Studies in Surface Sciences and Catalysis, 130 (2000) 2693-2698

Catalysis of palladium salt reduction in a gas-liquid membrane reactor

Sylvain MIACHON*, Arnaud MAZUY and Jean-Alain DALMON**.

Institut de Recherches sur la Catalyse, CNRS, 2, Av. A. Einstein F-69626 Villeurbanne.
*miachon@catalyse.univ-lyon1.fr, **dalmon@catalyse.univ-lyon1.fr

This paper deals with a new way to prepare a palladium - alumina nanoscale composite membrane, using a catalytic membrane reactor of the gas - liquid contactor type.

1. INTRODUCTION

Catalytic Membrane Reactors (CMRs) work by allying the separating effect of a membrane and the kinetic effect of a catalyst. They can be divided into three types .
Distributors are used to mix in a controlled way reactants by distributing uniformly one of them through the membrane all along the catalyst bed. This allows a controlled contact between reactants and limits the concentration of the distributed reactant into the reactor, thus limiting secondary reactions. One example of reaction currently studied in this type of CMR is selective oxidation [1], the control of the oxygen concentration all along the reactor limiting over-oxidation.
Active contactors are basically membranes including a catalyst that make an active interface between reactants which are, in general, non-miscible species, like a gas and a liquid. The purpose of this configuration is to make easier the three-phase contact between gas and liquid reactants and the solid catalyst. This contactor effect is achieved by locating the reaction into the catalytic pore in a peculiar way. As a matter of fact, as the catalytic pore is part of the membrane porosity, it can be fed from one side of the membrane by the gas phase, and on the other side by the liquid phase. This is a unique configuration of catalytic membranes, when conventional catalyst have pores presenting only one entrance and therefore need premixed reactants. Thus in the membrane, the gaseous reactant must not face a long way through into the solvent as a solvated species in order to proceed to the catalytic sites. Using such contactors based on mesoporous membranes, it has been shown [2] that the gaseous reactant can no more be the limiting partner of a gas-liquid-solid reaction.

The third type of CMR is the most currently known and called "equilibrium shift reactor". The principle is to use a very permselective membrane to evacuate one of the reaction products from the reaction zone, in order to shift the equilibrium. Well-known examples are dehydrogenation reactions. Dense palladium membranes are commonly used in these applications, as this metal is highly selectively hydrogen-permeable.

This work will focus mainly on a reactor of the second type (gas-liquid active contactor) used to produce a composite Pd-alumina membrane, which might then be mounted in a reactor of the third type.

Palladium-based membrane, such as that produced here, may be used for other purposes than equilibrium-shift dehydrogenation CMRs, as for instance pure separation applications. This work is part of a European Union project (JOE3/CT97-0075) that deals with hydrogen purification. This kind of membranes, when exempt from defects, can offer a very high selectivity towards hydrogen, while letting through large fluxes if they are thin enough. In the present project, this purified hydrogen should feed an on-board polymer electrolyte fuel cell to power an electrical vehicle.

Such membranes have been widely studied for many years for the production of pure hydrogen but their main drawback is their thickness, leading to reduced hydrogen fluxes [3-8]. In an attempt to reduce thickness (i.e. to reach higher flux and lower cost), current membranes are usually prepared by making a film on top of a porous support, with different techniques: chemical vapour deposition [9], electroless plating [10-13], magnetron sputtering [5, 14], etc. However, they often suffer from several limitations.

i) It is difficult to avoid defects when large plated films are prepared.

ii) Thermal stability of the deposited film may be compromised due to the difference between thermal expansion coefficients of the porous support and the metal layer.

iii) Palladium encounters a hydride phase separation under 300°C under common hydrogen pressures (hydrogen embrittlement), that destroy the membranes.

Our approach here is to work around these problems by making a nanometer scale composite $Pd-Al_2O_3$ structure. This can be done by plugging the pores of an alumina mesoporous support tube with palladium metal. Hence, the sizes of the defects are limited to the support pore size, while thermal expansion differences are minimised. Phase separation can be avoided, as the Pd phase is present only as small crystallites.

