

Development of metallic supported Pd-based membranes for H2 separation

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Development of metallic supported Pd-based membranes for H₂ separation

Design and application in membrane reactors

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus prof.dr. S.K. Lenaerts,

voor een commissie aangewezen door het College voor Promoties, in het openbaar te verdedigen op dinsdag 7 mei 2024 om 13:30 uur

door

Serena Agnolin

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De uitkomst zal het leren

Summary

Pd-based membranes are well known in literature for their unique solution diffusion H_2 transport mechanism, high H_2 selectivity, and high permeating flux, which make them perfect candidates for membrane separation in membrane reactors (MRs) for in-situ, selective H_2 removal. The introduction of membranes in the reaction environment promotes the continuous removal of H_2 , resulting in equilibrium shift towards the H_2 production owing to Le Chatelier's principle. In this way, the process operating temperature can be decreased, thus increasing overall energy efficiency and reducing operational costs. Similarly, the use of MRs promotes CAPEX reduction as downstream separations are not required.

Thin Pd layers have been successfully deposited and optimized onto ceramic supports with controlled surface characteristics (i.e. narrow pore size distribution, low surface roughness, no interaction with Pd). However, while they ensure adequate surface quality for thin layer deposition, ceramic supports prove to be fragile when introduced in the reaction environment. Particularly difficult is their connection and sealing to the steel parts of most reactors, making them prone to breakage and/or leaks and thus rendering the scale-up of Pd-based membrane modules a difficult task.

For these reasons, a variety of steel and steel alloy supports have gained interest as possible substitutes. These, in fact, do not require complicated sealing (substituted by a simple weld), are way less prone to breakage or crack formation thanks to their high mechanical stability, and can be easily introduced in the reactor via tube fitting. Steel-based supports, however, display large surface roughness, wide pore size distribution, and diffusive interaction with Pd films, making the preparation of metallic supported Pd-based membranes with high H₂ permeation and selectivity a challenging task. A few suppliers are able to deliver metallic supports with the desired surface characteristics for membrane preparation, achieved by tailor-made supplier treatments to reach suitable surface morphology. However, the complicated surface treatments make the final costs of the supports too high for economically interesting membrane applications.

In this Thesis, low-cost metallic filters are modified via suitable pre-treatments to achieve a sufficient surface quality for deposition of a selective Pd-based layer in a more economically convenient way. In Chapter 1, a general review on the state of the art concerning Pd-based membranes is reported, summarizing the main findings in relevant literature for their preparation and optimization on both ceramic based and metallic based supports, as well as their main applications in methane reforming and ammonia cracking membrane reactors. In Chapter 2, commercial unrefined porous Hastelloy X filters with large surface roughness, wide pore size, and high nominal media grade are acquired and characterized. A technique to improve the surface roughness is developed by combining a wet-polishing mechanism and the deposition via dip-coating of a boehmite-based interdiffusion barrier, optimizing each preparation step to reach the desired roughness target. Finally, a Pd-Ag layer is added onto the prepared supports via electroless plating technique, proving that the roughness reduction increases their suitability for Pd deposition. In Chapter 3, the H₂ selectivity of the newly developed membranes is increased to >10000 by adding two additional preparation steps, thoroughly characterized. In particular, a support filling step (with α -Al₂O₃ of decreasing particle size) is developed by ANOVA (ANalysis Of VAriance) assisted laser-optical microscopy,

