ELSEVIER

Catalysis Today 67 (2001) 33–42

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Preparation and characterization of palladium composite membranes for hydrogen removal in hydrocarbon dehydrogenation membrane reactors

Volker Höllein [a], Matthew Thornton [a], Peter Quicker [b,1], Roland Dittmeyer [a,*]

[a] *DECHEMA e.V., Karl-Winnacker-Institut, Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany*
[b] *ATZ EVUS Applikations- und Technikzentrum für Energieverfahrens-, Umwelt- und Strömungstechnik,*
Kropfersrichterstraße 6-8, 92237 Sulzbach-Rosenberg, Germany

Abstract

Palladium composite membranes were prepared by high velocity oxy-fuel flame spraying (HVOF) and electroless plating, respectively. Palladium was deposited onto porous stainless steel and alumina tubes. High-temperature permeation tests (350–650°C) were carried out to determine the permeation properties as well as the thermal and mechanical stability of the prepared membranes. The membrane morphology was characterized by scanning electron microscopy. Thicknesses of the Pd-layers ≥ 3 (electroless plating) and ≥ 50 μm (HVOF) were necessary to get defect-free films. The membranes showed a good hydrogen permeability and selectivity for both preparation methods. However, the experimental results indicate that the separation behaviour — for membranes prepared by electroless plating — depends on the thickness of the Pd-layer. The N_2-permeation of membranes with Pd-layers less than or equal to about 7 μm thickness increased significantly in presence of hydrogen at temperatures above 400°C. In contrast membranes having a Pd-layer well above 7 μm thickness proved to be stable at high temperatures, which is one of the prerequisites for employment of these membranes in industrially relevant dehydrogenation reactions. This was evident from a comparison of the data of permeation runs with H_2/N_2-mixtures and single gases.

Keywords: Composite membrane; Palladium membrane; Hydrogen permselective membrane; Hydrogen permeation; Membrane preparation

---

1. Introduction

In recent years, the application of high-temperature membrane reactors (e.g. for the catalytic dehydrogenation of hydrocarbons) has received growing attention. It is well known, that membranes have the potential to surpass the equilibrium conversion by selective removal of one of the reaction products, usually hydrogen [1–4]. A successful implementation of membrane reactors in industrial processes requires membranes with high hydrogen permeability and selectivity, linked with chemical, mechanical and thermal long-term stability.

In principle three different kinds of membranes can be employed to remove hydrogen in high-temperature applications: microporous membranes [5,6], dense metal membranes [7,8] or composite membranes [9,10]. With regard to a high hydrogen permeability and selectivity, combined with good mechanical properties, metal composite membranes seem to be

---

[*] Corresponding author. Tel.: +49-69-7564-428; fax: +49-69-7564-388.
E-mail address: dittmeyer@dechema.de (R. Dittmeyer).

[1] On leave from the University of Erlangen-Nürnberg, Lehrstuhl für Technische Chemie I, Egerlandstr. 3, 91058, Erlangen.

0920-5861/01/$ – see front matter
PII: S0920-5861(01)00279-6

Nomenclature

E_A	apparent activation energy (kJ/mol)
J	transmembrane flux (mol/m^2 s)
l	membrane thickness (palladium layer) (m)
n	hydrogen partial pressure exponent in Eq. (1) (–)
p_i	partial pressure of species i (Pa)
Q, Q_0	permeability coefficient (mol/m^2 s m Pa^n)
R	universal gas constant 8.314 (J/mol K)
T	temperature (K)

Indices

ret	retentate
per	permeate

the most reasonable choice. Composite membranes consist of a thin metallic layer — only permeable to hydrogen — supported on a porous substrate. Palladium and its alloys are the most common metals used for these hydrogen selective films. Porous vycor glass, porous ceramic or porous stainless steel membranes can be used as supports. In view of the reactor design, stainless steel membranes offer the most promising perspectives.

Several techniques have been investigated to deposit palladium and Pd-alloys on porous supports. Magnetron sputtering [11,12], electroplating [13], spray pyrolysis [14] and chemical vapour deposition [15,16] were suggested for the preparation of Pd-based composite membranes. However, the most successful method so far is electroless plating [17–20].

The objective of our work is the employment of metal composite membranes in catalytic dehydrogenation reactions, especially the dehydrogenation of ethylbenzene to styrene. The present paper is focussed on the investigation of the separation behaviour of palladium composite membranes with respect to a potential application in industrial dehydrogenation reactions. Palladium composite membranes were prepared by high velocity oxy-fuel flame spraying and electroless plating, respectively. The permeation properties of the membranes were examined in gas permeation measurements up to 650°C and for transmembrane pressure differences up to 4 bar. Experiments with pure gases (hydrogen or nitrogen) as well as with binary mixtures (hydrogen and nitrogen) were carried out.

2. Experimental

2.1. Membrane preparation

Tubular asymmetric porous stainless steel and alumina (α-Al_2O_3) membranes were used as supports for the preparation of the palladium composite membranes. The alumina tubes consist of four layers (pore size of the finest layer = 100 nm) whereas the stainless steel tubes consist of two layers (pore size of the finest layer <500 nm). The membranes have an o.d. of 10 mm and an i.d. of 6 mm. The SEM micrographs in Fig. 1 show cross-sectional views of the employed supports. The stainless steel membranes have the fine layer on the shell side, the alumina membranes have it on the tube side. The surface quality and the pore structure of both layers are quite different. The metal layer is produced by wet powder spraying followed by sintering whereas the ceramic layer is made by slip coating and sintering. Submicron metal particles cannot be processed with acceptable efforts. Therefore, the surface of the metal layer is less even and less regular compared to the surface of the ceramic layer. Moreover, the pore size distribution of the metal layer is broader.

