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# Hydrogen selective palladium-alumina composite membranes prepared by Atomic Layer Deposition

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## **Abstract:**

We report a novel strategy enabling the fabrication of hydrogen selective palladium-alumina (Pd/Al<sub>2</sub>O<sub>3</sub>) composite membranes using Atomic layer Deposition (ALD). The ALD of palladium was based on the reaction of Pd(hfac)<sub>2</sub> and formalin at 220°C, and allowed for the preparation of embedded Pd nanoclusters confined within the pores of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane layer on a tubular ceramic support. Gas permeation and separation measurements of the prepared membranes were carried out and values above 1000 GPU were measured for the hydrogen flux. Promising permselectivities have been obtained at a moderate temperature of 188°C ( $\alpha^*_{\text{H}_2/\text{N}_2} \sim 23$  and  $\alpha^*_{\text{H}_2/\text{CO}_2} \sim 13$ ) together with attractive separation factors of  $F_{\text{H}_2/\text{N}_2} \sim 16$  and  $F_{\text{H}_2/\text{CO}_2} \sim 9$ . The presented results demonstrate the proof of concept for the fabrication of low-cost hydrogen selective Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes using ALD. Furthermore, this strategy could be extended to the design of other gas selective or catalytic membrane materials, composed of different metals and their alloys conformally deposited on tubular ceramic supports with high surface to volume ratio.

**Keywords:** palladium, composite, ceramic membranes, hydrogen separation, Atomic Layer Deposition

## **ToC**



## **Introduction:**

Hydrogen gas is crucial for upcoming transportation technologies and is key for many chemical processes. Moreover, hydrogen is considered as one of the best clean energy carriers which could contribute to tackle the major environmental issues our society is facing. Nowadays, the first world scale liquid hydrogen production unit dedicated to the hydrogen energy market is being built,[1] requiring cost-effective and efficient means to separate hydrogen gas from other species. The principal route to produce pure hydrogen is based on membrane separation/purification technologies. In this context, hydrogen selective membranes represent an attractive opportunity, and many membrane materials have been designed for selective hydrogen extraction, including pure inorganic or polymer membranes and their composites, hybrid membranes (silicon-based membranes, MOFs), metal alloys etc.[2] In the area of metal-based membranes, palladium represents a particularly attractive material thanks to its high selectivity towards hydrogen enabling the production of pure H<sub>2</sub>. [3] Indeed, the mechanism of hydrogen purification through dense palladium membranes is based on the selective transport of atomic H through the dense metal layer,[4] which blocks the transport of all other gas molecules. In addition, these membranes are highly resistant to oxidation[5] and exhibit good thermal stability (up to ~550°C[6]), allowing their applications at high operating temperatures.[7,8]

Considerable research work was carried out on Pd-based membranes with thick foils or bulk tubes,[3,9,10] although these designs are not well adapted for large scale applications. In fact, self-supported Pd membranes are costly, as palladium is nowadays even more expensive than gold and its resources are limited.[11] In addition, the competitive adsorption of even small amounts of CO, CO<sub>2</sub>, steam or sulfur compounds (e.g. H<sub>2</sub>S, SO<sub>x</sub>), strongly reduces the H<sub>2</sub> permeating flux.[12] As a result, many research efforts have been undertaken to fabricate more stable and economically viable Pd membranes. A relevant strategy to reduce the impact of poison species and which could also reduce the adsorption activation energy of H<sub>2</sub>, consists in coating Pd-based membrane surface with a protective film.[13,14] In order to prepare relatively cheap and highly permeable Pd-based membranes, thin dense Pd layers have to be deposited on top of porous supports. In addition to a reduced consumption of the precious metal, such supported membranes also permit to offer high hydrogen flux.[3] Porous alumina is an attractive support for the deposition of this type of membrane material, as alumina offers a good thermal stability enabling its utilization for hydrogen separation/purification up to 400-500°C.