introducing a statistical method for membrane preparation parameters evaluation. Additionally, Capillary Flow Porometry (CFP) is introduced as tailored characterization technique for tubular porous membranes. In Chapter 4, the best performing membranes obtained with the preparation procedure optimization studied in Chapter 2 and Chapter 3 are selected, thoroughly characterized, and tested for methane steam reforming and ammonia cracking applications. Relevant gas permeation phenomena through the membranes are elucidated via single gas and mixed gas tests, followed by reaction in a fixed-bed membrane reactor, whose main performance indicators are thoroughly discussed. In both cases the membranes showed the ability to promote the overcoming of the thermodynamic conversion of the conventional processes. In Chapter 5, an additional y-Al₂O₃ mesoporous layer is added to the metallic supported Pd membranes. firstly in order to improve their defects distribution (and thus H₂ selectivity) and finally to promote their functionalization in terms of catalytic activity via impregnation and seeding with Ru nanoparticles, a known NH₃ decomposition catalyst. Each preparation step is thoroughly characterized and the developed layer is employed as part of a catalytic membrane for ammonia cracking. The Thesis is completed by Chapter 6, in which the reproducibility of the membrane supports pre-treatments is analyzed with a hybrid observational-statistical approach, using ANOVA as rigorous statistical method on a large sample of Hastelloy X supports. Information are provided on the key outcome variables of the pre-treatments and their repercussion on the final membrane performance, setting suitable support reproducibility targets to be used for further optimization.

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Chapter 1 Pd-based membranes for H₂ production in membrane reactors

1.1 Sustainable process engineering

Global warming is a direct consequence of human activities related to releasing greenhouse gases into the atmosphere. It is widely accepted that in Earth's history, this marks the first era in which the activities of a species (Human, Anthropos) can directly impact the planet's climatic evolution. This impact is so profound that the current geological era itself has been named after us: Anthropocene [1]. In Anthropocene, global temperature is rising, and the Earth's climate is changing at an unprecedented rate.

One of the consequences of the rising Earth's temperatures is the melting of polar ice caps and glaciers, causing sea levels to rise. For instance, in a 2023 brief comunication published in Nature Climate Change, the accelerating retreat of Greenland's peripheral glaciers has been documented with historical and aerial satellite-photography imagery. Over the last two decades, South Greenland's glaciers lost 18.5% of their 20th century lengths. A retreat that was shown as unprecedented in over a century [2]. In the Nature Climate change article by Box et al. [3], Greenland has been recognized as the largest contributor to sea level rise, and its glaciers' ablation has already contributed to at least 274 mm of global sea level rise.

The global sea level rise directly threatens low-lying coastal areas, such as The Netherlands. So much that Utrecht University, under request of the Dutch Delta Commissioner as part of the Dutch Sea Level Rise programme, mapped the consequences of 2 to 5 m sea rise in Figure 1.1 [4]



Figure 1.1. Schematic representation of the geological consequences on The Netherlands promoted by a 2-5 m global sea level rise, mapped by Utrecht University's researchers.

This brief example shows how much interest there should be in reducing the impact that the Anthropos species is exerting on their own planet.

The primary driver of global warming is the increase in greenhouse gas emissions, such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), largely stemming from human activities. Particularily, the burning of fossil fuels for power and industrial processes contributes significantly to the rising levels of these gases in the atmosphere. The result is a thick atmospheric blanket of greenhouse gases that traps heat, leading to an overall warming of the Earth's surface.

Chemical industry is one of the main responsibles for both direct and indirect CO_2 emissions in industrial processes. Indirectly, fossil fuels are still the preponderant feedstock for the energy demands of chemical plants, and plants with the current energy efficiency result in significant CO_2 emissions from inefficient energy consumption. More than that, the production of plastics, fuels, fine chemicals, fertilizers can all involve CO_2 as byproduct, which is directly emitted in the atmosphere in large amounts, daily.

The increased awareness towards the causes of climate change in Anthropocene leads to the growth of research areas aimed at mitigating greenhouse gases emissions. Specifically, for chemical and process engineering, the alternative is posed by the growth of sustainable process engineering research. Sustainable process engineering is aimed at reducing emissions and increasing energy efficiency of the currently employed chemical processes worldwide.

The reduction of emissions can be achieved directly by finding new alternatives to fossil fuels burning, producing sustainable plastics from different feedstocks, researching alternative fuels/energy carriers (i.e. biofuel, hydrogen, electricity, etc.), or indirectly by increasing process energy efficiency and reducing its needs for excessive energy input, thus promoting less CO_2 emissions. This second, parallel route to a sustainable process industry can be paced through process intensification.