The membranes were prepared by high velocity oxy-fuel flame spraying (HVOF) and electroless plating. In both cases palladium was coated onto the surface of the layer with the finest pores. Electroless plating is a standard technique to prepare palladium layers preferably on substrates having smooth surfaces. HVOF has advantages first of all for coating of stainless steel substrates because it can tolerate relatively rough surfaces and is expected to give a better adhesion of the Pd-film to the support. The surface morphology and microstructure of the substrates and deposited films were examined using a scanning electron microscope (Philips XL40). The thickness of the Pd-films was estimated from the weight gain after the plating ($\rho_{Pd} = 11.96$ g/cm) and from SEM micrographs.

2.1.1. High velocity oxy-fuel flame spraying

HVOF is a thermal spraying technique. The palladium powder is injected into the nozzle of a spray gun using nitrogen as a carrier gas. It is partially molten in a fuel/air flame at temperatures between 2600 and 2900°C, accelerated to high velocities (500–600 m/s),

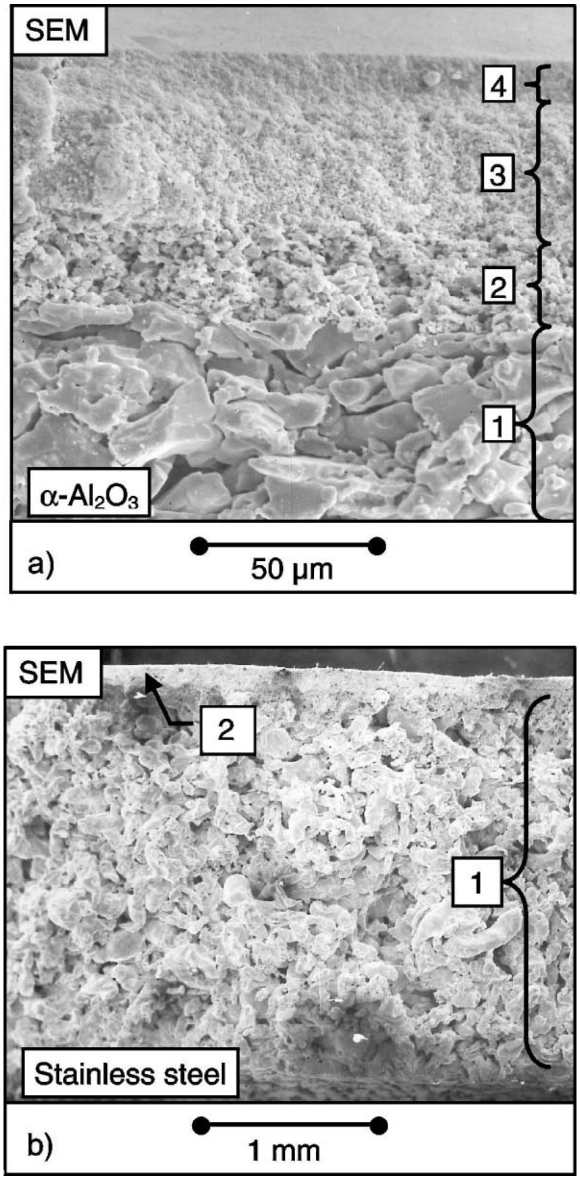

Fig. 1. SEM micrographs of the porous supports: (a) cross-section of an asymmetric four-layered alumina tube showing the coarse support (1), two intermediate layers (2 and 3) and the top layer with 100 nm nominal pore diameter (4); (b) cross-section of an asymmetric two-layered stainless steel tube showing the coarse support (1) and the top layer with 500 nm nominal pore diameter (2).

and propelled onto the surface of the substrate. Despite the high flame temperature the thermal load of the substrate is still moderate ($\Delta T = 50$–200°C). The experiments were carried out in cooperation with ATZ EVUS (Vilseck, Germany). The palladium powder used had a grain size ≤45 µm. An ethylene/air mixture served as fuel gas. The substrates were cleaned with ethyl alcohol prior to the coating. The coating took place in a normal air atmosphere, neither protective gas nor vacuum were applied. To receive a uniform coating the substrate was rotated in front of the spray gun which was moved by computer control over the longitudinal axis of the tube at a distance of 260 mm. The optimum linear velocity of the spray gun was below 25 mm/s at a rotational frequency of about 60 rpm. In general four successive coatings were applied.

2.1.2. *Electroless plating*

Electroless plating relies on the autocatalytic reduction of a metastable metal salt complex. The composite membranes were prepared using a plating bath which contained an EDTA stabilized palladium metal complex with hydrazine as reducing agent and ammonia to stabilize the bath and maintain the pH value. Table 1 shows the plating bath composition and the plating conditions. Prior to the plating step the tubes were first cleaned and afterwards — to pre-seed the microporous layer of the supports with palladium nuclei — sensitized (acidic $SnCl_2/SnCl_4$-solution) and activated (acidic $PdCl_2$-solution). The plating solution temperature was kept constant at 60°C. After the palladium deposition the membranes were rinsed with deionized water and then dried overnight at 140°C.