In the past, few authors have tried to make such a real Pd-alumina composite membranes [15-17], and then with limited success in terms of permeation rates, hydrogen permselectivity and stability.

2. EXPERIMENTAL

This work basically presents the reduction of palladium complex by hydrogen gas, both reactants being contacted through a porous catalytic membrane.

Palladium is a well-known hydrogenation catalyst. As such it can be used with hydrogen to reduce tetramminepalladium (II) chloride ($Pd(NH_3)_4Cl_2$) into palladium metal to produce the composite palladium-ceramic membrane.

2.1. Materials

The tubular ceramic supports used in this work were provided by ECN (The Netherlands), partner of the Joule program. They were made of four porous alumina layers of different thickness, pore sizes decreasing from the inner to the outer layer (see fig. 1). The top layer, on the external side of the tube, was made of gamma-alumina and was modified by application of small particles of catalyst (Pd) in its mesoporous structure (see preparation step 1).

Precursors for palladium application were $Pd(NH_3)_4Cl_2$ and $PdCl_2$ from Alfa, 99.9% purity.

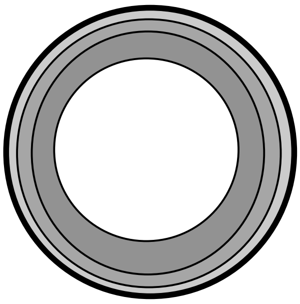

Figure 1: Cross section schematic of the ECN porous alumina support membrane. Outer diameter 14 mm. From inside to outside, the three first layers are made of α-alumina with respective thicknesses of 6400, 60 and 60 μm and average pore sizes of 5, 0.28 and 0.18 μm. The final mesoporous γ-alumina top layer has a thickness of ca. 2 μm and an average pore size of 4 nm.

2.2. Preparation

Step 1

This first step of the composite preparation was of prime importance. It dealt with the deposition of small Pd particles into the mesoporous top-layer, and only into this layer. In fact, the location of these small catalyst particles determined the location of the reaction during the second step. These particles can be seen as seeds for the later growth of the palladium crystallites. The applied procedure was a traditional anionic impregnation in acidic solution of palladium chloride, followed by hydrogen reduction at 650 K.

Step 2
The second step of the preparation procedure consists of salt reduction in the gas-liquid CMR. The pores of the membrane were filled with a solution of $Pd(NH_3)_4Cl_2$. A hydrogen pressure of about 0.1 MPa was applied onto the external side (see fig. 2).

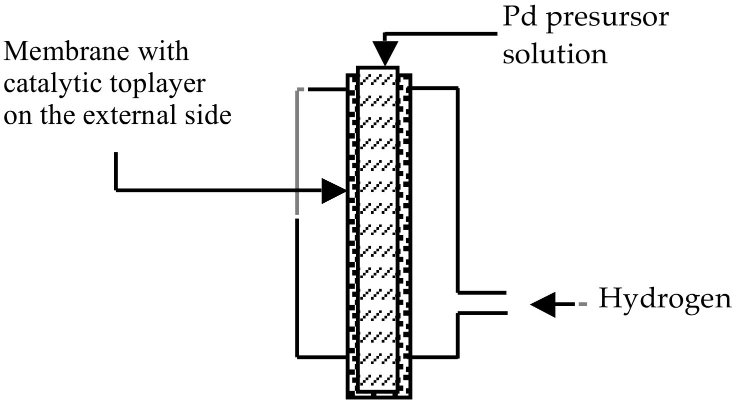

Figure 2: Schematic of the gas-liquid catalytic membrane reactor used to reduce the palladium complex and built the composite palladium - alumina membrane.

To be more precise, the liquid phase was located only in the tube wall pores. After a few minutes, most of the salt was reduced and formed a black composite with the gamma alumina top layer. The reaction temperature was 80°C.