Already in the 1990's, different research groups successfully used magnetron sputtering and chemical vapor deposition (CVD) to synthesize dense Pd-films on top of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

membrane substrates, aiming to prepare H<sub>2</sub>-selective membranes.[15–18] In 1994, Yan et al. were the first to show the feasibility of a dense (5 microns thick) Pd/Al<sub>2</sub>O<sub>3</sub> composite membrane prepared by deposition of Pd inside the macropores of an alumina support using low-pressure metallorganic CVD.[19] Employing Pd-acetylacetonate as a metallic precursor, Uemiya et al. reported the synthesis of a Pd membrane by deposition of Pd inside the pores of α-Al<sub>2</sub>O<sub>3</sub> using atmospheric pressure CVD.[16] Xomeritakis et al. reported the deposition of Pd inside the pores of mesoporous alumina supports using a CVD process with both PdCl<sub>2</sub> and H<sub>2</sub>. Despite being confirmed as an attractive approach for the preparation of supported dense (composite) membranes on/in inorganic supports, neither CVD nor sputtering could achieve the high conformality required to coat uniformly the pores within alumina substrates. Finally, CVD limits its applications only to small disk membrane supports.[17,18,20] Indeed, for industrial applications with tubular membrane designs, a Pd deposition technique offering both a good uniformity and excellent conformality of the films is required. In the last decade, electroless plating (ELP) has been considered as a promising technique for this purpose, since it provides higher uniformity of the films when compared to their CVD and PVD counterparts. Using this method, thin dense Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes with fine and uniform microstructures[7,21,22] were prepared by different research groups for H<sub>2</sub> separation applications. Composite membranes containing Pd particles prepared by ELP were developed by Tanaka et al.[23] However, these membranes are generally quite thick (several microns) and the synthesis procedure requires at least two steps (support seeding, ELP...). Hence, a simple and direct deposition technique enabling the preparation of thin, uniform and conformal Pd nanomaterials on commercial porous substrates with complex geometry is desired.

In this respect, Atomic Layer Deposition (ALD) is a very attractive technique. It is a CVD derived route allowing the direct preparation of thin films of a large range of materials on high aspect ratio substrates with precise thickness control at the nanometer scale, high uniformity and excellent conformality.[24–26] The technique is based on sequential pulses of precursors and co-reactants in the gas phase, leading to self-limiting chemical reactions at the substrate surface.[25,27] The nanomaterials typically synthesized by ALD are metal oxides,[27] although metals[28–31], nitrides[32–34] and other more complex materials could be prepared as well. Because ALD enables subnanometer control of the film thickness, this technique became a key technology for the deposition of thin films in numerous applications, ranging from microelectronics[35] to photovoltaics,[36] and from biosensing[37] to membranes.[38,39] Due to the excellent conformality of the ALD films, this route is particularly suited for both pore tailoring and modification of membrane support microstructure.[38–42] Despite the great potential of this synthesis route, there are very few studies reporting ALD of metals for gas selective membrane preparation.[43,44] To the

best of our knowledge, ALD has not been applied yet for the synthesis of Pd-based hydrogen selective composite membrane materials on/in tubular ceramic supports.

ALD of metals is challenging but has been already achieved in the past. According to literature reports, the best results have been obtained when using palladium hexafluoroacetylacetonate ( $\text{Pd}(\text{hfac})_2$ ) as the metallic precursor, which is also the most classically adopted precursor for Pd ALD.[31,45–48] Starting from this metalorganic precursor, our research group recently synthesized a large variety of Pd-based nanomaterials for both catalysis and sensing applications.[49–51] The applied ALD protocol was based on both  $\text{Pd}(\text{hfac})_2$  and formalin as a co-reactant, as recommended by Elam's group.[45]

In the present work, we report for the first time a proof of concept for the preparation of hydrogen selective membranes by ALD of Pd within the pores of a  $\gamma\text{-Al}_2\text{O}_3$  top-layer covering the inner side of a tubular ceramic support. The ability of ALD to coat high aspect ratio substrates with high uniformity and excellent conformality has been advantageously applied to embed the Pd material within the pores of tubular supports having higher S/V ratio compared to classical disc supports. The physical and chemical properties of the prepared Pd/ $\text{Al}_2\text{O}_3$  composite membranes were determined together with their gas transport properties and separation performance for hydrogen purification.

## **EXPERIMENTAL SECTION**

### **1. Membrane support**

The tubular membrane supports used for Pd deposition were purchased from Pall-Exekia, France. The supports present an asymmetric structure composed of a mesoporous  $\gamma\text{-Al}_2\text{O}_3$  inner top-layer with mean pore sizes in the range 5-8 nm, deposited on a macroporous support (1.5 mm thick) consisting of 3 layers with mean pore sizes of  $\sim 0.2 \mu\text{m}$ ,  $0.8 \mu\text{m}$  and  $10 \mu\text{m}$  from the inner to the outer side of the tubes. The support dimensions were as follows: OD/ID=10/7 mm with a total length of 50 mm. In order to avoid any gas leakage during permeation tests, both tube extremities (1 cm length) were sealed with a commercial enamel at a temperature of  $\sim 900^\circ\text{C}$ .

