

Hydrogen Permeable Palladium Membrane Catalysts

AN AID TO THE EFFICIENT PRODUCTION OF ULTRA PURE CHEMICALS AND PHARMACEUTICALS

By Professor V. M. Gryaznov

A. V. Topchiev Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences, Moscow

The catalytic properties of selected palladium binary alloy membranes have been studied during hydrogenation and dehydrogenation reactions. When hydrogen, from a variety of hydrogen-rich sources, is introduced through such membrane catalysts the yield and selectivity of hydrogenation products may be increased, the energy requirement reduced and finite natural resources conserved.

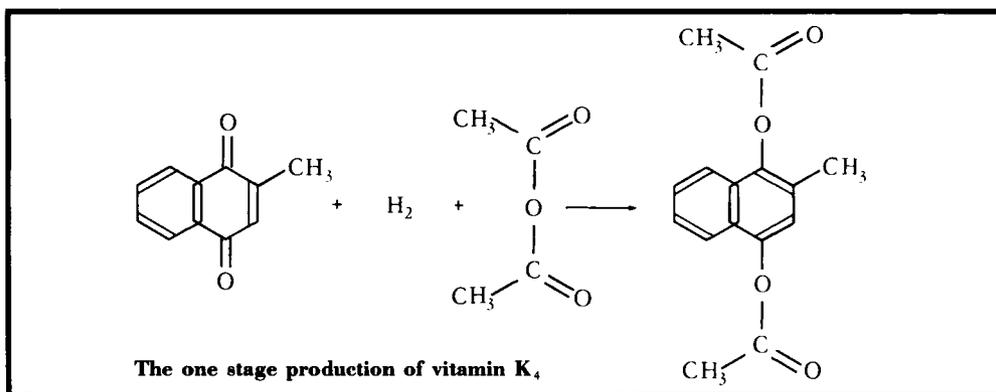
Some palladium rich alloys are only permeable to hydrogen and have catalytic activity for hydrogenation and dehydrogenation reactions. Hydrogen transfer through such membrane catalysts, in the form of foil or thin-walled tube, provides a new method of influencing hydrogen addition or removal processes, and this technique is compared with the use of traditional catalysts (1, 2). The hydrogenation rate and selectivity depend on the concentration ratio of hydrogen and the hydrogenated substance on the catalyst surface. For a conventional catalyst this ratio is a function only of the initial mixture content, and is not constant along the catalyst bed. For a membrane catalyst the situation is quite different. The hydrogenated substance is adsorbed on that surface of the catalyst to which atomic hydrogen penetrates through the sheet or a tube wall of the membrane catalyst. Dihydrogen is adsorbed on the opposite surface of the membrane catalyst. Thus the surface concentration of both reagents may be controlled independently, so suppressing the adsorption competition which is harmful for catalysis. Another means of increasing the hydrogenation rate is by the input of highly active atomic hydrogen to the hydrogenated compound. There is one more important advantage of a membrane catalyst over conventional ones — it

provides a desirable hydrogen concentration on the whole surface. This is particularly important during the manufacture of products of incomplete hydrogenations, which are thermodynamically unstable in excess hydrogen.

Many liquid-phase hydrogenation processes are carried out on supported or Raney catalysts. However these catalysts are dispersed during the reaction and their small size makes them difficult to separate from the reaction products. Membrane catalysts do not have this disadvantage due to their high mechanical strength. Additionally they are corrosion resistant, which is why selective hydrogenation may be combined with esterification by highly corrosive agents, for example by acetic anhydride. The usual process for the production of vitamin K₄ (2-methyl-1,4-diacetoxynaphtholene) involves four steps:

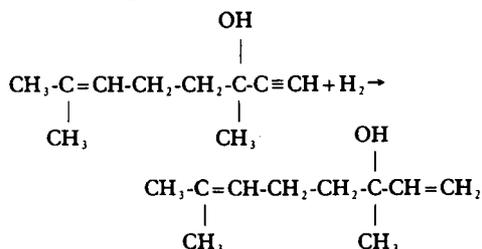
- [i] 2-methylnaphthoquinon-1,4 hydrogenation into 2-methylnaphthohydroquinone-1,4;
 - [ii] filtration of the product from the catalyst;
 - [iii] solvent evaporation;
 - [iv] boiling with acetic anhydride;
- and the yield of vitamin K₄ is 80 per cent.

