by P. M. Maitlis of McMaster University; in non-hydroxylic solvents, hexaphenyl-benzene is obtained almost quantitatively from diphenyl-acetylene. Dimethylacetylene in methylene chloride solution on the other hand reacts with palladium chloride to give only about 10 per cent of hexamethylbenzene, the remainder of the product being polymeric in nature.

G. C. B.

Iridium Coatings in Ion Engines

HIGH WORK FUNCTION AND THERMAL STABILITY

In their traditional miserly role, metals with a high work function are reluctant to part with electrons although when heated they accept them with great alacrity from materials of lower electron affinity. As an electron acceptor iridium is now being seriously considered as an improved ioniser material for use in caesium ion engines. This work is being carried out under the auspices of NASA by the Hughes Aircraft Company Research Laboratories, Malibu, California, and a recent report by R. R. Turk and W. E. McKee (1) describes some of the preliminary results obtained.

Thrust is obtained in these ion engines by the reaction of a stream of electrostatically accelerated caesium ions and an appreciable un-ionised flux rapidly destroys the accelerating electrodes. Although solid tungsten has been used as an ioniser it is easily flooded by the high flow rates of caesium now normally employed.

Porous tungsten with its high surface area is less liable to flooding but is unfortunately somewhat unstable and loses its permeability at the normal temperature of operation involved in these devices.

Attempts to produce complete ionisers of higher work function and improved thermal stability involved powder metallurgy studies on iridium and rhenium alloys. Porous compacts based on the 50 per cent iridium, 50 per cent tungsten composition had the hexagonal epsilon crystal structure and a high resistance to densification. Economic and practical considerations finally indicated that better results would be obtained by the appli-

cation of thin layers of iridium and rhenium to porous tungsten substrates.

Iridium coatings were obtained by spraying dilute solutions of iridium trichloride on to heated tungsten compacts which were subsequently reduced in hydrogen. Half-micron coatings of iridium so obtained were stable for at least 200 hours in vacuum at 1500°C and work functions of $5.28 \pm 0.03\text{eV}$ were measured on such deposits.

Electroplated rhenium surfaces were also effective. Although the work function of $5.20\text{eV} \pm 0.03$ determined for rhenium was comparable to that of iridium, it was found that rhenium, because of its high solubility in tungsten, provided a less stable coating than iridium.

Much further work will be required before the true effectiveness of these noble metal coatings can be properly assessed. It is interesting to speculate, however, upon the way in which osmium might behave under such conditions. The work function of osmium has been recently determined (2) as $5.93 \pm 0.05\text{eV}$ a value higher than that of iridium and rhenium. Osmium also forms a carbonyl which might facilitate the deposition of uniform thin deposits on the tungsten substrate.

A. S. D.

References

- 1 R. R. Turk and W. E. McKee, "Alloy Ioniser Fabrication", NASA Contract No. NAS 3 - 6272, Hughes Aircraft Company, Malibu, California
- 2 P. Zalm and A. J. A. Van Stratum, *Philips Tech. Rev.*, 1966, 27, (3/4) 69-75