### **2. ALD of Palladium**

The ALD of palladium process allowing for the synthesis of the selective composite membrane was achieved by using a low-pressure (home-built) hot-wall ALD reactor. The precursors  $\text{Pd}(\text{hfac})_2$  (Sigma-Aldrich, CAS 64916-48-9) and formalin (Sigma-Aldrich, 37 wt. % in  $\text{H}_2\text{O}$ , containing 10-15% methanol as stabilizer, CAS Number 50-00-0) were used as received without any further purification. The

bubbler containing the Pd(hfac)<sub>2</sub> precursor was heated at 70 °C to provide sufficient vapor pressure, and the formalin container was kept at room temperature. The deposition chamber was set at the temperature of 220 °C, and the feed lines were heated at 100 °C to avoid any condensation. A typical ALD cycle consisted of 5 s pulse of Pd(hfac)<sub>2</sub>, 15 s exposure, and 10 s purge, followed by a 1 s pulse of formalin, 15 s exposure and 60 s purge with Ar. Further details about both this deposition protocol and the associated ALD reactor can be found elsewhere.[49,52]

### 3. Physico-chemical characterization and permeation measurements

The morphology, thickness and homogeneity of the composite membrane materials were studied at different locations on/in the supports using a scanning electron microscope (SEM, Zeiss Evo hd15) with LaB6 source at 1.5 keV. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB 250 spectrometer (Thermo Electron, monochromatic radiation source Al K $\alpha$  = 1486.6 eV). The high-resolution spectra were recorded at a step of 0.1 eV (transition energy: 20 eV). The binding energy (BE) measurement was corrected on the basis of the energy of C1s at 284.4 eV, and the quantification was carried out from the corresponding XPS peak area after correction with a suitable sensitivity factor. X-ray diffraction (XRD) patterns were recorded using a PANalytical Xpert-PRO diffractometer equipped with a X'celerator detector using Ni-filtered Cu-radiation. Energy dispersive X-ray spectroscopy (EDX) (Silicon Drift Detector (SDD), X-MaxN, Oxford Instrument) coupled to Zeiss EVO HD15 SEM analyzer was used to determine the location and degree of Pd infiltration into the mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> inner top-layer.

### 4. Gas permeation and separation experiments

The permeance and selectivity of the prepared membranes have been measured both for different single gas series (He, H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub>) and a selected gas mixture containing H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>. The H<sub>2</sub> (99.9992%) and CO<sub>2</sub> (99.995%) gases were provided by Air Products while N<sub>2</sub>, He and CH<sub>4</sub> with purities 99.995%, 99.999% and 99.995%, respectively were provided by LINDE.

Membranes were equipped with silicon o-rings (Sephatec), placed in a stainless steel module and outgassed under vacuum.

Single gas flow through the membrane was evaluated by a bubble flowmeter connected to the atmosphere enabling a rapid screening of the membrane permeance values. Additional 30 minutes outgassing treatment in vacuum was operated after each change of gas. Ideal selectivities were calculated as the ratio of single gas permeances. Single gas permeance values were measured in the temperature range 35 °C – 188 °C, at transmembrane pressures in the range  $\Delta P$  = 1-3 bar. The stabilization time before each gas flow measurement was typically fixed at 30 min and the gas

permeation was always carried out from the highest to the lowest transmembrane pressure. For all the measured single gas permeance values, the estimated error was ~12%.

Gas separation experiments were performed with a gas mixture containing 80.8% N<sub>2</sub>, 15.4% H<sub>2</sub> and 3.8% CO<sub>2</sub>, at  $\Delta P = 3$  bar and temperatures of 103 and 188°C. Helium was used as a sweep gas and the gas concentration in the permeate was measured using TCD-GC (PerkinElmer-Clarus 400) equipped with one column (Shincarbon ST,100/120 mesh,2m ,1 mm ID micropacked). Gas mixture compositions were analyzed by continuous dosing of the permeate diluted with He (sweep gas) and transported to the sampling loop of the gas chromatograph. The transmembrane flux was measured with an electronic flow-meter (PE 1000 Perkin Elmer). Before each measurement, the membranes were outgassed under vacuum.

## **RESULTS AND DISCUSSION**

The strategy developed in this work aimed to the fabrication of hydrogen selective Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes with Pd-clusters confined within the pores of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> top-layer covering the inner side of a tubular ceramic support. This novel type of membrane material was prepared by Atomic layer Deposition (ALD) and the characteristics of the as-obtained membranes are described hereafter in relation with their morphology, structure, composition, single gas permeation properties and gas mixture separation performance.