Membrane separation technology

A chemical plant is mainly an organized process whose ultimate goal is to produce a valuable product via one or more chemical reactions. However, most of the chemical reactions in nature do not lead to a sole, pure product, but rather a conglomerate of different ones, from which the one of interest must be separated. In a chemical plant, this is achieved via separation technology, usually right after the reactor zones.

The most widespread separation technique employed in chemical plants is distillation. Distillation is carried out in large columns, and its main principle revolves around the different boiling points of components leaving the reaction zone. As it requires heat, distillation is one of the most energy intensive parts of the chemical plant, significantly contributing to indirect CO_2 emission by intensive energy consumption. To tackle this part of the industry, alternative separation methods arise in the sustainable process engineering field. In a 2016 Nature article by Sholl & Lively, membrane-assisted separation is praised as a promising alternative to energy intensive conventional industrial processes [5].

Membrane separation technology relies on the basic definition of membrane: a permselective barrier which can separate one component or phase from another. As the separation of components is not heat-driven, the usage of a membrane significantly contributes to the reduction of the plant's energy consumption by virtually eliminating the distillation columns. To achieve this ideal scenario, extensive research on membrane design, engineering, optimization and manufacturing is carried out in the sustainable process engineering field. Besides the efforts in product purification applications such as nano-ultrafiltration and reverse osmosis, membrane separation technology finds an interesting application in membrane reactors (MRs) for membrane assisted chemical processes. Suitable membranes can infact be integrated in a reaction zone in order to directly separate a reaction product in-situ, without requiring extra equipment or energy. This strategy is particularly suitable for equilibrium reactions [6], reactions in series [7], or when a product requires selective dosage [8].

1.2 Membrane reactors for H₂ production

Hydrogen (H_2) has emerged as possible alternative energy carrier to mitigate direct CO_2 emissions from fossil fuels. Besides being a key component in many chemical processes, it holds the potential to power society as the main clean, carbon-free energy carrier.

MRs have proven themselves as a promising alternative to conventional H_2 production processes by integrating both reaction and separation in a single unit and thus avoiding the purification steps required by a conventional process [9][6][10]. The introduction of membranes in the reaction environment promotes the continuous removal of H_2 , resulting in an equilibrium shift towards the H_2 production reaction, owed to the Le Chatelier's principle. In this way, the process operating temperature is reduced, increasing overall energy efficiency and thus reducing operational costs [11][12][13].

These promising results have been employed in the Sustainable Process Engineering (SPE) group of Technical University of Eindhoven for two different H₂ production applications: Steam Methane Reforming (SMR) and Ammonia Decomposition (AD), funded by the two European projects MACBETH [14] and ARENHA [15], respectively. In both these applications, membranes which are able to selectively remove H₂ are submerged in the desired reaction catalyst, promoting direct H₂ separation.

Steam methane reforming

In the European project MACBETH, two prototypes for H₂ production via membraneassisted autothermal biogas reforming and membrane-assisted natural gas steam reforming are to be demonstrated at Technology Readiness Level 7 (TRL 7), to promote the utilization of the membrane reactor technology in the contemporary industrial scenario. Methane steam reforming is a fundamental chemical process widely employed to produce hydrogen and synthesis gas (syngas), which are essential feedstocks in various industrial applications, including ammonia production, petrochemical processes, and clean energy technologies such as fuel cells. The SMR process is endothermic, requiring high temperatures and substantial energy input, often achieved through the combustion of fossil fuels, which results in significant greenhouse gas emissions.

Hydrogen production via SMR is summarized by Eq. 1, and it involves two main contributions. Methane (CH₄) reacts with steam to form hydrogen (H₂) and carbon monoxide (CO) (Eq. 2), which is also converted into carbon dioxide (CO₂) and more

hydrogen with a water–gas-shift reaction (Eq. 3). Currently, SMR is a consolidated process performed in a reformer reactor at high temperatures (800-900 °C) and 14-20 bar of pressure, followed by two water-gas-shift reactors and hydrogen separation and purification steps (i.e., pressure-swing adsorption, cryogenic separation) [16][17].

