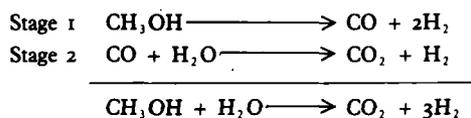


Hydrogen Recovery from Waste Methanol

AN APPLICATION OF SILVER-PALLADIUM MEMBRANES

Over the years a number of papers have been published in this journal describing a method of hydrogen production that uses silver-palladium membranes to separate hydrogen from hydrogen-rich gas mixtures (1, 2, 3). Hydrogen generators based on this principle have been commercially available for over a decade. They use a mixture of methanol and water as a gaseous feedstock which is catalytically cracked to produce a mixture of hydrogen and carbon dioxide in a two stage reaction:



High purity hydrogen is then recovered by diffusion through silver-palladium membranes.

Applications for such hydrogen generators include the provision of the hydrogen component of the reducing gas used as a protective atmosphere during the annealing of stainless steel wire, and also for the reducing atmosphere when sintering uranium oxide pellets for nuclear fuel assemblies.

Another major use of these generators is for the on-site production of the hydrogen which serves as the cooling fluid for the alternators in electric power stations; here the high thermal conductivity of hydrogen allows heat to be removed from the alternators three times faster than is possible with any other commercially available gas. Perhaps more topical is the on-site generation of hydrogen at research stations in Antarctica, the gas being used to fill meteorological balloons that lift instruments to study the upper atmosphere, part of the programme of work which recently led to the discovery of the hole in the ozone layer.

The variety of these applications show that hydrogen generation by cracking a methanol-water mixture is now a well established

technology, successfully filling its special niche in the hydrogen supply market. The hydrogen produced is better than 99.99 per cent pure, because of the diffusion process. Only hydrogen can dissociate into single protons, and it is these that pass through the lattice of the silver-palladium while the larger atoms of the other components of the hydrogen-rich gas mixture are left behind. Frequently such purity is associated with high production costs, but here it is the natural outcome of the diffusion stage, and the hydrogen produced is often cheaper than that obtained from other sources.

In the production of fine chemicals, or during the separation of some of the rarer metals, it is often necessary to use a wet chemical process that produces a precipitate of the metal as an insoluble salt. When this precipitate is filtered, a wet filter cake is formed. This may take a long time to dry, and one method of accelerating the drying process is to douse the cake in methanol. The effect of this is to replace the water of association in the cake with methanol which can then be readily removed by suction, and the process is especially suitable for unstable salts which cannot be heated.

One major disadvantage of the methanol drying technique is the production of a waste methanol-water solution which is costly to dispose of. However, in processes where hydrogen is also used, for example when metals separated by wet chemistry are sintered under a hydrogen atmosphere, it is possible to use this waste solution to produce very cheap, very pure hydrogen.

Another source of waste methanol occurs during the manufacture of silicon chips, where methanol is used to clean and dry the silicon before it is impregnated with activating elements transported to its surface by a carrier gas of hydrogen.

This sort of waste methanol-water mixture



Fig. 1 The hydrogen generator at ABB Atom AB, Vasteras, Sweden is housed in a building equipped with alarms for fire and hydrogen detection. Should the latter ever be positive then the double doors open automatically to increase ventilation. The small door gives access to the separately housed electrical controls. The white tank on the right is the pure hydrogen store, from which the unlagged (smaller) horizontal pipe carries the pure hydrogen to the factory; the lagged pipe beneath brings the waste methanol supply to the generator

may contain other impurities such as heavy metals or ammonium salts. Generally it is not difficult to remove the heavy metals, and often it is a necessary economic requirement. The ammonium salts do not have to be removed because they can be vaporised and then pass through the hydrogen generator system, provided the conditions are controlled to prevent blockage. Before the waste methanol-water mixture is fed to the generator the ratio of methanol to water is analysed and then adjusted

to the ideal ratio of 63.5:36.5 by adding the requisite amount of water or, more usually, methanol.

