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Pd-based Diffusion Membranes as Ethylene Hydrogenation Catalysts*

I. T. CAGA[†], J. M. WINTERBOTTOM

Department of Chemical Engineering, University of Birmingham, P.O. Box 363, Birmingham, BI5 2TT, U.K.

and I. R. HARRIS

Department of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham, BI5 2TT, U.K.

Some Pd-rich alloys are only permeable to hydrogen and have catalytic activities for hydrogenation and dehydrogenation reactions [1–5]. Hydrogen permeating through such membrane catalysts in the form of foils or thin-walled tubes presents a new way of introducing hydrogen to the reactions, involving the activation and transfer of hydrogen together with new concepts in reactor design. The diffusion of hydrogen through such membranes has also fundamental importance in understanding the interstitial diffusion in transition metal alloys. They are widely used for the separation and purification of hydrogen gas.

Their use in catalytic systems may be advantageous as: (i) they can suppress the competitive adsorption with a better control of surface concentrations; (ii) they can increase the reaction rate by supplying the highly active atomic hydrogen to the reactant with a desirable concentration on the whole surface; (iii) the removal of spent catalyst from the product is eliminated by their use in liquid-phase hydrogenations; and (iv) it is also possible to carry out a hydrogen evolution reaction on one side and a hydrogen addition reaction on the other side of the membrane.

In this study, the aims were to search for Pd-based alloys with high permeability to hydrogen and good mechanical properties and to correlate their catalytic activities with their structural and sorptional properties.

Experimental

The experiments were carried out in a stainless steel reactor which was divided by the membrane into two compartments of equal volume, a high pressure hydrogen and a low pressure reaction side.

The membrane itself was clamped between two copper gaskets and a thermocouple was sited very close to the low pressure side. The reactants were passed through a stainless steel tube into the low pressure side, the outlet being approximately 3 mm away from the membrane surface, and were kept at a constant pressure of 1 bar.

Two Pd-rich membranes (Pd–23 at% Ag and Pd–7.8 at% Y) were used. The former was kindly supplied by Johnson Matthey plc., as a sheet of 0.005 cm in thickness, whereas the latter was prepared by the similar methods cited in refs. 6 and 7, *i.e.* by argon arc-melting of the constituent metals, homogenized in a vacuum furnace and cold-rolled to the thickness of 0.005 or 0.01 cm, with several intermediate anneals in between. The alloy composition was verified by X-ray diffraction methods [8]. Discs with a diameter of 2.47 cm were cut from this sheet and given a final anneal at 900 K for 3 h.

For the permeability studies, the membrane was activated by abrading its surface and heating it to 250 °C in dry hydrogen at 2 bars, then furnace-cooling to room temperature. It was then pressurized to give the required differential pressure, whilst the low pressure side was kept at a constant 1 bar hydrogen pressure. A very sensitive microflowmeter was used to monitor the outflow rate of the gas on the low pressure side.

The catalytic activities of the membranes were investigated. First, the self-hydrogenation of ethylene on the low pressure side of the untreated membrane (*i.e.*, not previously activated by hydrogen treatment) was studied whilst keeping the high pressure side under vacuum. Secondly, ethylene was hydrogenated on the low pressure side of the untreated and/or treated membrane (*i.e.*, activated by hydrogen treatment then outgassed prior to the ethylene introduction) as a function of temperature and differential pressure across the membrane.

The reactants and products of these reactions were analysed by gas chromatography using a Pye series 104 unit fitted with dual f.i.d. and a 1.5 m × 3 mm i.d. glass column packed with 80–100 mesh silica gel.

Results and Discussion

The permeability results are in good agreement with published results [6, 7, 9]. The permeabilities of the Pd–7.8 at% Y membrane are greatly in excess of those of the Pd–23 at% Ag membrane as the temperatures and differential pressures increase; for example at 300 °C and 6.8 bars the permeability of the Pd–7.8 at% Y is 3.65 times that of the Pd–23 at% Ag membrane.

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[†] Author to whom correspondence should be addressed.