CH₄ + 2H₂O ↔ CO₂ + 4H₂,
$$\Delta H^0 = 165 \text{ kJ mol}^{-1}$$
 (1)

$$CH_4 + H_2 O \leftrightarrow CO + 3H_2, \ \Delta H^0 = 206 \text{ kJ mol}^{-1}$$
 (2)

$$CO + H_2O \leftrightarrow CO_2 + H_2, \ \Delta H^0 = -41 \text{ kJ mol}^{-1}$$
(3)

To address the environmental and energy efficiency challenges associated with conventional SMR, membrane reactors have emerged as a promising approach. In the context of SMR, membrane reactors hold the potential to mitigate the environmental impact of hydrogen and syngas production while enabling efficient resource utilization [6][18][19]. Membrane reactors combine catalysis and selective permeation within a single unit, allowing for simultaneous reaction and hydrogen separation via a selective membrane. In this way, the shift reactors and pressure-swing adsoprtion or cryogenic distillation units are avoided, enhancing conversion rates, reducing energy consumption, and potentially achieving high-purity product streams. For these reasons, Membrane Assisted Steam Methane Reforming (MA-SMR) was widely investigated in literature (both in fixed-bed and fluidized-bed conditions) since the early 2000's [6][10]; [19]–[23].

For instance, in the work of Gallucci et al. [11] of 2004, a simulation study of the methane steam reforming reaction was carried out, showing the possibility to reach the same CH₄ conversion of a traditional process at lower operating temperatures thanks to the equilibrium shift promoted by the insertion of a membrane in the system. The membrane reactor configuration was further investigated in the study of Patil et al. [12], where a model for MA-SMR in fluidized-bed conditions was proposed and validated by experimental data, showing improved CH₄ conversion, decreased CO selectivity, improved power output and H_2 product yield with respect to a conventional SMR reactor. Further comparisons with conventional SMR processes were carried out by Bernardo et al. in 2010 [13], where the membrane reactor configuration was found to promote extremely compact and intensified production units, with a lower mass intensity associated to the membrane reactor reformers, especially when steam is fed as sweep gas. The promising conceptual results led to the interest of the European Union (EU) in funding the technology. In the work of Di Marcoberardino et al. (2017) [19] the SMR membrane reactor concept is extensively discussed, summarizing all the main results from EU-funded projects FERRET and BIONICO. In FERRET, the SMR was integrated in a micro-combined heat and power system, achieving a net electric efficiency 8% points higher than the conventional reactor case. In BIONICO, the hydrogen production from biogas through a membrane reactor configuration was investigated, proving that the adoption of the membrane reactor increased the system's efficiency by more than 20% with respect to benchmark cases, promoting lower H₂ prices ($4 \in Kq_{H2}^{-1}$ vs $4.2 \in Kq_{H2}^{-1}$) at the same hydrogen delivery pressure. Finally, a recent work by Ongis et al. [18] further investigates the economical feasibility of the MA-SMR technology for small-scale hydrogen production at TRL7, presenting the biogas as most convenient feedstock choice for realistic industrial application.

Ammonia decomposition

In the European project ARENHA, the promising route for the storage, transportation, and on-site production of sustainable hydrogen via decomposition of green ammonia (NH₃) [24]—[26] is investigated. This process, which involves the breakdown of ammonia into nitrogen (N₂) and hydrogen, has in fact several advantages compared to conventional systems for H₂ production. In particular, the process is not responsible for carbon emissions [27]–[30], and it allows to overcome the challenges related to hydrogen storage and distribution. The ease of liquefaction of ammonia compared to compressed hydrogen, its lower cost per unity of energy stored and the already existing infrastructure for its storage and transportation make this molecule a promising energy carrier and ammonia decomposition an attractive solution for decentralized hydrogen production [25][26][27]. Moreover, the fact that ammonia is a carbon-free molecule makes it attractive for the production of carbon-free hydrogen to be used in carbon-sensitive applications such as Polymer Electrolyte Membrane (PEM) fuel cells [27]–[36].