2.2. *Membrane permeation*

To determine the separation behaviour of the prepared membranes, permeation measurements were conducted. Experiments were carried out — to evaluate if the hydrogen permeability and selectivity of the membranes depends on the feed composition — using both single gases and a gas mixture. The membranes

Table 1
Composition of the electroless plating bath and plating conditions

$PdCl_2$	5 g/l
$Na_2EDTA\cdot 2H_2O$	70 g/l
NH_4OH (28%)	500 ml/l
$N_2H_4\cdot H_2O$	10 ml/l
pH value	10
Temperature	60°C

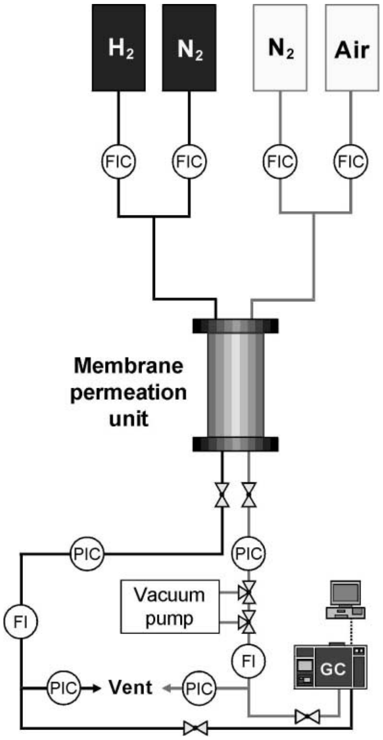

Fig. 2. Schematic of the experimental setup used for the permeation measurements.

were tested with pure hydrogen or nitrogen and with an equimolar mixture of both gases.

A schematic of the experimental setup and a detailed structure of the membrane permeation unit are shown in Figs. 2 and 3, respectively. The unit consists of the tubular membrane and a surrounding dense tube of the same material. The length of both tubes is 110 mm. They are clamped between two metal flanges using graphite seals. Thermal mass flow controllers served to feed the required gases. The axial temperature profile is monitored using thermocouples that are situated inside the unit, on the retentate and the permeate side. The gas flows leaving the unit were measured using a thermal mass flow meter or a digital bubble-flow meter. The pressure on both sides of the membrane was regulated by back pressure controllers. For the experiments with the gas mixture, the composition of the permeate and retentate was analysed using a gas chromatograph (Varian-CP 3800).

The measurements were conducted at temperatures between 350 and 650°C and transmembrane pressure differences up to 4 bar. The permeation side was kept at atmospheric pressure and no sweep gas was used during the experiments. The heating rate was set to 1°C/min to prevent cracking of the membrane. During the startup both sides of the membrane were kept under a nitrogen atmosphere to avoid hydrogen embrittlement at temperatures below the critical temperature of 300°C [21].

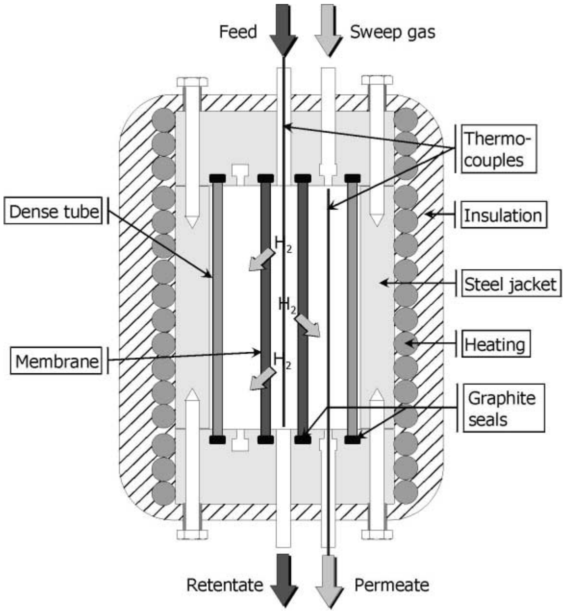

Fig. 3. Schematic of the membrane permeation unit.

3. Results and discussion

3.1. Membrane preparation

Fig. 4 compares the morphology of the Pd-surface of composite membranes prepared (a) by electroless plating and (b) by HVOF. As seen in Fig. 4a, the membrane possesses a good adherent film of palladium. The micrograph shows the typical morphology for this preparation method. The Pd-clusters are packed together resulting in a dense layer without any pinholes. The absence of pinholes was verified by nitrogen pressure hold tests at room temperature with polymeric seals prior to the permeation experiments. Pd-layers thicker than 3 μm are necessary to obtain defect-free membranes using the electroless plating technique.