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Ethylene hydrogenation was chosen to test the catalytic activities of these membranes. However, ethylene is known to decompose and/or self-hydrogenate on catalytic metal surfaces at elevated temperatures and pressures [10, 11].

This process can even poison the catalytic surface for further reactions. Hence, the effects of temperature, ethylene pressure and feed rate were investigated in the self-hydrogenation of ethylene on the low pressure side of the untreated materials. The results are shown in Figs. 1 and 2. Although the self-hydrogenation of ethylene was not observed with both membranes up to 300 °C at 1 bar of ethylene pressure, in the 300–350 °C range methane, ethane and n-propylene were common products to both systems and n-butylene appeared additionally with the Pd–7.8 at% Y alloy which yielded 3 times higher concentrations than those with the Pd–23 at% Ag. On the other hand, increasing the pressure of ethylene suppressed the methane and ethane formation and shifted the n-butylene formation to higher temperatures with the Pd–7.8 at% Y alloy, but with the Pd–23 at% Ag their concentrations were increased along with the additional formation of n-butane. Doubling the ethylene feed rate again depressed the methane and ethane formation for the Pd–7.8 at% Y alloy, the latter being about 5 to 10 times lower than those with the Pd–23 at% Ag. The higher hydrocarbon formations were again shifted to higher temperatures.

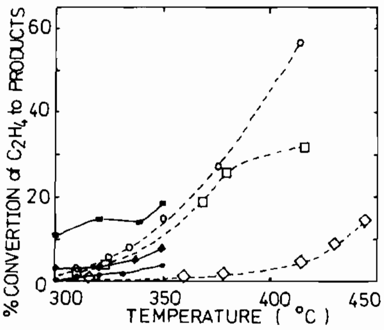

Fig. 1. The self-hydrogenation of ethylene on the low pressure side of Pd–7.8 at% Y (– – –, open), Pd–23 at% Ag (——, closed). Temperature effects (○), pressure effects (□), ethylene feed rate effects (◇).

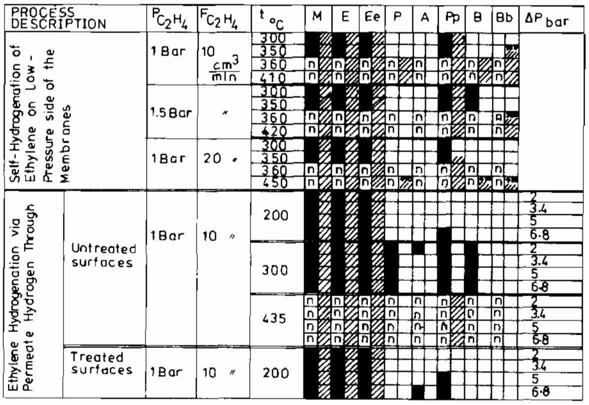

Fig. 2. Comparison for product analysis of the self-hydrogenation and/or hydrogenation via permeate hydrogen under various conditions with Pd–7.8 at% Y (▨), Pd–23 at% Ag (■). M = methane, E = ethane, Ee = ethylene, P = propane, A = acetylene, Pp = propylene, B = butane, Bb = butylene, ΔP = differential pressure, $P(C_2H_4)$ = ethylene pressure, $F(C_2H_4)$ = ethylene feed rate, (n) = not examined, (□), not formed.

Figs. 2 and 3 show the collective results of the hydrogenation of ethylene via permeating hydrogen through the untreated and/or treated surfaces of the membranes as a function of temperature and differential pressure across the membranes.

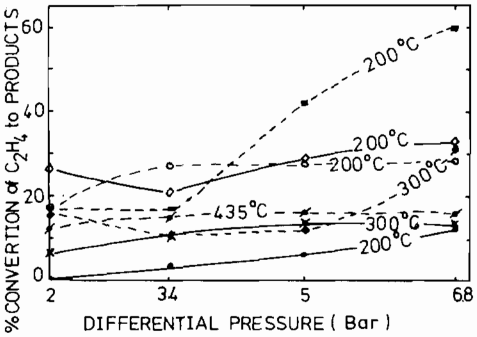

Fig. 3. The ethylene hydrogenation via permeate hydrogen through untreated (closed), and treated (open) surfaces of Pd–7.8 at% Y (– – –) and Pd–23 at% Ag (——) at various temperatures and differential pressures.