To produce H₂, NH₃ has to be decomposed into H₂ and N₂ (Eq. 4). Then, H₂ must be separated from N₂ and unconverted NH₃. While these two steps require dedicated units in a conventional system, they can be simultaneously performed in a single membrane reactor. Moreover, while in a conventional process ammonia conversion is favored at high temperature and low pressure, the usage of a membrane reactor was proven to reduce the reactor operating temperature and increase the operating pressure compared to the conventional process, with advantages in terms of energy efficiency and compactness of the system, respectively [32]; [37]–[40]. The selective separation of H₂ from the reaction products, therefore increasing the conversion of the feedstock.

NH₃ ↔
$$0.5N_2 + 1.5H_2$$
, $\Delta H^0 = 45.92 \text{ kJ mol}^{-1}$ (4)

 H_2 production via NH₃ decomposition has already been experimentally investigated in several works available in literature [32]; [37]–[52]. Particularily, in the recent works of Cechetto et al. [48][40] the best performance in terms of NH₃ conversion, H₂ recovery, and purity of H₂ have been obtained when using a Ru-based catalyst to promote the ammonia decomposition reaction, coupled with ultra-thin, double-skinned ceramic supported Pd-based membranes for the H₂ separation.

1.3 Pd-based membranes

For all the previously discussed membrane reactors applications, extensive membrane engineering and optimization efforts are required. Particularily, the study of suitable membrane materials is essential to bring the MRs closer to industrial applications. For H_2 production, the most widely investigated membranes are dense metal membranes. Specifically, Pd-based thin films have been subjected to extensive studies due to their peculiar solution diffusion H_2 transport mechanism.

In Figure 1.2, the main steps of H₂ transport through dense Pd films [53] are shown:

- i. H_2 gas migrates from the media bulk to the membrane surface.
- ii. H_2 molecules are adsorbed on the membrane surface.
- iii. H₂ molecules dissociate on the palladium surface.
- iv. Atomic hydrogen is chemisorbed and migrates through the Pd layer, driven by a pressure gradient.
- v. Atomic hydrogen desorbs and recombines in molecular form.



Figure 1.2. Illustration of the solution diffusion H₂ transport mechanism through Pd films.

The diffusion of H₂ through the metal layer is pressure-driven. Specifically, the conventional equation utilized to depict the hydrogen permeation flux (J_{H_2}) through a Pd-based membrane is referred as Richardson's equation:

$$J_{H_2} = \frac{k_{H_2}(P_{H_2,ret}^n - P_{H_2,perm}^n)}{\delta}$$
(5)

Which is a function of hydrogen permeability (k_{H2}), metal thickness (δ), and pressure driving force ($P_{rel}^n - P_{perm}^n$). In the scenario where the Pd-based membrane is completely dense, devoided of defects and/or external layers contributions, hydrogen permeation is governed by diffusion in the bulk metal, and the exponential factor takes on the value of n = 0.5, characterizing the equation as Sieverts' law:

$$J_{H_2} = \frac{k_{H_2}(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5})}{\delta}$$
(6)

In both cases, it is evident how the reduction of the Pd layer thickness would improve the permeation properties of the membrane, while reducing the cost implied by the usage of a large amount of Pd. However, the preparation of self-supported thin palladium layers poses two principal challenges:

- i. Limitations in mechanical resistance.
- ii. Difficulty in obtaining optimized, defect-free, thin films [54] [58].

To mitigate these issues, the utilization of porous supports is preferred to maintain adequate mechanical properties while saving palladium expenditure. Various commercially available support configurations and materials exist, however tubular supports are preferred due to their larger surface/volume ratio compared to disk-shaped substrates, and to their ease of integration through a reactor flange [59]—[63]. For the preparation of extremely thin and defect-free supported membranes, the selection of a suitable porous substrate is crucial. The characteristics of the support play infact a pivotal role in determining the required thickness of the selective layer to achieve a defect-free, thin Pd-based membrane [55].