2.3. Materials characterisation
The prepared samples were observed using SEM-EDX technique. A dedicated XRD set-up was used to obtain diffractograms of the external surface of the tube after step 2. This method provided information on about 1 μm deep material.

Membranes were also characterised by gas permeation. As palladium is permeable only to hydrogen, nitrogen permeation measurements supplied an estimate of the membrane defects. In order to obtain the hydrogen to nitrogen permselectivity, hydrogen permeation was also measured, within the same set-up. All these permeation measurements were carried out at room temperature, with a pressure difference of 1-4 kPa (rough tubes) or 10-50 kPa (composite tubes).

3. RESULTS

The following results were obtained from a series of more than six samples, which show a fair reproducibility.

3.1. Characterisations after step 1
Step 1 lead to Pd loading of 4 to 6wt% Pd/Al_2O_3 as measured by elemental analysis of the impregnation solutions and by SEM-EDX. This last technique also showed that the Pd was only present in the mesoporous top layer of the membrane support.

Nitrogen permeation measurements showed about the same figures on step 1 samples (8.4 μmol/s/m^2/Pa) that on raw supports (8.6).

3.2. Characterisations after step 2

The equivalent thickness of the obtained palladium - alumina composite layer, measured by gravimetry and analysis of the precursor solution before and after reaction, was about 300 to 400 nm. It has been checked by SEM-EDX that the palladium is located mostly in the 2.5 μm top layer in which the catalyst was placed after step 1.

XRD experiments showed a crystallite average size in the order of 10 nm.

Room temperature nitrogen permeance was reduced by a factor of 200 to 600 (13 to 36 nmol/s/m^2/Pa) after step 2. At that point, hydrogen permeance was in the order of 400-500 nmol/s/m^2/Pa.

A sixty hour treatment under room temperature hydrogen atmosphere did not affect the permeation rate of both gases.

4. DISCUSSION

The fact that step 1 did not change the permeation rate of nitrogen indicates the porous structure of the support was not affected. A very rough calculation can show that step 1 deposited particles account for a small fraction of the porous volume.

The very large reduction of nitrogen permeation after step 2 showed the pores of the support were plugged for most, if not all, of them. In fact, all the pores might well be plugged, but nitrogen permeation measurements are not so reliable in this range. A very tiny leak at the sealing endings could be in the same order of the observed nitrogen permeation.

The same remark applies to the figures of hydrogen to nitrogen selectivity obtained here. The measured ratio is about 12, but may have been under estimated.

Hydrogen permeation results have been obtained at room temperature. Moreover, the membrane resisted without consequences the stay for a relatively long duration (60 hours) at room temperature under hydrogen atmosphere. No hydrogen embrittlement was observed. To our knowledge, it is the first time this has been demonstrated for pure palladium (i.e. non alloy) dense membranes. The results exposed in the literature with pure palladium usually restrain to high temperature (more than 300°C), in order to avoid hydrogen embrittlement. Only a very few authors have succeeded in making a pure palladium based membrane, i.e. a composite with ceramic, that could withstand temperatures as low as 100°C [15, 17], but these author do not quote room temperature hydrogen treatment or permeance measurements.

Such a resistance to hydrogen embrittlement can be explained by the nanometric scale composite structure of the membrane. The composite was made of particles of γ-alumina and palladium of about 10 nm, as observed by XRD for the latest. One can think that for such small crystallites, the hydride phase separation that usually causes hydrogen embrittlement can not take place. As a matter of fact, recent experiments carried out here on even larger crystallites (26 nm) deposited onto α-alumina powder support, showed they don't collapse after hydrogen treatment at room temperature.

When considering the hydrogen to nitrogen permselectivity value obtained at room temperature (12), one has to keep in mind the dramatic increase with temperature of hydrogen permeation in palladium [15, 17]. Not only the present data compare well with those obtained at 100°C by others [15, 17], but they may increase by orders of magnitude for high temperatures, as typically used in dehydrogenation reactions.