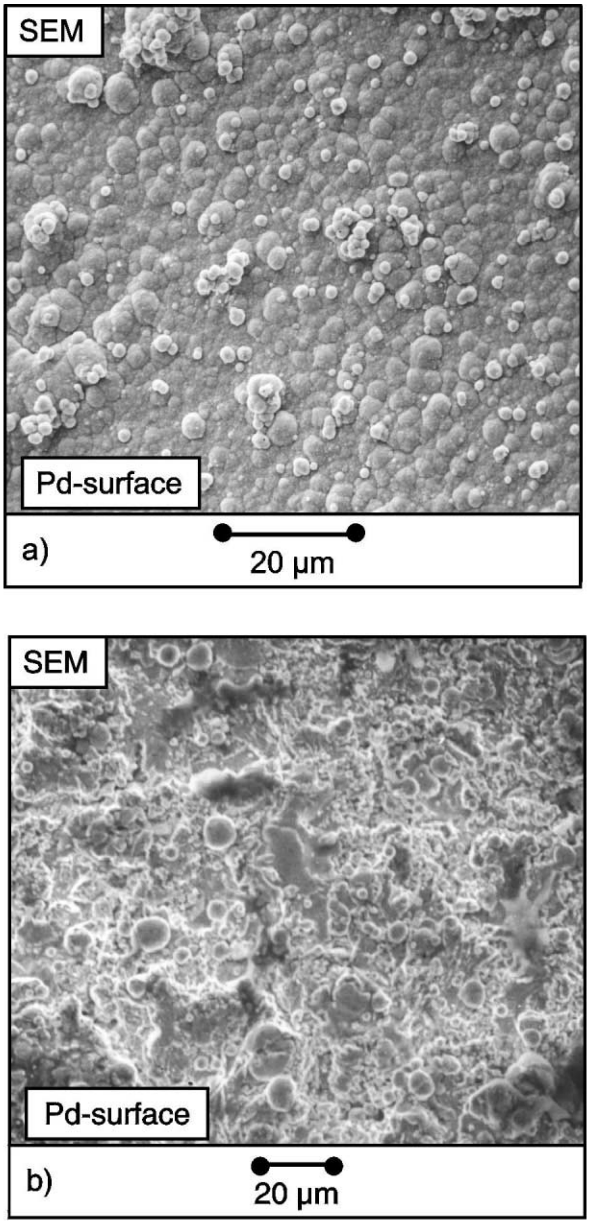

Fig. 4. SEM micrographs of palladium composite membranes: (a) Pd-surface of an electroless plated alumina membrane; (b) Pd-surface of a HVOF-plated stainless steel membrane.

In contrast to an electroless plated membrane, Pd-films deposited by HVOF are not compact. Due to the fast impact of the molten palladium powder on the cold substrate surface the particles deform and become "disc-shaped". The Pd-layers show a high residual porosity. To get a Pd-film without open pores on the support, a layer thickness ≥50 µm proved to be necessary.

3.2. Membrane permeation

The hydrogen permeation through a palladium composite membrane is a complex, multistep process [21]. It can be expressed by the following equation:

$$J = \frac{Q}{l}(p^{n}_{\mathrm{H_2,ret}} - p^{n}_{\mathrm{H_2,per}}) \tag{1}$$

where J is the hydrogen flux, Q the permeability coefficient, l the thickness of the Pd-layer, $p_{\mathrm{H_2,ret}}$ the hydrogen pressure on the retentate side, $p_{\mathrm{H_2,per}}$ the hydrogen pressure on the permeate side, and n is a constant power of the pressure. The quantity Q/l is called permeance or pressure normalized flux.

The value of n is often used as an indication of the rate-determining step of the hydrogen permeation through a metal composite membrane. Assuming that the diffusion of atomic hydrogen through the palladium is rate-limiting, the hydrogen flux should be directly proportional to the difference of the square root of the hydrogen partial pressure on either side of the membrane (Sieverts's law) [22].

The hydrogen transport through a metal composite membrane is an activated process. Under the assumption, that the value of n is independent of temperature, the relationship between hydrogen flux, permeance or permeability and temperature can be described by an Arrhenius law:

$$Q = Q_0 \exp\left(\frac{-E_{\mathrm{A}}}{RT}\right) \tag{2}$$

3.2.1. High velocity oxy-fuel flame spraying

The temperature dependency of the hydrogen flux through a palladium stainless steel membrane is plotted in Fig. 5 (single gas experiments). The thickness of the Pd-layer of this membrane was about 60 µm. Despite this thick layer the hydrogen flux is relatively high. For example, due to the characteristics of the Pd-film ("sponge structure"), the transport resistance in the Pd-film is supposed to be lower, in comparison with electroless plated membranes.

The nitrogen flux through the membrane at 100 kPa overpressure at room temperature was

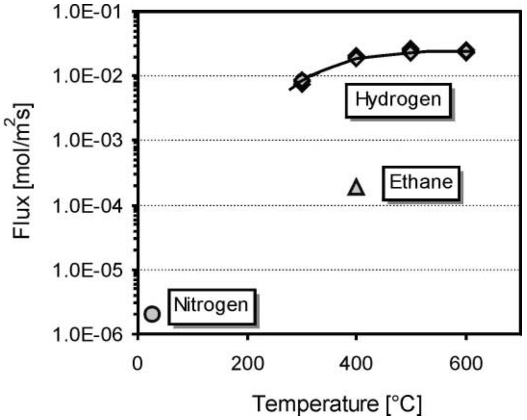

Fig. 5. Hydrogen flux through a HVOF-plated palladium stainless steel membrane as a function of temperature (graphite seals). Data from experiments with pure hydrogen flow in the retentate (316–631 ml/min) and nitrogen sweep in the permeate (600–1800 ml/min). Equal retentate and permeate pressure. Hydrogen partial pressure difference in the range of 120–280 kPa. Fluxes converted to a partial pressure difference of 100 kPa ($n_{H_2} = 0.5$). Comparison with the nitrogen flux during a pressure hold test at room temperature (polymeric seals). Pd-film thickness ≈60 μm.

2×10^{-6} mol/m^2 s. However, due to an inevitable leakage at the graphite seals the single gas H_2/N_2-separation factors detected in the membrane permeation unit are around 100–150 only as witnessed, e.g., by a permeation test with ethane at 400°C (cf. Fig. 5). The membranes were thermally and mechanically stable up to 600°C.

As shown in Fig. 5, no significant increase of the hydrogen permeation can be observed at temperatures above 500°C. Several explanations may be given for this behaviour. One possibility, though not proved experimentally here, is that intermetallic diffusion between the Pd-layer and the stainless steel support compensates the increase of the hydrogen permeance at high temperatures. Intermetallic diffusion can be expected at temperatures that are about half of the melting temperature of the metal (for stainless steel ≈550°C). It has been reported that the hydrogen flow through palladium composite membranes can be obstructed by intermetallic diffusion [23,24].