Amongst other alternatives (cold rolling [56][57][58], physical vapour deposition [64][65][66], chemical vapour deposition [67][68], electrochemical plating [69][70][71]), the deposition of thin pd layers onto suitable supports can be achieved via ELectroless Plating (ELP) technique. The technique relies on the autocatalytic reduction of coordinated Pd to Pd metallic onto a suitable support in presence of a reducing agent, without the aid of any external current. The salt precursor of the coordinated Pd is dissolved and stabilized with a ligand (ammonium hydroxide, ethylenediaminetetraacetic acid), and the membrane support is introduced in the plating environment in presence of hydrazine, which initiates the reduction of Pd or additional alloying metal precursors, according to Eq. 7 below:

$$2Pd(NH_3)_4^{2+} + N_2H_4 + 40H^- \rightarrow 2Pd^0 + 8NH_3 + N_2 + 4H_2O$$
(7)

This procedure is widely employed due to its low cost, the absence of electrodes, and the possibility to prepare homogeneous metal films on complex geometries and non conductive substrate materials [72]–[77]. For these reasons, electroless deposition of Pd was preferred for the membrane development carried out in this Thesis.

Ceramic supported Pd-based membranes

Crucial characteristics of porous supports for depositing very thin, defect-free selective Pd-based layers via electroless plating include:

- i. Smooth surface.
- ii. Thermal and chemical stability.
- iii. Small superficial pore size.

In particular, the pore size determines the minimum material required to completely cover the support's pores and form a continuous surface. Mardilovich et al. [78] demonstrated

that the thickness needed to achieve a dense Pd layer is three times the diameter of the largest superficial pore of the support. However, the minimum thickness of palladium required for depositing a dense layer on top of porous supports with a distribution of pores of different sizes can be significantly larger [79].

Considering the aforementioned points, porous, tubular ceramic supports are appealing for Pd layers deposition due to their favorable surface properties (narrow pore size distribution, small superficial pores, low surface roughness) and chemical compatibility. However, their sealing and integration into a membrane reactor proves complex, while they exhibit mechanical weakness particularily to sollicitations, which can make the transport of membrane reactor units quite a challenging task.

Porous alumina (Al₂O₃) supports are widely employed for highly H₂ selective, ultra-thin Pd membranes preparation, as they are easily supplied with tunable superficial characteristics. Pacheco Tanaka et al. [60] prepared several membranes by vacuum assisted ELP onto porous α -Al₂O₃ supports with an average pore size of 100 nm. Similarily, Fernandez et al. [59] achieved ultra-thin Pd membranes onto the same α -Al₂O₃ supports provided by Rauschert. Arratibel et al. [80][48][81], successfully prepared thin Pd-Ag membranes via ELP deposition onto α -Al₂O₃ double skin layer and reaching outstanding H₂ selectivities. The stability of the α -Al₂O₃ supported thin Pd membranes was studied by De Nooijer et al. [82], highlighting the difficulty in rendering the membranes gas tight and in coupling them to the reactor for long term leakage-free operation.

Metallic supported Pd-based membranes

The need for ease of sealing and integration into the reactor system, as well as resistance to solicitations, leads to the study of suitable, more resistant metallic supports. For this purpose, a variety of steel and steel alloys supports have gained rising interest as possible substitutes to ceramic alternatives. They in fact do not require sealing (which can be substituted by a simple weld) and are way less prone to breakage or crack formation thanks to their high mechanical stability [54][83][84].

Unlike their ceramic relatives, metallic supported Pd films are proven to be inclined to atomic migration within the support structure, a phenomenon known as intermetallic diffusion or Pd-support interaction [85][86]. To solve the intermetallic diffusion issue, an additional barrier is required between the Pd layer and the metallic support [87]. Several interdiffusion barriers have been extensively investigated in literature, mostly ceramic-based (Al₂O₃[88][62][89], ZrO [90]—[93], CeO [94], SiO₂ [95][66], YSZ [96], TiO₂ [83], zeolites [97][98], or even pencil coatings [99]), or oxidation-based (controlled metal oxides growth [100]).