### **1. Fabrication and physico-chemical characterization of the Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes**

A porous alumina tube presenting an asymmetric structure with a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> inner top-layer (pore size ~ 5-8 nm) has been used as a support for Pd deposition. It should be noted that the pore sizes (5-8 nm) of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer in the sample tubes are slightly larger than those (3-5 nm) in the original support, due to the thermal treatment at 920°C required for sealing the tubes extremities with enamel. The heating protocol leads to slight pore opening (resulting in more open porous structure) but does not alter the integrity of the alumina top-layer. The tubular alumina support has been considered as more attractive membrane geometry for industrial applications compared to the simple disc supports classically used for Pd composite membrane preparation by PVD or CVD methods. Indeed, tubular supports offer higher S/V ratio and enhanced mechanical robustness, facilitating their handling and ensuring membrane stability under demanding operation conditions (temperature and pressure).

The ALD of Pd has been carried out applying a process based on alternate pulses of Pd(hfac)<sub>2</sub> and formalin, separated by argon (Ar) purges (cf. Experimental section). Typically 2000 ALD cycles have been applied to obtain a sufficient amount of Pd forming a selective membrane, and being confined within the pores of the mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. Figure 1 compares a bare and Pd-coated alumina membrane support by ALD.

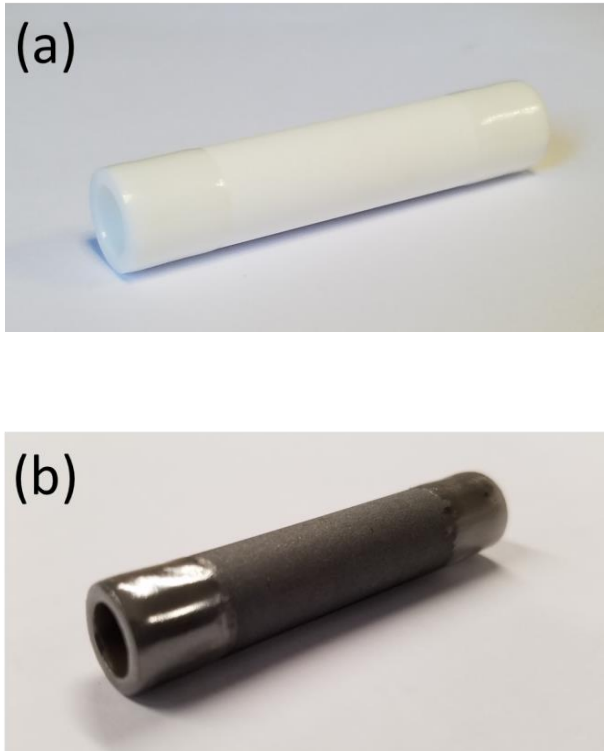
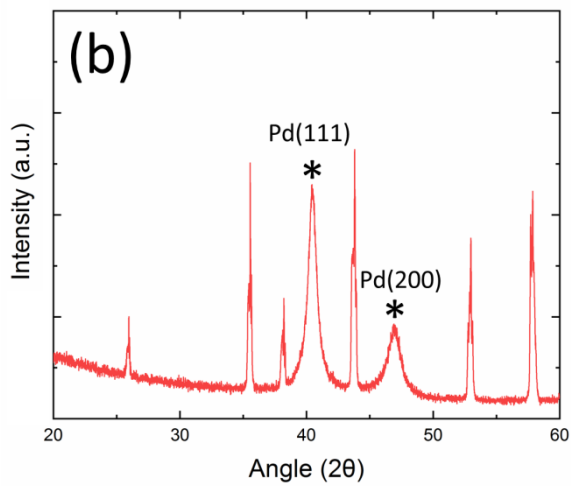
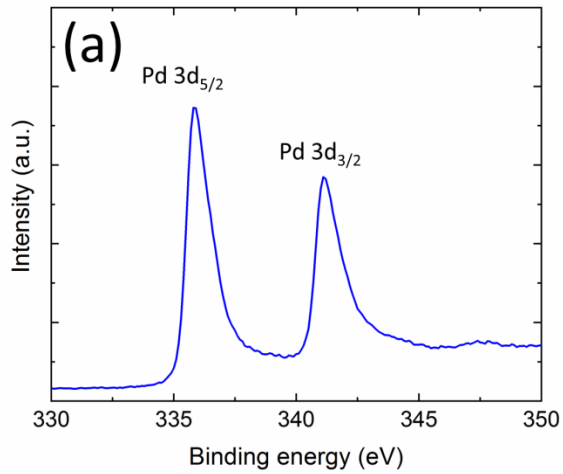


Figure 1: Images of (a) bare and (b) Pd-coated alumina membranes by ALD.