On the other hand the use of a membrane catalyst makes vitamin K₄ production a one stage process and in addition it increases the vitamin K₄ yield to 95 per cent.



The hydrogenation of acetylenic alcohols into ethylenic alcohols, which are synthetic perfumes and intermediate products of vitamins, takes place on a palladium-ruthenium membrane catalyst with a selectivity of 0.98 to 0.99 (3). 2-Butynediol-1,4 is converted into cis-butenediol (95 to 96.5 per cent), trans-butenediol (2.5 to 3.0 per cent) and butandiol (1 per cent only). It has been shown that direct hydrogenation of the triple bond in butynediol into the single bond does not take place during the passage of hydrogen through the membrane catalyst. However in the presence of the same catalyst hydrogen bubbling through the butynediol solution gives butandiol from the start of the reaction. This suggests that molecular hydrogen adsorbed on the membrane catalyst participates in direct hydrogenation of the triple bond into a single bond. This does not occur during atomic hydrogen transfer through the membrane catalyst.

Additionally acetylenic alcohols of higher molecular weights are hydrogenated selectively into ethylenic alcohols by the membrane catalysts. The synthetic perfume linalool has a yield of 98 per cent for the reaction:



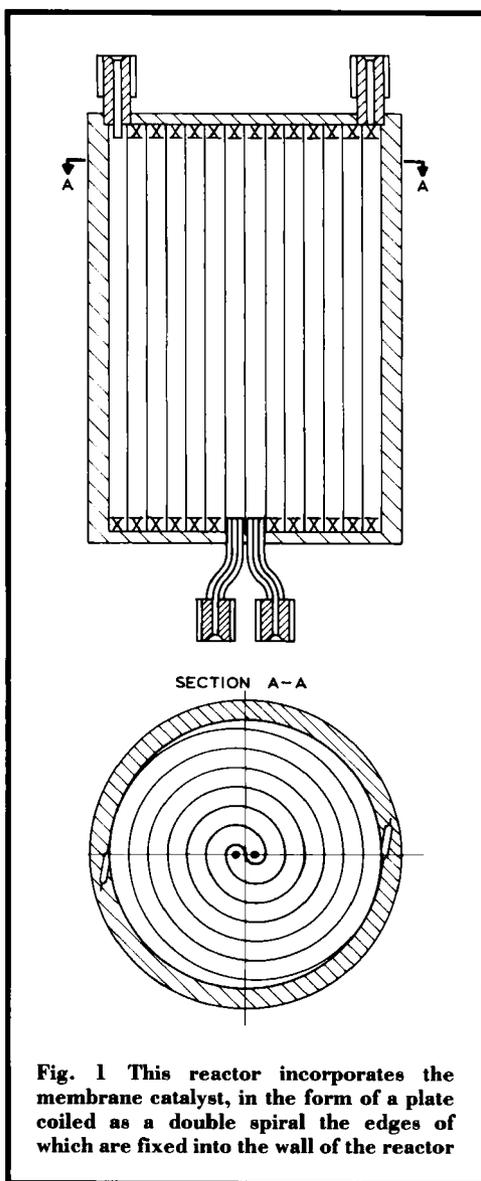
The initial rate equals 4 mol/m² hour.

Hydrogen evolution reactions such as dehydrogenation and dehydrocyclisation give more of the required products as a result of hydrogen discharge through the membrane catalyst. Selectivity is higher than on conventional catalysts because side reactions are depressed by the lowering of the hydrogen partial pressure.

The previously noted advantages of membrane catalysts may be combined by performing the hydrogen evolution reaction on one side of the catalyst and the hydrogen addition reaction on the other side (4, 5). Such coupling of the two reactions does not result in mixing of all reactants. The selective hydrogen transfer from the volume of its evolution to the volume of its consumption increases the yields of both reaction products. These effects are most pronounced for atomic hydrogen transfer without the recombination of hydrogen atoms which have been split from organic molecules on one surface of the membrane catalyst, and for dissociation of dihydrogen on the other surface of the catalyst. All these conditions are realised using palladium alloys as the membrane catalysts. Pure palladium is not as good, because it is embrittled by repeated hydrogen sorption and desorption cycling.

