



Unravelling the transport mechanism of pore-filled membranes for hydrogen separation



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ABSTRACT

The permeation characteristics of palladium pore filled (PF) membranes have been investigated with gas permeation and structural characterization of the membranes. PF membranes have been prepared by filling with Pd the nanoporous γ -Al₂O₃/YSZ (or pure YSZ) layer supported onto porous α -Al₂O₃ and ZrO₂. The number of nanoporous layers and the applied vacuum level during the electroless plating process have been studied. Gas permeation properties of the PF membranes have been determined in a temperature range of 300–550 °C. The measured hydrogen permeances have been found to be lower than previously reported for similar membranes. It has been found that the hydrogen fluxes do not depend on the thickness of the nanoporous layers (γ -Al₂O₃/YSZ or pure YSZ) or on the vacuum pump employed for filling with Pd. The physicochemical characterization performed showed that the palladium deposited does not form a percolated network across the mesoporous layer(s), leading to low hydrogen permeances and thus low H₂/N₂ perm-selectivities.

1. Introduction

Several reports on the use of Pd-based membranes for hydrogen separation in fluidized bed membrane reactors have been published in the last few years [1–5]. When particles are in continuous contact with the (thin) hydrogen selective layer, depending on the gas velocity, particles can erode the membrane surface by creating pinholes, leading to a decrease in the membrane perm-selectivity.

The pore-filled (PF) type membranes avoid direct contact of fluidized particles with the hydrogen selective material, since the Pd is located inside the nano-pores of the substrate [6,7], protected by a mesoporous layer composed of γ -Al₂O₃/YSZ or pure YSZ. Another advantage of this membrane configuration is that the embrittlement due to α - β phase transition is prevented due to the nanometric size of the palladium clusters, where the hydrogen loading preferentially occurs on the surface rather than on the interior of the particles [8].

It has been reported that, when Pd is filled in the nanopores composed of only γ -Al₂O₃ the membranes are not stable at temperatures above 400 °C due to the large difference in the thermal expansion coefficient of Pd and alumina; in addition, the hydrogen permeance of conventional Pd alloy membranes supported on alumina showed a

decay when they were exposed to hydrogen at high temperature (650 °C) [9]. Inclusion of YSZ into the mesoporous layer diminishes the probability of alloying of Pd with alumina, while the thermal expansion is closer to that of palladium [10]. For these reasons, in a previous paper [7] the study was focused on the preparation of Pd PF membranes with a nanoporous layer made out of γ -Al₂O₃/YSZ with more than 50 wt% of YSZ. The permeation performance of this PF membrane was studied in the temperature range of 500–550 °C and the ideal H₂/N₂ perm-selectivity was around 50. The ideal perm-selectivity is defined as the ratio of the permeability of two gas species, $\alpha_{ab} = Pe_{(a)}/Pe_{(b)}$, measured separately under same conditions. This low value was attributed to the low hydrogen flux through the membrane. The aim of the present work is to extend the study on PF membranes and understand the reason for the very low permeation rates observed in the previous work.

In the present work, the permeation properties of pore-filled membranes have been studied by varying the porous support material, thickness and composition of the nanoporous layers and the vacuum level applied during VA-ELP (vacuum-assisted electroless plating), among other parameters. Physicochemical characterization has been performed on the nanoporous layers containing a different YSZ content

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and calcined at 550 °C or 650 °C.

2. Experimental

2.1. Membrane preparation

The γ - Al_2O_3 /YSZ layers were deposited onto porous α - Al_2O_3 (OD/ID 10/7 and 10/4 mm) with a pore size of 100 nm, provided by Rauschert Kloster Veilsdorf, according to the procedure reported in a previous work [7]. Calcination of the deposited layers was carried out at 550 °C or 650 °C, which allows studying the effect of the pore-size of the layer on the membrane performance. Then the support is activated with nano-palladium nuclei and another porous layer (the so-called protective layer) was deposited, as reported previously. Afterward, the nano-palladium particles in the first mesoporous layer were forced to grow by vacuum-assisted electroless plating using a rotatory (Edwards RV3) and a turbomolecular pump (Edwards T-Station 75), where the maximum vacuum measured was $2 \cdot 10^{-2}$ mbar and $1 \cdot 10^{-6}$ mbar, respectively. Finally, the membrane was annealed at 550 °C for 4 h under 10 vol.% H_2 /90 vol.% N_2 . The VA-ELP and annealing processes were repeated until the nitrogen leakage at room temperature of the membrane was below $8 \cdot 10^{-9}$ mol m^{-2} s^{-1} Pa^{-1} (this value is considered as the maximum acceptable value for preparing a good membrane).

The nanoporous layer was also deposited onto porous supports composed of asymmetric α - Al_2O_3 (OD/ID 10/7 mm) with an intermediate TiO_2 layer and a ZrO_2 top layer with 3 nm pore size (see Fig. 1). In this case, the top porous support layer was first activated with palladium nuclei and then a protective layer of YSZ was deposited, which is possible owing to the similar thermal expansion coefficient with the top layer of the support (ZrO_2). Then, Pd nano-seeds were forced to grow by VA-ELP as in the case of the α - Al_2O_3 support, followed by the annealing process. As described for α - Al_2O_3 supports, the cycle (VA-ELP and annealing process) was repeated until the nitrogen permeance was below $8 \cdot 10^{-9}$ mol m^{-2} s^{-1} Pa^{-1} .