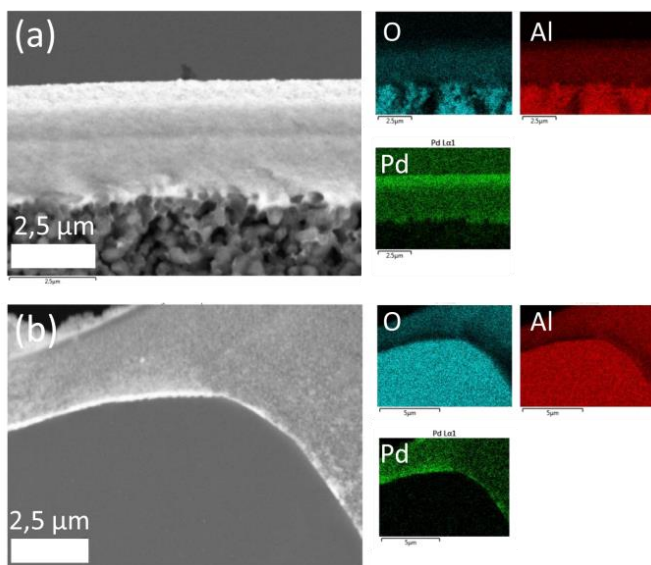
The metallic appearance of the Pd-coated membrane clearly reveals the successful deposition of Pd, which has been further assessed by XPS measurements confirming the presence of metallic palladium (Pd<sup>0</sup>) deposited on the alumina membrane support. The 3d region of the XPS spectra is shown in Figure 2a. X-ray diffraction analysis has been performed in order to gain understanding on the Pd crystallinity. The XRD pattern shown in Figure 2b revealed fcc crystal structure with the (111) and (200) peaks of the palladium, at respectively  $\sim 40^\circ$  and  $\sim 47^\circ$   $2\theta$ . The (111) peak is sharper than the (200) one, implying that the (111) oriented grains have a larger average grain size than the crystals with other orientations. The other diffraction peaks in the pattern correspond to the (crystalline) Al<sub>2</sub>O<sub>3</sub> support.





**Figure 2:** (a) High-resolution XPS spectrum of the Pd 3d region, depicting the Pd 3d<sub>3/2</sub> and Pd 3d<sub>5/2</sub> peaks, and (b) XRD pattern of the Pd-coated alumina membrane (the characteristic Pd peaks are annotated\*).

Obviously, due to the conformality of ALD coatings, Pd metal was deposited not only at the surface but also within the porous volume of the asymmetric support structure. In order to gain further information on the deposit morphology and degree of Pd infiltration, both SEM observations and EDX measurements have been performed on the obtained Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes.



**Figure 2:** SEM images and corresponding EDX mapping of a) inner part of the tubular membrane support depicting Pd infiltrated in both  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> top-layer ( $\varnothing_{\text{pore}} = 5\text{-}8\text{ nm}$ ) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ( $\varnothing_{\text{pore}} = 200\text{ nm}$ ) intermediate layer, b) outer part of the tubular membrane support ( $\varnothing_{\text{pore}} = 10\text{ }\mu\text{m}$ ) also coated with Pd.

Both FESEM observations and EDX analysis (Figure 2a) evidenced a uniform composite membrane design, with fully confined metallic Pd in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous layer. As observed on both the FESEM image (retro-diffusion mode) and the corresponding Pd-mapping, the preferential location of Pd was in the upper part of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, reaching depth of  $\sim 700\text{ nm}$ . The notable conformality feature of ALD allows the coatings to be uniformly deposited in the whole porous support, however because gradual pore closing progressively hinders the diffusion of reactants (Pd(hfac)<sub>2</sub> and formalin), lower amount of confined Pd nanoclusters were found in deeper locations of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer (i.e.  $> 700\text{ nm}$  from the membrane surface). EDX analysis of the cross-section revealed that when taking into account the mass % of Pd, Al and O elements and the density of Pd and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (11.9 and 3.7 g/cm<sup>3</sup>, respectively), the total volume of Pd occupying the space in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer represents about  $\sim 40\%$  of the total layer volume (700 nm thick infiltrated area). This result nicely fits the theoretical porosity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous layer which is expected to be in the range 35-40 %. Hence, this observation supports the presumption of well infiltrated Pd clusters filling up the majority of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer porosity to a depth of 700 nm. Beneath this compact composite layer (beyond a depth of 700 nm), the volume of Pd represents only about 20% of the total membrane layer volume, suggesting that only half of the available  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pore volume is filled up with Pd clusters.