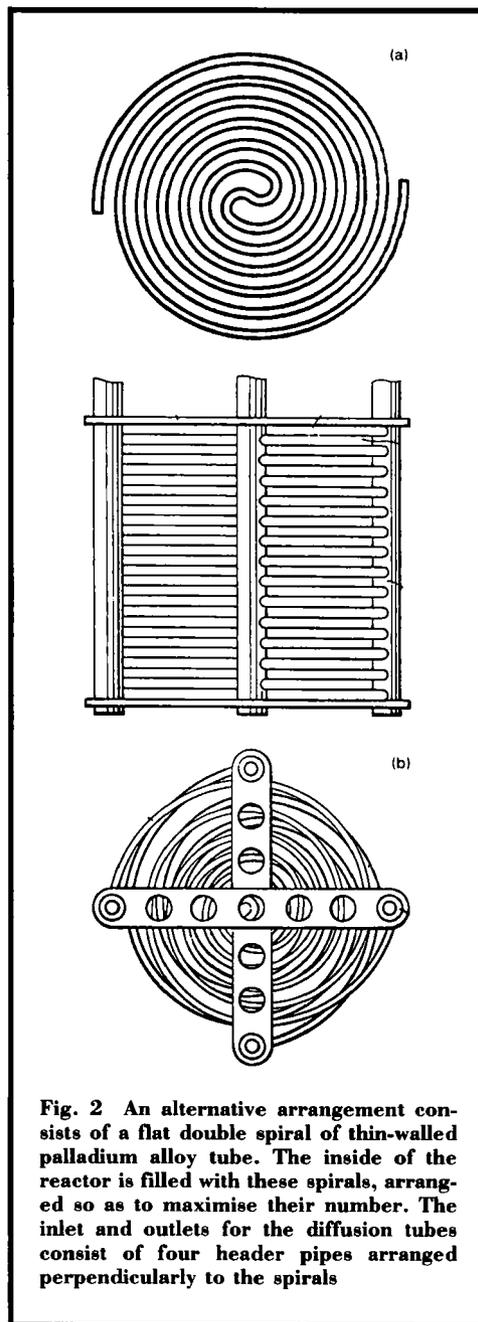
Binary Palladium Membranes

Thus it became a matter of identifying palladium alloys with high permeability to hydrogen which would not suffer mechanical



damage and which were catalytically active in hydrogenation or dehydrogenation reactions. For this reason the influence of the second component in palladium alloys upon these properties has been systematically studied in the A. V. Topchiev Institute of Petrochemical Synthesis of the U.S.S.R. Academy of Sciences, the P. Lumumba Peoples' Friendship University and the A. A. Baikov Institute of Metallurgy of the U.S.S.R. Academy of Sciences.

The study of binary alloys of palladium with twelve other metals — aluminium, titanium, nickel, copper, molybdenum, ruthenium, rhodium, silver, indium, tungsten, rhenium and platinum — revealed that the catalytic



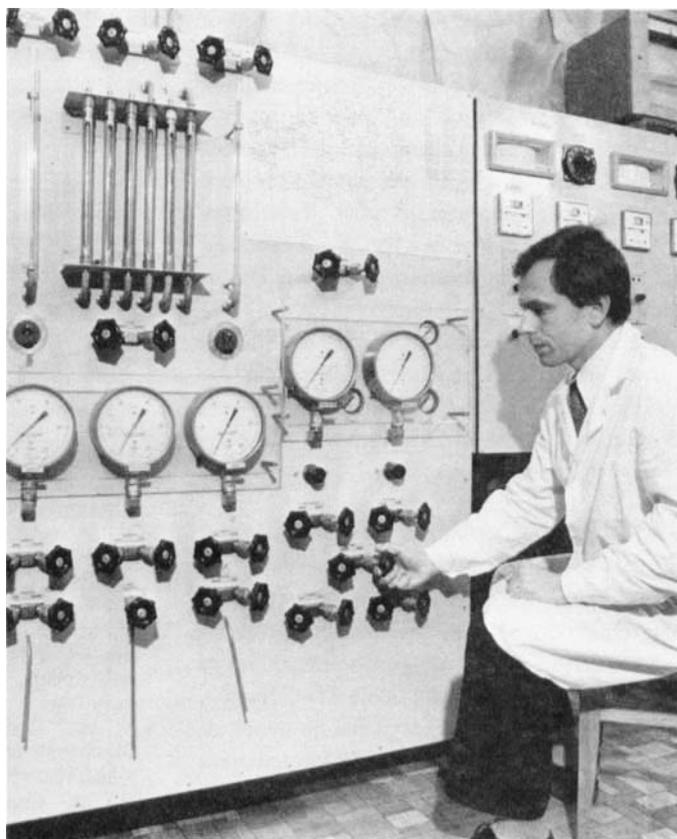


Fig. 3 A pilot plant which incorporates hydrogen permeable palladium alloy membrane catalysts has now been employed for selective hydrogenation