The pressure dependence of the hydrogen permeation rate was found to be almost proportional to $n = 0.5$ (cf. Eq. (1)), which indicates that the rate-determining step is the hydrogen diffusion through the palladium, according to Sieverts's law.

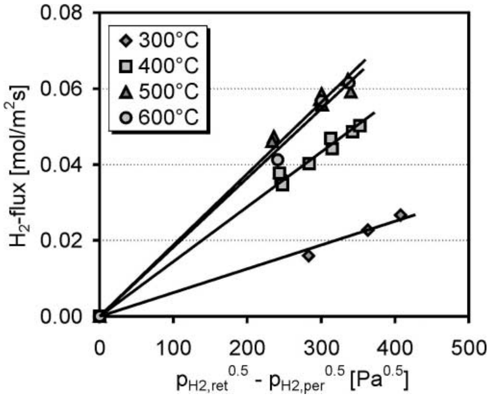

Fig. 6. Hydrogen flux through an HVOF-plated palladium stainless steel membrane as a function of the transmembrane pressure difference (Pd-film thickness ≈60 μm, see Fig. 5 for experimental conditions).

Fig. 6 shows a plot of the hydrogen flux versus the partial pressure difference of hydrogen for various temperatures and a hydrogen pressure exponent of $n = 0.5$. Agreement between experiment and theory seems reasonable as witnessed by the good approximation of the data points by the straight lines in Fig. 6. A separate estimation of n by regression of the different data sets obtained at constant temperature yielded values for n between 0.4 and 0.6.

3.2.2. Electroless plating

Before the high-temperature permeation experiments the palladium composite membranes were tested for nitrogen leakage at ambient temperature. At pressure differences up to 4 bar with gas-tight polymeric sealings the nitrogen flow through membranes with Pd-layers thicker than 3 μm normally was less than 0.01 cm^3/cm^2 min (i.e. 7.5×10^{-5} mol/m^2 s).

Fig. 7 shows the hydrogen and nitrogen fluxes through a palladium alumina membrane as a function of the temperature (thickness of the Pd-layer ≈4 μm; single gas experiments). The hydrogen flux increases with temperature. Initially the nitrogen flux is low. As already stated above the greatest part of this nitrogen flux can be attributed to leaks at the end seals. The measured single gas H_2/N_2-separation factors for the palladium composite membrane were usually in the range of 100 to several 1000. Nevertheless temperatures over 500°C lead to a significant decrease

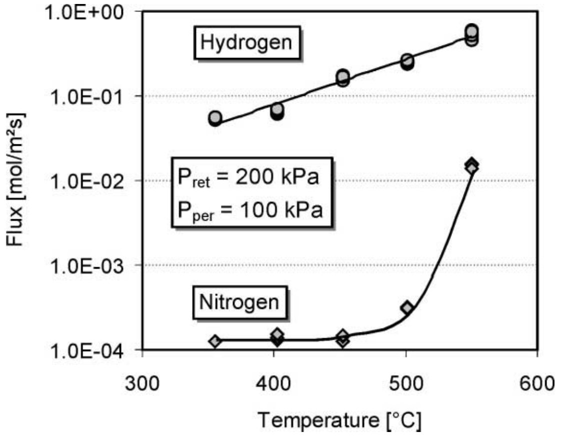

Fig. 7. Hydrogen and nitrogen fluxes through an electroless plated palladium alumina membrane as a function of temperature (Pd-film thickness ≈4 μm). Single gas permeation experiments. Retentate pressure: 125–350 kPa. Permeate pressure: 115 kPa. No sweep gas.

in the H_2/N_2-permselectivity. This behaviour can be observed with membranes having Pd-layers of about 7 μm or less.

Fig. 8 shows SEM micrographs of such a thin palladium alumina membrane after a permeation test. The high temperatures led to annealing and sintering of the metal layer. Pinholes can be seen in the surface of the Pd-film.

Similar results were reported previously by Collins and co-workers [25]. They suggest that a combination of the following processes could cause the formation of pinholes and lead to the deterioration in the H_2/N_2-separation:

- Stress induced by differences in the thermal expansion coefficients of the deposited palladium and the support.
- Intermetallic diffusion of Sn particularly along the grain boundaries.
- Contaminations and voids trapped in the Pd-layer during the sensitizing/activation and the electroless plating procedure which lead to pore formation at higher temperatures.

Fig. 9 shows the N_2-flux through a palladium alumina membrane (thickness of the Pd-layer ≈5 μm) as a function of time after switching the retentate feed flow from hydrogen to nitrogen and sweeping the retentate compartment for about 10 min with nitrogen.