Figure 2b shows that Pd also penetrated the tubular support through the outer (macroporous) side, confirming the conformality of the ALD route. Advantageously, the ALD precursors can penetrate from the support side across its whole thickness and infiltrate the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane layer at its

interface with the macropores. This has been confirmed by EDX measurements revealing higher Pd concentrations at the interface between the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane layer and the 200 nm pore size intermediate support layer. This phenomenon could be useful for the synthesis of double-side membranes able to limit concentration–polarization phenomena.[53] In fact, the advantages of double-sided membranes have been already evidenced elsewhere,[54,55] suggesting that, under specific conditions, the flux through membranes can be significantly higher when the selective films are located on both sides of the porous support rather than on a single side. Consequently, for separations in which selectivity increases with membrane thickness, double-sided membranes could yield fluxes and selectivities that are higher than those of single supported films. Currently, we are studying the possibility of a controlled selective layer deposition to obtain double-side membranes of the same thickness in order to confirm the benefit of this kind of composite membranes. Such novel membrane design will be subject of future communications.

## 2. Performance of Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes for single gas permeation

With the optimized Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes, different permeation tests have been performed in order to assess their potential for hydrogen separation. Initially, the prepared membranes were tested in single gas permeation measurements to ensure their good quality in terms of absence of any macro-defects (viscous flow contribution) in the membrane structure. In order to select the best membranes, helium permeance has been first measured at room temperature on membrane series prepared with different numbers of ALD cycles. The increasing of ALD cycles led to gradual decrease of He permeance, although the He permeance after 500 – 1000 cycles of Pd ALD still remains in the range of the virgin support permeance ( $\sim 10^{-5}$  mol.s<sup>-1</sup>.m<sup>-2</sup>.Pa<sup>-1</sup> or  $\sim 10^5$  GPU). Such high permeance values reveal that the pores of mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are only partially filled with Pd-clusters and the permeating gas can easily flow through the remaining open pathways (non-selective pores). After applying 1500 ALD cycles, the He permeance was found to decrease significantly (more than 100x) reaching the values  $\sim 1 \times 10^{-7}$  mol.s<sup>-1</sup>.m<sup>-2</sup>.Pa<sup>-1</sup> ( $\Pi_{\text{He}} \sim 1000$  GPU) confirming more important (but still partial) closing of the membrane pores. Further increase of the number of ALD cycles ( $\sim 2000$  cycles) led to a decrease of permeance by more than 1000x ( $\Pi_{\text{He}} \sim 100$  GPU) with Pd-clusters fully confined within the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pores. Such composite membranes were considered having an optimum design as any further increase of the number of ALD deposition cycles was found to lead to a gradual growth of a pure Pd top-layer on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface. Such a Pd top-layer was not desired for the targeted composite membrane design where Pd-clusters have to remain confined within the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesopores. The fact that the as-prepared composite membrane

was not completely gas-tight was attributed to the presence of remaining small pathways between the Pd-clusters and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pore walls. However the very low helium flux obtained after 2000 ALD cycles confirmed the formation of an extremely compact composite membrane layer inside the tubular ceramic support. Hence, for any further tests, single gas permeation measurements and gas mixture separation experiments have been carried out on the membranes prepared by applying 2000 ALD cycles of Pd.

It must be noted that virtually zero contribution of viscous flow was detected for all the measured gases, as the membrane permeances were never found to increase with the transmembrane pressure. This result confirms no damage of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> mesoporous layer during both the tube sealing treatment and the ALD deposition process.

Single gas permeation measurements with H<sub>2</sub>, He, N<sub>2</sub> and CO<sub>2</sub> (table 1) were used to evaluate the membranes reproducibility and their performance in terms of Pd-clusters contribution to the selective transport of hydrogen.