Various vacuum levels were applied during the vacuum-assisted electroless plating (VA-ELP) step. A vacuum is applied at the inner side of the tubes in order to force the Pd^{2+} ions present in the plating

Table 1

Capabilities of the vacuum pump during VA-ELP of pore-filled membranes.

| Parameter | Rotatory pump | Turbomolecular pump |
|-------------------------------------|-------------------|---------------------|
| Measured pressure during ELP (mbar) | $2 \cdot 10^{-2}$ | $1 \cdot 10^{-6}$ |
| Number of VA-ELP | 4–15 | 2–6 |
| Plating time (min) | 4–12 | 8–60 |

solution to pass through the pores; therefore, the plating will be carried out inside the pores where Pd (catalyst for the reaction) is present. As the vacuum level increased, the number of cycles (VA-ELP and annealing) needed to fill the pores decreased (see Table 1), so that the plating time can be increased while still avoiding growth of palladium on the surface.

2.2. Gas permeation measurements

The membranes have been tested with pure gases (hydrogen and nitrogen) in an empty reactor in the temperature range of 300–550 °C and with a transmembrane pressure difference of 30–400 kPa. The setup used for single gas measurements was described in our previous work [7]. The pressure difference between retentate and permeated side (at atmospheric pressure) was regulated by a back-pressure regulator (Horiba Stec. UR-7340 model) at the retentate side. Permeated fluxes were measured with an automated soap film flow meter (Horiba STEC VP-1, VP-2 and VP-3).

2.3. Characterization

The pore size and surface area of the mesoporous materials calcined at different temperatures were obtained from the BET nitrogen adsorption isotherm obtained with a Thermo Scientific Surfer. The crystal structure of γ - Al_2O_3 /YSZ powders was obtained by powder X-ray diffraction (Rigaku MiniFlex 600) in the 2θ range of 20–90° with a step size of 0.02° 2θ , operating at 40 kV and 15 mA with Cu-K α radiation. The crystallite size was calculated using the Scherrer equation. The carbon content has been determined by the infrared absorption method after combustion in an induction furnace using a CS400 LECO analyzer, where the produced CO_2 volume was measured. The membrane thickness was measured using cross-sectional images with a SEM (FEI Quanta 250 FEG).

Preparation of a sample for the transmission electron microscope (TEM) was undertaken using a Thermo Scientific Helios 660 focused ion beam (FIB) dual-beam instrument. A cross-sectional sample was taken from the surface of a cut sample, using a 30 kV Ga ion beam to prepare an approximately 150 nm thick lamella.

Characterization of the Pd distribution was carried out with a Thermo Scientific Talos F200A scanning transmission electron microscope (STEM), possessing a high brightness X-FEG electron source and Super-X energy dispersive X-ray (EDX) silicon drift detectors (SDDs). The microscope was operated at an accelerating voltage of 200 kV with a beam current of 260 pA, a convergence angle of 12 mrad and a HAADF acceptance inner angle of 50 mrad. EDX spectrum images were acquired with the Thermo Scientific Velox software (version 1.6.0), with a total per pixel dwell time of approximately 2.5 ms and an image size of 387×439 pixels. A tilt series for HAADF-STEM tomography was acquired using Xplore3D acquisition software at angular increments of 1° from -75° to $+75^\circ$. Image alignment was performed using patch tracking in the IMOD software package, followed by the use of a simultaneous reconstruction technique (SIRT) to perform the reconstruction with 20 iterations. Segmentation of Au and Pd voxels was performed using an auto threshold in Avizo. Visualization of the 3D reconstructions was also performed in the Avizo software package.

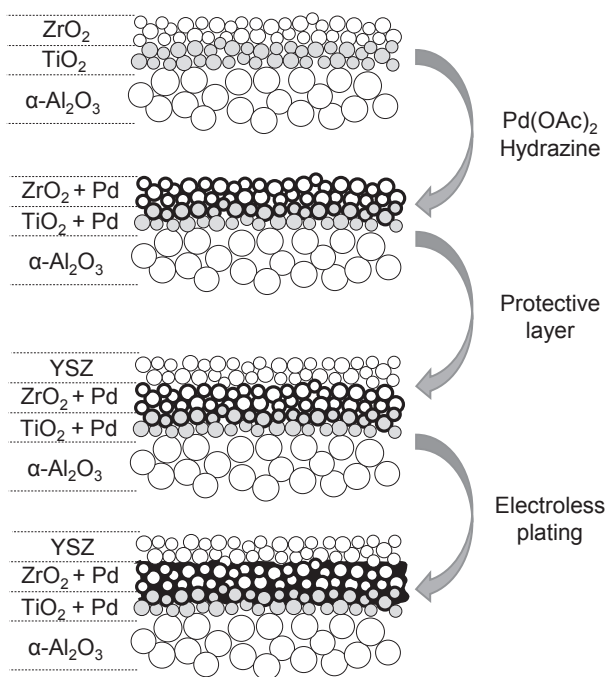


Fig. 1. Schematic representation of the preparation of Pd pore-filled membranes using porous α - Al_2O_3 support with an intermediate TiO_2 layer and a ZrO_2 top layer with a pore size of 3 nm.

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