The same experiment carried out without step 1, i.e. without catalyst in the membrane reactor, needed hours of reaction time and resulted into a much lower quality membrane in terms of permselectivity, together with a higher dispersion of reduced Pd along 120 μm deepness into the support.

It was then concluded that the presence of the step-1 catalyst seeds was essential to achieve a thin palladium-alumina small-scale composite membrane.

5. CONCLUSION

A nanoscale composite palladium - alumina membrane was obtained by plugging pores of a porous ceramic tubes with palladium. Plugging was obtained by catalytic reduction of a palladium salt in a gas-liquid Catalytic Membrane Reactor. The presence of a catalyst was necessary to achieve quick and efficient membrane fabrication.

This original way of preparation leads to materials which are resistant to hydrogen-embrittlement at room temperature (a major problem of conventional Pd membranes) and present a rather good hydrogen permselectivity.

Perspectives concentrate on improving the method and measuring the performance of the membrane at higher temperatures, typical of those used in dehydrogenation reactions.

6. ACKNOWLEDGEMENTS

This work has been conducted with the help of the European Union Joule project, ref. JOE3/CT97-0075.

Many thanks to Dr Gérard Bergeret for his invaluable help in achieving XRD experiments on tubular samples.

References

1. Mota S., Abon M., Volta J-.C. and Dalmon J.-A., Catalysis Today 1999, in press.
2. Peureux J., Torres M., Mozzanega H., Giroir-Fendler A. & Dalmon J-A., Catalysis Today, 1995. **25**: p. 409.

3. Athayde A.L., Baker R.W., & Nguyen P., Journal of Membrane Science, 1994. **94**: p. 299.
4. Booth J.C.S., Doyle M.L., Gee S.M., Miller J., Scholtz L-A., Walker P.A., in *11th World hydrogen energy conference*. 1996.
5. Gryaznov V.M., Serebryannikova O.S., Serov Yu. M., Ermilova M.M., Karavanov A.N., Mischenko A.P. & Orekhova N.V., Applied Catalysis A : General, 1993. **96**: p. 15.
6. Kusakabe K., Yokoyama S., Morooka S., Hayashi J.-I. & Nagata H., Chemical Engineering Science, 1996. **51**(11): p. 3027.
7. Li A., Liang W. & Hughes R., Journal of Membrane Science, 1998. **149**(2): p. 259.
8. Shu J., Granjean B.P.A., Van Neste A. & Kaliaguine S., Canadian Journal of Chemical Engineering, 1991. **69**: p. 1036.
9. Aoki K., Yokoyama S., Kusakabe K. & Morooka S., Korean Journal of Chemical Engineering, 1996. **13**(5): p. 530.
10. Collins J.P. & Way J.D., Industrial & Engineering Chemistry Research, 1993. **32**: p. 3006.
11. Ilias S., Su N., Odoaka U.I. & King F.G., Separation Science & Technology, 1997. **32**(1-4): p. 487.
12. Li A., Liang W., & Hughes R., in *Workshop "Applications & future possibilities of catalystic membrane reactors"*. 1997. Turnhout (B).
13. Shu J., Granjean B.P.A., Kaliaguine S., Ciavarella P., Giroir-Fendler A. & Dalmon J.A., Canadian Journal of Chemical Engineering, 1997. **75**: p. 712.
14. Jarayaman V. & Lin Y.S., Journal of Membrane Science, 1995. **104**: p. 251.
15. Konno M., Shindo M., Sugawara S. & Saito S., Journal of Membrane Science, 1988. **37**: p. 193.
16. Hongbin Z., Anwu L., Jinghua G. & Guoxing X., Cuihua Xuebao, 1997. **17**(6): p. 483.
17. Morooka S., Yan S., Yokoyama S. & Kusakabe K., Separation Science & Technology, 1995. **30**(14): p. 2877.