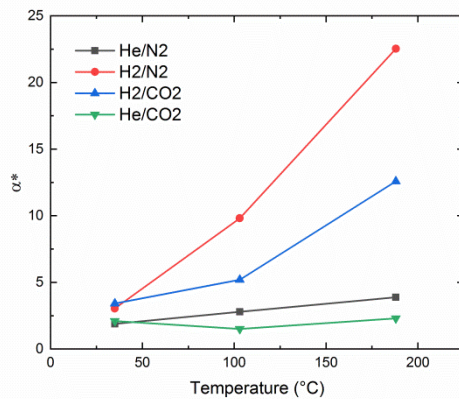
Table 1: Gas permeance and permselectivity values of Pd/Al<sub>2</sub>O<sub>3</sub> composite membrane, for different temperatures ( $\Delta P=1$  bar).

Temperature (°C)	Permeance (GPU)				Permselectivity $\alpha^*$			
	He	H <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	He/N <sub>2</sub>	He/CO <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>
<b>35</b>	84	136	45	40	1.9	2.1	3.0	3.4
<b>103</b>	129	453	46	87	2.8	1.5	10.0	5.2
<b>188</b>	171	991	44	79	3.9	2.3	23.0	12.5

It can be observed in table 1 that the H<sub>2</sub> permeation is strongly favored through the composite Pd-alumina membrane, in comparison with other gases. This effect is further enhanced when the temperature increases.

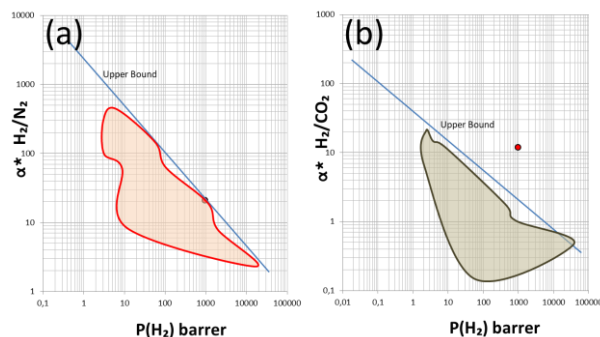
At 188°C, the order of gas permeances ( $\pi_i$ ) for He, N<sub>2</sub> and CO<sub>2</sub> clearly follows the order of their kinetic diameters:  $\pi_{\text{He}} (2.60 \text{ \AA}) > \pi_{\text{CO}_2} (3.30 \text{ \AA}) > \pi_{\text{N}_2} (3.64 \text{ \AA})$ . This effect is still observed at lower temperature although the permeance of N<sub>2</sub> is the only one which remains stable in the whole studied temperature range. This result should reveal that N<sub>2</sub> is able to diffuse through mesopores, although He (and CO<sub>2</sub>, with lesser extent) is able to access smaller pores (micropores) more and more easily when the temperature increases. This results in the activated transport of He beyond room temperature, thus leading to increasing permselectivity values  $\alpha^*_{\text{He/N}_2}$  (from = 1.9 at 35°C, up to 3.9 at 188°C). Interestingly, a strongly marked activated transport was evidenced for H<sub>2</sub>. Considering the kinetic diameter of H<sub>2</sub> (2.89 Å) which is larger than He (2.60 Å), the higher permeances of the former could only be explained by the active contribution of Pd species which have a strong affinity with H<sub>2</sub> and

might form PdH<sub>x</sub> species facilitating hydrogen transport. Hydrogen transport through the composite Pd/Al<sub>2</sub>O<sub>3</sub> membrane results from a complex contribution of transport through remaining meso/micropores coupled with the chemical diffusion of (atomic) hydrogen through the metallic Pd network. The evolution of membrane permselectivity for selected gas pairs (Figure 3) clearly evidences an exponential increase of the membrane selectivity values towards H<sub>2</sub> which are an order of magnitude higher than membrane selectivity values towards He.



**Figure 3.** Evolution with temperature of the Pd/Al<sub>2</sub>O<sub>3</sub> membrane permselectivity for selected gas pairs.

In order to estimate the potential interest of such Pd-alumina composite membranes, their performance has been reported on a Robeson plot.[56] A membrane thickness of ~1 μm (over-evaluated) has been considered for converting H<sub>2</sub> permeances to permeability values (under-evaluated) expressed in Barrers. As shown in Figure 4, the membrane performance is just on the upper bound for α\*<sub>H<sub>2</sub>/N<sub>2</sub></sub> permselectivity vs. H<sub>2</sub> permeability and well above upper bound for α\*<sub>H<sub>2</sub>/CO<sub>2</sub></sub> permselectivity vs. H<sub>2</sub> permeability. Promising performance could thus expected for such composite membrane materials for both.