activity of the alloys containing metals of Groups VI to VIII of the Periodic System towards dehydrogenation (6) and hydrogenation (7) is usually higher than the activity of pure palladium. In contrast to this, alloys containing metals of Group IB are less active than palladium.

The catalytic activity of several palladium alloys may be significantly increased by holding the samples at 973 K for 20 minutes in an atmosphere that is inert to the catalyst, such as nitrogen, argon or helium and thereafter cooling the catalysts rapidly down to the temperature of the catalytic reaction. Quenching a palladium-10 weight per cent rhodium catalyst in this way doubles the yields of benzene and toluene during *n*-heptane dehydrocyclisation. The hydrodealkylation of toluene over a palladium-5.5 per cent nickel alloy is also enhanced (5).

Unlike conventional catalysts the membrane catalyst is a part of the reactor construction. The inner space of the catalytic reactor is subdivided into two compartments by a partition in the form of a plate or tube. The plate is fabricated from palladium alloy coiled as a double spiral, as shown in Figure 1. The edges of the plate are built into the walls of the reactor shell (8). To prevent deformation of the plate, corrugated sheets of the same alloy may be inserted into both compartments (9). Seamless thin-walled tubes may have the shape of a double flat spiral, Figure 2(a). The spirals are positioned one on top of the other so that each succeeding spiral is in a mirror symmetry with the adjacent one. This simplifies the bank assembly and enables the reactor volume to be filled with the maximum number of spirals. The inlet and outlet ends of the spirals are fitted into four headers constructed in the form of

tubes positioned perpendicularly to the plane of the spirals, Figure 2(b), (10). Palladium-ruthenium tubes three metres long with an external diameter of 1.0 mm and an internal diameter of 0.8mm are commercially available in the U.S.S.R., and are resistant to pressure drops of up to 100 atm. A pilot plant incorporating such tubular reactors has been used for selective hydrogenation processes; this is shown in Figure 3.

Membrane catalysts with smaller amounts of palladium per unit of reactor volume may be produced by covering a hydrogen-permeable support with a film of palladium alloy which is several microns thick (11).

An Efficient and Environmentally Acceptable Production Route

Very pure chemicals and pharmaceuticals may be produced with the help of the membrane catalysts. The hydrogenation reactions of triple C≡C bonds into double C=C bonds, NO₂ groups into NH₂ groups and quinones into hydroquinones have been performed with better results than on the same catalyst but without hydrogen transfer through the membrane catalyst. Hydrogen-rich gases from refineries and ammonia synthesis plants may be used for hydrogenation instead of more expensive pure hydrogen. All of these factors are important in keeping the environment clean and in making best use of non-renewable hydrocar-

bon resources. Additionally, reaction coupling on the membrane catalysts also reduces the energy consumption.

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A Further Compendium on Organometallic Compounds

Dictionary of Organometallic Compounds, First Supplement

EDITED BY DR. JANE E. MACINTYRE, Chapman and Hall, London, 1985, 564 pages, £135

The original three-volume Dictionary of Organometallic Compounds was reviewed in this journal in July last year (*Platinum Metals Rev.*, 1985, **29**, (3), 130). This outstanding work of reference has now been followed by the first supplementary volume, bringing the survey of the literature down to mid-1984 with many additional entries, some 2300 in all, and including a list of recent books and review articles, while some of the original entries in the main work have been revised and updated.

Compounds of the platinum metals listed

with their molecular formulae, CAS registry number, brief description and literature reference total 450, platinum being represented by 118 entries, rhodium by 90, ruthenium 83, iridium 74, palladium 48 and osmium 37.

The editor has had the co-operation of a distinguished international advisory board as well as a group of specialist editors for individual metals. This addition to the main dictionary makes a most useful compendium for all those engaged in any way in organometallic chemistry.

L.B.H.