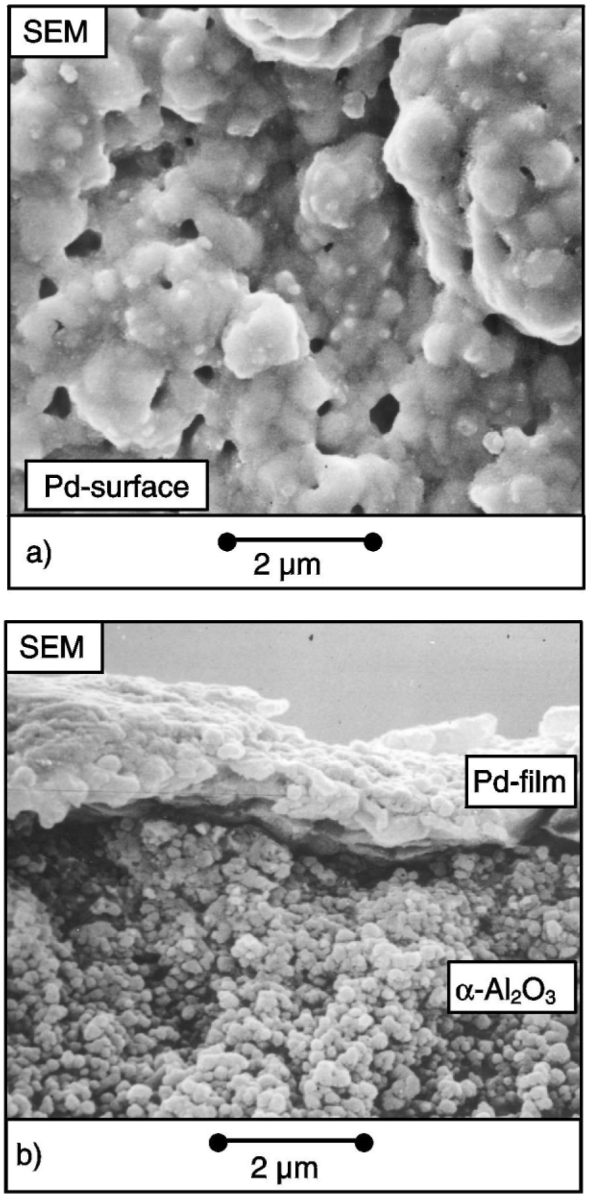

Fig. 8. SEM micrographs of an electroless plated palladium alumina membrane after a hydrogen permeation test at 500°C: (a) Pd-surface; (b) cross-section.

The initial N_2-flux is higher than that found in a nitrogen test performed before the hydrogen permeation measurements. However, it decreases with time. Roughly after 10 h the N_2-flux returns to approximately the same value as in the previous nitrogen

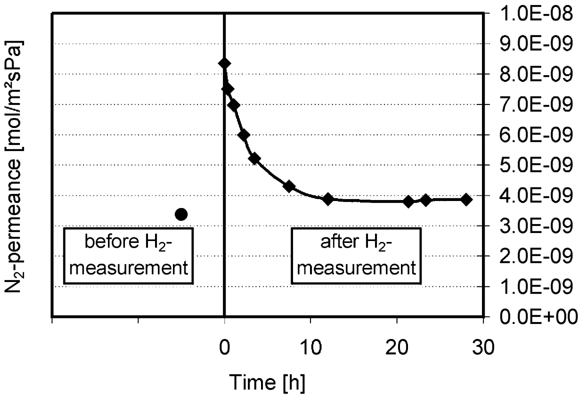

Fig. 9. Change of the nitrogen permeance through an electroless plated palladium alumina membrane before and after measurements with pure hydrogen. Time = 0 indicates first nitrogen measurement carried out 10 min after switching the retenate feed from pure hydrogen to pure nitrogen ($T = 450°C$, $\Delta p = 100\,kPa$, Pd-film thickness ≈5 μm).

permeation test. This indicates that an atmosphere of hydrogen at high temperature can lead to the formation of small channels in thin Pd-films which allow nitrogen to pass through the membrane. Moreover, with continued exposure to high temperature, but under nitrogen atmosphere, these leaks in the palladium layer seem to disappear again. The same effect can be seen in Fig. 10. This shows the hydrogen and nitrogen permeance through a palladium stainless steel membrane (thickness of the Pd-layer ≈5 μm) for different retentate feed gas compositions.

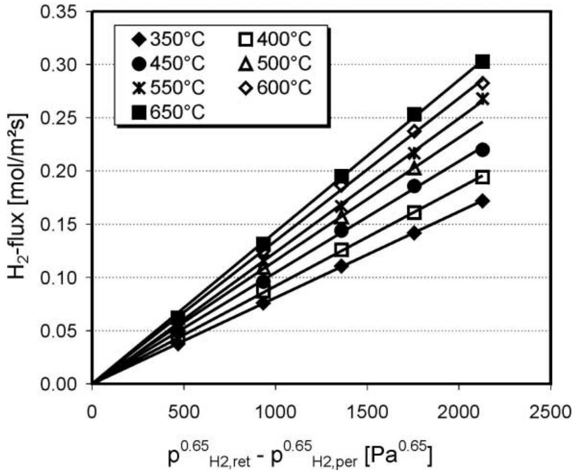

Fig. 11. Hydrogen flux through an electroless plated palladium alumina membrane as a function of the temperature and the transmembrane pressure difference (Pd-film thickness ≈15 μm). Single-gas hydrogen permeation (retentate pressure: 150–350 kPa; permeate pressure: 105 kPa; no sweep gas).

Measurements with pure H_2 and pure N_2 before and after use of a H_2/N_2-mixture were conducted. The N_2-permeation increases significantly when using a binary H_2/N_2-mixture instead of the pure gases.