**Figure 4:** Representation of the performance (red dot) at T=188°C, ΔP=3 bars of the Pd/Al<sub>2</sub>O<sub>3</sub> composite membrane (1 μm thick selective layer), on the Robeson plot and its upper bound[56]: (a) α\*<sub>H<sub>2</sub>/N<sub>2</sub></sub> permselectivity vs. H<sub>2</sub> permeability, (b) α\*<sub>H<sub>2</sub>/CO<sub>2</sub></sub> permselectivity vs. H<sub>2</sub> permeability.

### 3. Evaluation of membrane performance for gas mixture separation

Finally, the performance of the developed Pd/Al<sub>2</sub>O<sub>3</sub> membranes has been measured for the separation of the components in a gas mixture containing 80.8% N<sub>2</sub>, 15.4% H<sub>2</sub> and 3.8% CO<sub>2</sub>. Due to detection limitation, gas permeance and separation factors have only been measured for sufficiently high H<sub>2</sub> permeance values, i.e. above 100°C.

As shown in table 2, the permeance values with the gas mixture are similar to the values measured with single gases, yielding promising separation efficiency for both H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO<sub>2</sub> gas pairs. The typical separation factors are in the range 10-15 and the H<sub>2</sub> permeance is ~1000 GPU at 188°C. It must be recognized that such performance is below those typically reported in the literature for Pd membranes. However, it should be underlined that the present membranes exhibit promising separation performance in a temperature window lower than those typically reported in the literature (>300°C). In addition, the originality of this membrane bears also on its preparation method enabling the deposition of much lower quantity of expensive metallic Pd and thus decreasing significantly the membrane cost. Higher membrane stability could also be expected upon thermal cycling of these composite membranes in which the Pd material is confined within a ceramic matrix.

Numerous parameters still need to be investigated in order to fully evaluate the potential of this new concept for the preparation of nanocomposite membranes as an alternative to classical supported palladium gas selective barriers. For example, further improvement of the membrane performance in terms of higher permeance should derive from a judicious adjustment of the membrane architecture, e.g. decreasing the thickness of the mesoporous support layers and consequently the depth and location of the infiltrated Pd clusters. The latter parameters could be achieved by optimizing the ALD process parameters for ensuring effective pore plugging only at the pore entrance and thus improving the membrane performance in terms of gas permeance/selectivity ratio.

Table 2: Gas permeance and separation factors of Pd/Al<sub>2</sub>O<sub>3</sub> composite membrane for a gas mixture containing 80.8% N<sub>2</sub>, 15.4% H<sub>2</sub> and 3.8% CO<sub>2</sub> ( $\Delta P=3$  bar).

Temperature (°C)	Separation factor			Permeance GPU		
	H <sub>2</sub> /N <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>	N <sub>2</sub> /CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	CO <sub>2</sub>
103°C	6	5	1	37	251	38
188°C	16	9	1	41	1124	68

## CONCLUSIONS

In this work, we reported for the first time the synthesis of hydrogen selective Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes by ALD. The Pd ALD process was based on the reaction of Pd(hfac)<sub>2</sub> and formalin at 220°C. The as-prepared Pd clusters were confined within the pores of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane layer, thus demonstrating the successful use of this ALD nanomanufacturing route for the fabrication of Pd-based composite membrane materials in tubular ceramic supports. The gas permeation measurements showed promising permselectivities ( $\alpha^*$  H<sub>2</sub>/N<sub>2</sub>  $\sim$  23 and  $\alpha^*$  H<sub>2</sub>/CO<sub>2</sub>  $\sim$  13) together with attractive separation factors ( $F$  H<sub>2</sub>/N<sub>2</sub>  $\sim$  16 and  $F$  H<sub>2</sub>/CO<sub>2</sub>  $\sim$  9) and reached values above 1000 GPU for the H<sub>2</sub> flux at 188°C.

The presented proof of concept, reporting the fabrication of low-cost hydrogen selective Pd/Al<sub>2</sub>O<sub>3</sub> composite membranes using ALD is a considerable improvement over similar membrane materials reported in the literature in which gas-selective layers prepared typically by CVD or sputtering techniques were much thicker (in the micron range) and deposited on flat disk supports. This work showed that the conformality benefit of ALD can be applied to tune the gas selective properties of membrane materials, thus opening prospects for the separation of different gas mixtures. In fact, this strategy could be further extended to the design of other gas selective or catalytic membranes composed of various composite materials conformably deposited on/in ceramic supports with high surface to volume ratio.

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