

Platinum Group Metal Coatings for Metal Hydrides

THE MODIFICATION OF SURFACE PROPERTIES

Many metals which are capable of forming metal hydrides suffer problems due to low surface affinity for hydrogen, the formation of inhibitory surface oxides, hydroxides and carbonates, or slow diffusion of hydrogen from the surface to the bulk. Therefore the net result is often to limit the conditions under which their hydrides will form.

Magnesium Hydride

Magnesium, although capable of storing hydrogen up to the composition MgH_2 , presents a considerable surface activation barrier to hydrogen (50 kJ/mol) and this means that the hydrogenation reaction usually requires temperatures above 500 K, and pressures of tens to hundreds of bars. In a recent publication by A. Krozer and B. Kasemo, of Chalmers University of Technology, Sweden, a palladium coating was used to extend the available information on the magnesium-hydrogen phase diagram to pressures 10^5 times lower than was previously possible, and to temperatures down to 290 K (1). Their approach involved the deposition of a palladium layer (5–20 nm thick) on a magnesium sample which was vacuum evaporated onto a piezo-electric quartz crystal microbalance. Hydrogen uptake was measured by the weight increase of the sample registered as a change in the resonant frequency of the quartz crystal.

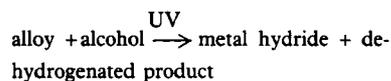
The palladium film on the magnesium sample removed the kinetic barrier for converting gas phase H_2 to atomic hydrogen prior to bulk absorption, thus allowing the establishment of equilibrium at pressures below 20 Torr and temperatures in the range 330 to 370 K. At lower temperatures, kinetic limitations appeared due to hydride formation at the interface between the palladium and the magnesium, whereas at higher temperatures intermixing/

alloying of these two metals began to occur.

Hydrogen uptake was characterised by Sievert's law behaviour up to hydrogen:magnesium ratios <0.01 . Slow kinetics and deviations from Sievert's law at higher hydrogen contents pointed to the increased importance of H-H attractive interactions as more sites in the metal are filled.

Photo-assisted Hydrogen Storage

In another recent paper H. Imamura, M. Futsutara and S. Tsuchiya of Yamaguchi University, Japan, reported photo-assisted hydrogen storage in the rare earth intermetallic compounds RCo_5 (R = lanthanum or samarium) using alcohol as a hydrogen source (2). The work relies on the transfer hydrogenation of a metal hydride as a method of producing useful hydrogen from industrial waste alcohol, and presents an interesting possibility for the conversion and storage of solar energy. The reaction is:



Their standard procedure involves a solution containing 0.3 g of RCo_5 and 0.01 – 0.1 cm^3 carbon tetrachloride in 220 cm^3 of alcohol. In one experiment irradiation of $LaCo_5$ in 2-propanol for four hours resulted in the formation of the hydride $LaCo_5H_{1.4}$ and acetone.

In order to assess the possibility of enhanced surface reactions contributing to the effect, some $LaCo_5$ was treated with chloroplatinic acid to produce an electroless surface deposit of platinum. When placed in the reactor, platinum coated alloys showed faster hydriding rates and remarkable ease of conversion into the metal hydride when compared with non-coated material, under the same conditions.

It was concluded that, since there were no

differences in the LaCo₃ used, the rate limiting processes must be exterior to the bulk, with the deposited platinum being active as an alcohol dehydrogenation catalyst.

The use of the catalytic and other special properties of platinum group metals in association with metal hydrides has long been known, with coatings of palladium being effectively employed to activate metals such as tantalum, niobium and vanadium (3). Both the above recent papers illustrate the continued use of platinum group metals as modifiers of the sur-

face properties of metal hydrides, opening up the possibility of developing useful metal hydride systems capable of operating in new, more favourable conditions of temperature and pressure.

M.L.D.

References

- 1 A. Krozer and B. Kasemo, *J. Less Common Met.*, 1990, **160**, (2), 323
- 2 H. Imamura, M. Futsuhara and S. Tsuchiya, *Int. J. Hydrogen Energy*, 1990, **15**, (5), 337
- 3 N. Boes and H. Zuchner, *J. Less Common Met.*, 1976, **49**, 233

Uses of Platinum Metals Catalysts

Catalysis of Organic Reactions, Chemical Industries Series Vol. 40

EDITED BY DALE W. BLACKBURN, Marcel Dekker, New York, 1990, 354 pages, ISBN 0-8247-8286-0, U.S.\$115.00 (U.S. and Canada), \$138 (elsewhere)

This book summarises a series of papers presented at the Twelfth Conference on the Catalysis of Organic Reactions held in San Antonio, Texas, U.S.A., during April 1988. These meetings provide a useful forum where industrial and academic chemists together with catalyst manufacturers can discuss the state-of-the-art and industrial relevance of catalysis. No fewer than thirteen of the twenty chapters refer to the use of platinum group metal catalysts.

It is timely that a special chapter on chiral catalysis is included as regulatory bodies are requiring more stringent controls on the purity of chiral products and the area is becoming of greater interest to the pharmaceutical and fine chemical industry.

The enantioselective reduction of prochiral alkenes, imines and ketones using variants such as hydrogen gas, transfer hydrogenation and silanes in the presence of homogeneous rhodium catalysts is described by H. Brunner. B. R. James continues this theme by discussing the enantioselective hydrogenation of imines and ketones with catalysts comprising rhodium, iridium or ruthenium and inexpensive ligands derived from naturally occurring acids.

The stereospecific reduction of cinnamic acid is addressed by J. G. Andrade, and D. F. Taber deals with the regio and diastereoselective formation of cyclopentanoids via rhodium acetate-catalysed intramolecular arrangements.

R. L. Augustine traces the development of an understanding of olefin hydrogenation using heterogeneous catalysts including analogies with homogeneous rhodium catalysts. Further

chapters refer to the use of supported palladium catalysts. The use of carbon disulphide titrations as a method of testing for mass transfer limitations is exemplified for palladium-on-silica and platinum-on-alumina catalysts by G. V. Smith. V. L. Mylroie considers the reduction of sulphonyl halides to thiols using sulphided palladium-on-carbon catalysts. The development of a palladium-on-silica catalyst for the hydrogenation of acetylenes, which has culminated in the widespread use of this catalyst for the production of vinyl chloride monomer, is reviewed by K. M. Deller.

For palladium catalysed carboalkoxylation reactions W. R. Moser describes the use of novel in situ infra red techniques in order to obtain a better understanding of ester formation. R. F. Heck discusses the catalytic dimerisation of styrene and isomerisation of allylbenzene by cyclopalladated azobenzene complexes.

Two chapters deal with carbonylations. J. F. Knifton describes the application of melt catalysis to the hydroformylation of both linear and internal alkenes, and in discussing the use of pyridine containing polymers in organic chemistry, G. L. Goe draws attention to a heterogenised rhodium catalyst which has higher activity than its homogeneous counterpart for the carbonylation of methanol to acetic acid.

The topics represented in this book are wide-ranging and include Chiral Catalysis, New Catalysis Technologies, Mechanisms in Catalysis and New Catalytic Chemical Processes. It should prove useful to organic chemists involved in catalysis. M.J.H.R.