On the other hand, Fig. 11 shows the H_2-flux through a palladium alumina membrane with a relatively thick Pd-layer (≈15 μm) as a function of the temperature and the pressure difference between retentate and permeate (single gas experiments). An

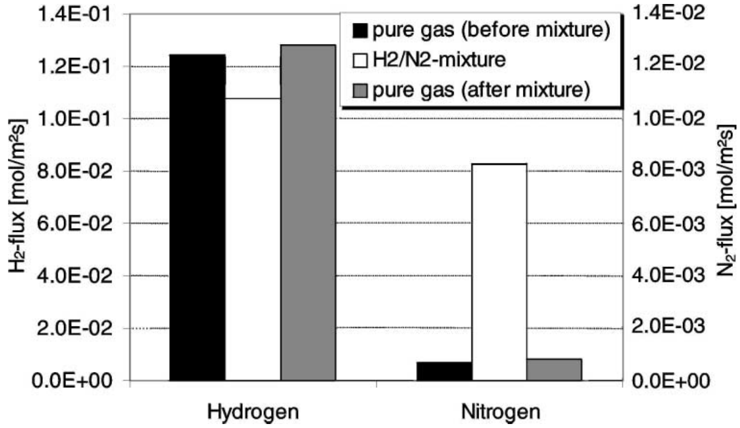

Fig. 10. Hydrogen and nitrogen fluxes through an electroless plated palladium stainless steel membrane. Difference between single-gas and mixture permeation experiments ($T = 400°C$, $\Delta p = 50\,kPa$, Pd-film thickness ≈5 μm).

increase of the temperature and the transmembrane pressure difference leads to an increase of the H_2-flux. Under the same conditions the nitrogen flux is much lower than that of hydrogen.

In contrast to membranes with Pd-layers <7 μm, membranes with thicker Pd-films show good thermal and mechanical stability. For example, the membrane of Fig. 11 was operated at temperature (350–650°C) and pressure cycles ($\Delta p = 0.5$–4 bar) for approximately 4 weeks with no significant changes in hydrogen permeability and H_2/N_2-permselectivity.

The pressure dependence of the hydrogen permeation for palladium composite membranes with a thickness of the Pd-layer >7 μm was found to be in the range 0.6–0.7 (cf. Eq. (1)). Thinner Pd-layers show slightly higher values for n. This indicates that effects other than the diffusion of atomic hydrogen through the palladium become important for the hydrogen transport through the membranes.

Many variations in the dependency of the hydrogen flux on the transmembrane pressure difference have been published so far [16,18,26,27]. Generally it can be said that with decreasing thickness of the Pd-layer the influence of surface reactions (adsorption/desorption) or surface diffusion of hydrogen becomes more important. Also the results from Figs. 9 and 10 make it clear that open channels in the Pd-film can contribute to the H_2-flux. These effects lead to a deviation from Sieverts's law.

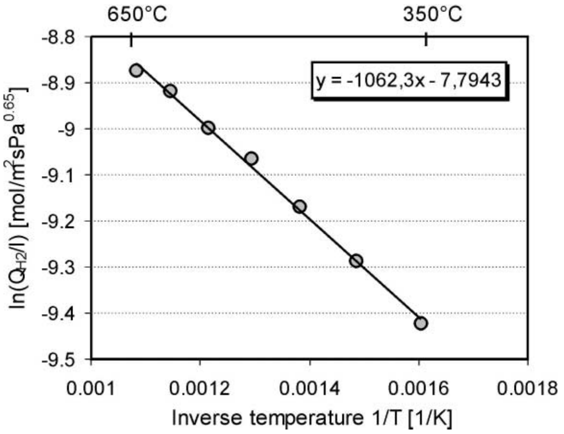

Fig. 12. Arrhenius plot of the hydrogen permeance Q/l (mol/m^2 s Pa$^{0.65}$) of an electroless plated palladium alumina membrane (Pd-film thickness ≈15 μm, see Fig. 11 for experimental conditions).

In Fig. 12, an Arrhenius plot for the hydrogen permeance through electroless plated palladium alumina membranes is shown. The apparent activation energy of hydrogen permeation calculated from the

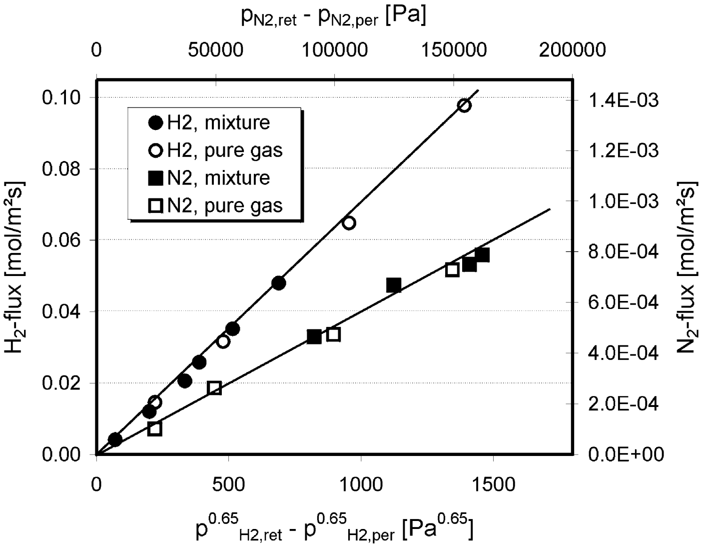

Fig. 13. Hydrogen and nitrogen flux through an electroless plated palladium alumina membrane for single-gas and mixture permeation experiments as a function of the partial pressure difference between retentate and permeate ($T = 400$°C, no sweep gas, Pd-film thickness ≈14 μm).

experimental results is about 10 kJ/mol (cf. Eq. (2)). This value is in good agreement with those obtained by other groups, e.g. Weyten et al. [3]: 11–12 kJ/mol, Li et al. [26]: 12.3 kJ/mol and Uemiya et al. [28]: 10.7 kJ/mol.