To enable the feasibility of recovering hydrogen from the waste produced by a particular process to be established, Johnson Matthey have constructed a small model hydrogen generator incorporating catalytic cracking and silver-palladium diffusion units. Thus trials can be conducted on samples of methanol-containing process waste collected from a

Fig. 2 These two hydrogen generator units together provide 50 Nm³/h of pure hydrogen. The interconnecting pipework is lagged to keep the system above 60°C, and so prevent ammonium salts building-up inside the system. The corner of the wall in the foreground is part of the bund in which a tank of pure methanol is contained. This is used to adjust the composition of the aqueous waste methanol solution, which is held in another tank inside the bund, in order to provide a fuel of stoichiometric ratio



potential user's site in container drums. The results from the trial, which should last for at least 1000 hours of continuous operation, will allow the viability of the process to be proven at small cost, before a full size plant is commissioned.

Where a trial is successful and when the operating variables are established, including, for example, the regularity of water rinsing necessary to prevent the build up of ammonium

salts during the methanol drying technique, then fast economic pay-back times can be anticipated and a remarkably cheap hydrogen source deployed. J.E.P.

References

- 1 J. E. Philpott, *Platinum Metals Rev.*, 1976, **20**, (4), 110; and references therein
- 2 M. J. Cole, *Platinum Metals Rev.*, 1981, **25**, (1), 12
- 3 J. E. Philpott, *Platinum Metals Rev.*, 1985, **29**, (1), 12; and references therein

Improved Catalyst System for the Wacker Process

The Wacker process for the palladium catalysed conversion of ethylene to acetaldehyde is one of the oldest industrial homogeneous catalyst systems. The original process was plagued by problems of corrosion within the reactor system, and has been replaced by a heterogeneous catalyst system which suffers, however, from the problem of poor catalyst utilisation.

Acetaldehyde used to be a major source of acetic acid and while this route has largely been superseded by rhodium catalysed carbonylation, the Wacker process remains a major route to acetaldehyde. The problems outlined above that are associated with the Wacker catalyst have been, to a large extent, circumvented by a new catalyst system developed by workers in the Department of Chemical and Materials Engineering at the University of Iowa (V. Rao and R. Datta, *J. Catal.*, 1988, **114**, (2), 377-387).

The supported liquid melt catalyst which they have used consists of a spherical silica support which contains a palladium chloride-copper(II) chloride catalyst in a eutectic melt of copper(I) chloride-potassium chloride. The location of the homogeneous catalyst within the pores of the support avoids the problems both of corrosion of the plant and also product/catalyst separation, which are associated with the conventional homogeneous system. However, the system remains in essence a soluble catalyst and retains the benefits of the rates and conversions achieved with the homogeneous catalyst. It shows a better utilisation of metal than the conventional supported liquid phase catalysts. In addition the use of a melt media avoids the rapid deactivation associated with supported liquid phase catalysis containing aqueous catalyst solutions. The use of a copper(I) chloride-potassium chloride with a melting point of 423K means that the com-

plete oxidation of ethylene to carbon dioxide and water is avoided.

The authors have combined a number of concepts which have been available for some time, and appear to have developed a system which avoids most of the pitfalls associated with other catalyst systems for the Wacker process. If it can be established that the catalyst maintains its activities for substantially greater than one week, does not cause corrosion, and if catalyst attrition is not a problem, then the system may have considerable commercial significance. However, the relative simplicity and high stability of the catalyst components in the Wacker catalyst system may mean that it is difficult to apply this technology in a more general fashion. M.J.H.R.

Hydrogen Storage Material

Although iron-titanium is an excellent material for hydrogen storage, it becomes deactivated after repeated charge-discharge cycles. The mechanism of this phenomenon has been determined by J. H. Sanders and B. J. Tatarchuk of Auburn University, Alabama, U.S.A., who have also investigated the use of thin palladium films to protect the alloy from deactivation (*Thin Solid Films*, 1988, **166**, 225-233; *J. Phys. F: Met. Phys.*, 1988, **18**, (11), L267-L270).

Deactivation is triggered by oxygen impurities in the hydrogen charging gas reacting with titanium in the surface layer of the iron-titanium matrix, forming titania and metallic iron crystallites which are inert to reversible hydrogen storage. However under the conditions of interest a thin 5nm layer of palladium provides an effective barrier to oxygen, preventing deactivation and so increasing the useful life of the alloy. The integrity of the coating has been verified by conversion electron Mössbauer spectroscopy.