With the untreated surfaces at 200 °C, increasing the differential pressure increased the ethane formation with both systems but with greater concentrations for the Pd–7.8 at% Y membrane, and while methane and ethane were the major products, n-propylene appeared only with the Pd–23 at% Ag at 6.8 bar differential pressure. Again at 300 °C, a similar effect was observed; n-propane, n-propylene and n-butane were also detected at all differential pressures and acetylene at 2 bar only with the Pd–23 at% Ag membrane. n-Propylene was observed at elevated temperatures (435 °C) with the Pd–7.8 at% Y, together with methane and ethane at all differential pressures.

When the membrane surfaces were hydrogen treated prior to the ethylene introduction, at 200 °C methane and ethane again were the common products. Traces of acetylene and n-propylene were also detected only with the Pd–23 at% Ag alloy at 5 and 6.8 bar. Increasing differential pressure slightly increased the ethane formation for both cases and their concentrations were comparable.

In general, the nature of the membranes, different surface conditions, availability of active sites, variation in adsorption of different hydrocarbons and possible poisoning of the surfaces by the hydrocarbons formed during the hydrogenation may provide some explanation for the formation of various products with interesting concentrations on these surfaces [3, 4] and the work of Somorjai [12] and Bandy *et al.* [13] on ethylidyne formation may shed some light on the differences in their behaviour. The hydrogenation activity for the Pd–7.8 at% Y membrane is greater than that of the Pd–23 at% Ag but not in the same ratio as in their permeability. The possible susceptibility of yttrium to oxidation may yield a slightly oxygen-contaminated surface which could affect the above factors and lead to modified product distributions compared with the Pd–23 at% Ag membranes, and future surface studies will be carried out to verify or otherwise these suggestions.

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References

1 H. Nagamoto and H. Inoue, *J. Chem. Eng., Jpn., 14*(5), 377 (1984).
2 B. J. Wood, *J. Catal., 11,* 30 (1968).
3 N. R. Roshan, A. P. Mishchenko, V. P. Polyakova, N. I. Parfenova, E. M. Savitsky, E. A. Voitekhova, V. M. Gryaznov and M. E. Sarylova, *J. Less-Common Met., 89,* 423 (1983).
4 V. M. Gryaznov, M. M. Ermilova, L. S. Morozova, N. V. Orekhova, V. P. Polyakova, N. R. Roshan, E. M. Savitsky and N. I. Parfenova, *J. Less-Common Met., 89,* 529 (1983).
5 V. M. Gryaznov, S. G. Gul Yanova, Yu. M. Serov and V. D. Yagodovskii, *Russ. J. Phy. Chem., 55*(5), 730 (1981).
6 D. T. Hughes and I. R. Harris, *Z. Phys. Chem., Neue Folge, Bd., 117,* 185 (1979).
7 R. C. J. Wileman and I. R. Harris, *J. Less-Common Met., 109,* 367 (1985).
8 I. R. Harris and M. Norman, *J. Less-Common Met., 15,* 285 (1968).
9 A. S. Darling, *Proceedings of the Symposium on Less-Common Means of Separation,* Institute of Chemical Engineering, Birmingham, April 1963.
10 J. Horiuti and K. Miyahara, 'Hydrogenation of Ethylene on Metallic Catalysts', *NSRDS-NBS-13,* U.S. Department of Commerce, 1968.
11 S. A. Miller, in S. A. Miller (ed.), 'Ethylene and Its Industrial Derivatives', Ernest Benn, London, 1969, pp. 1134–1145.
12 G. A. Somorjai, *Phil. Trans. R. Soc. London, Ser. A, 318,* 81 (1986).
13 B. J. Bandy, M. A. Chesters, D. I. James, G. S. McDougall, M. E. Pemble and N. Sheppard, *Phil. Trans. R. Soc. London, Ser. A, 318,* 141 (1986).