Fig. 13 shows the H_2- and N_2-fluxes through a palladium alumina membrane as a function of the partial pressure difference between retentate and permeate, feeding either hydrogen and nitrogen as pure gases or as a binary gas mixture. In this case, the thickness of the Pd-layer was about 14 μm. In contrast to membranes with thinner Pd-films (cf. Fig. 10) the H_2-permeation as well as the N_2-permeation and consequently also the H_2/N_2-permselectivity remain unchanged (within measurement accuracy) when using a binary H_2/N_2-mixture instead of the single gases.

4. Conclusions

Defect-free palladium composite membranes were prepared on porous stainless steel and alumina tubes by electroless plating with Pd-layers greater than 3 μm and on porous stainless steel tubes using HVOF spraying with Pd-layers greater than 50 μm.

The experiments have pointed out that both types of membranes show a good hydrogen permeability and selectivity combined with a sufficient mechanical and thermal stability. However, for electroless plated palladium composite membranes a thickness of the Pd-layer well above 7 μm is necessary to obtain a separation behaviour which is satisfactory for a later employment in dehydrogenation reactions. Those membranes show an apparent activation energy of about 10 kJ/mol with a value for the pressure exponent of the hydrogen permeation rate in the range between 0.6 and 0.7. Electroless plated membranes with Pd-layers thinner than 7 μm failed at temperatures over 500°C after several days of operation. In addition, their H_2-permselectivity declined when using a binary H_2/N_2-mixture instead of the pure gases.

Acknowledgements

The authors gratefully acknowledge financial support by the Bavarian Catalysis Research Network FORKAT II (Project C3.2). We thank Süd-Chemie AG for the excellent cooperation, GKN Sinter Metals Krebsöge Filters GmbH for the supply of membrane supports and ATZ EVUS for the HVOF-preparation work.

References

[1] N. Itoh, AIChE J. 33 (9) (1987) 1576.
[2] Y. Yildirim, E. Gobina, R. Hughes, J. Membr. Sci. 135 (1997) 107.
[3] H. Weyten, J. Luyten, K. Keizer, L. Willems, R. Leysen, Catal. Today 56 (2000) 3.
[4] J.P. Collins, R.W. Schwartz, R. Sehgal, T.L. Ward, C.J. Brinker, G.P. Hagen, C.A. Udovich, Ind. Eng. Chem. Res. 35 (1996) 4398.
[5] J.C.S. Wu, T.E. Gerdes, J.L. Pszczolkowski, R.R. Bhave, P.K.T. Liu, Sep. Sci. Technol. 25 (13–15) (1990) 1489.
[6] Z.D. Ziaka, R.G. Minet, T.T. Tsotsis, AIChE J. 39 (3) (1993) 526.
[7] M. Sheintuch, R.M. Dessau, Chem. Eng. Sci. 51 (1996) 535.
[8] J.K. Ali, A. Baiker, Appl. Catal. A 155 (1997) 41.
[9] P. Quicker, V. Höllein, R. Dittmeyer, Catal. Today 56 (2000) 21.
[10] T. Matsuda, I. Koike, N. Kubo, E. Kikuchi, Appl. Catal. A 96 (1993) 3.
[11] V. Jayaraman, Y.S. Lin, M. Pakala, R.Y. Lin, J. Membr. Sci. 99 (1995) 89.
[12] E. Gobina, R. Hughes, Appl. Catal. A 137 (1996) 119.
[13] S.-E. Nam, S.-H. Lee, K.-H. Lee, J. Membr. Sci. 153 (1999) 163.
[14] Z.Y. Li, H. Maeda, K. Kusakabe, S. Morooka, H. Anzai, S. Akiyama, J. Membr. Sci. 78 (1993) 247.
[15] G. Xomeritakis, Y.S. Lin, J. Membr. Sci. 120 (1996) 261.
[16] S. Yan, H. Maeda, K. Kusakabe, S. Morooka, Ind. Eng. Chem. Res. 33 (1994) 616.
[17] S. Uemiya, T. Matsuda, E. Kikuchi, J. Membr. Sci 56 (1991) 313.
[18] J.P. Collins, J.D. Way, Ind. Eng. Chem. Res. 32 (1993) 3006.
[19] Y.S. Cheng, K.L. Yeung, J. Membr. Sci. 158 (1999) 127.
[20] R.S. Souleimanova, A.S. Mukasyan, A. Varma, J. Membr. Sci. 166 (2000) 249.
[21] J. Shu, B.P.A. Grandjean, A. van Neste, S. Kaliaguine, Can. J. Chem. Eng. 69 (1991) 1036.
[22] G.L. Holleck, J. Phys. Chem. 74 (3) (1970) 503.
[23] P.P. Mardilovich, Y. She, Y.H. Ma, M.-H. Rei, AIChE J. 44 (2) (1998) 310.
[24] V.M. Gryaznov, O.S. Serebryannikova, M.Y. Serov, M.M. Ermilova, A.N. Karavanov, A.P. Mischenko, N.V. Orekhova, Appl. Catal. 96 (1993) 15.
[25] S.N. Paglieri, K.Y. Foo, J.D. Way, J.P. Collins, D.L. Harper-Nixon, Ind. Eng. Chem. Res. 38 (1999) 1925.
[26] A. Li, W. Liang, R. Hughes, Catal. Today 56 (2000) 45.
[27] V. Jayaraman, Y.S. Lin, J. Membr. Sci. 104 (1995) 251.
[28] S. Uemiya, N. Sato, H. Ando, Y. Kude, T. Matsuda, K. Kikuchi, J. Membr. Sci. 56 (1991) 303.