Contrary to their ceramic counterparts, metallic supports display large surface roughness, large superficial potholes, and wide pore size distribution, making the preparation of Pd-based membranes with high H₂ permeation and selectivity a complex task [101][72]. In order to acquire metallic supports with the desired characteristics, tailor-made supplier treatments and extremely low media grades must be requested, clearly increasing their final costs [63]. Commercially available Porous Stainless Steel (PSS) supports are made of stainless steel 316L or similar alloys with different Media

Grades (MG). It is important to remark that most suppliers of metallic supports do not provide an average pore size, but rather a nominal media grade, which corresponds to the particle size that is rejected in a 95% for a filtration carried out with the support. A lower media grade corresponds to a lower pore size. Typical media grades for commercial metallic supports are 0.1 μ m and 0.2 μ m, corresponding to an average pore size of 2–5 μ m and 10 μ m, respectively (measured by mercury intrusion). Larger media grades (~0.5 μ m), are not preferred due to their larger average pore size (10–20 μ m), which requires complex superficial pre-treatments and thicker Pd or interdiffusion barriers to reach complete surface coverage. Membrane-suitable stainless steel porous supports are commonly produced by Mott Metallurgical Corporation, which is able to supply:

- i. The smallest media grades available.
- ii. Suitably pre-treated supports to ease pore closure via Pd deposition [102][61][92].

However, commercial metallic filters with media grade >0.5 μm and unrefined surface characteristics prove more economically convenient (due to their untuned superficial characteristics) and less scarce on the market.

In Table 1.1 the surface characteristics of large media grade filters are compared with the ones of:

- i. Standard α -Al₂O₃ asymmetric support, commonly used for thin Pd-Ag membranes preparation.
- ii. More expensive metallic supports with most commonly used media grades for membrane preparation.

Rough, unrefined filters can be 4 to 5 times less expensive than pre-treated, low media grade metallic filters rendered suitable for membrane preparation. Their lower price makes these options more suitable for membrane industrial scale up. Unfortunately, these more economically viable alternatives lack both in the surface quality necessary for deposition of a continuous Pd-based layer, and in suitable pore size for rendering such layers highly selective.

In this Thesis, special effort is expended in studying suitable, cost-effective pretreatments to bring these unrefined, cheaper steel-based filters to the superficial quality that is necessary for defect-free Pd layers deposition.

Support material [-]	Supplier [-]	<i>Ra</i> [µm]	Average pore size [-]	N ₂ permeance [mol s ⁻¹ m ⁻² Pa ⁻¹]	Ref [-]	Price [Eur m ⁻²]
α -Al ₂ O ₃	Rauschert	0.58	100 nm avg. pore diameter; narrow PSD	8.0·10 ⁻⁵	[103]	[-]
Hastelloy X	Hebei Golden Flame Wire Mesh Co.	6.10	0.5 μm nominal media grade; 8 μm largest through pore; 1.8 μm mean flow pore	5.0·10 ⁻⁵	This work	18923*
Hastelloy X, treated	Mott Corp.	0.90	0.2 µm nominal media grade	3.5.10-5	[96]	44184*
Porous SS	Mott Corp.	3.20	0.1 µm nominal media grade	1.5.10-5	[88]	102805*
*prices from quotation requests for small amounts. Price may vary according to order volume.						

Table 1.1. Main superficial characteristics and prices of porous tubular membrane supports from different suppliers.

1.4 Thesis scope and outline

Porous stainless steel and steel alloys supports have gained interest as possible substitutes for ceramic supports for the fabrication of Pd-based membranes to be integrated in membrane reactors.

Such supports do not require complicated sealing (simple weld), are not prone to breakage or crack formation thanks to their high mechanical stability, and can be easily introduced in the reactor via tube fitting. However, as already mentioned, they display large surface roughness, wide pore size distribution, and diffusive interaction with Pd films, making the preparation of metallic supported Pd-based membranes a challenging task. A few suppliers are able to deliver metallic supports with the desired surface characteristics for membrane preparation, achieved by tailor made treatments to reach extremely low media grades. However, the complicated surface tratments to be operated make the final costs of the supports too high for economically interesting membrane applications.

In this Thesis, the focus is on modifying low-cost porous metallic filters via suitable and easily reproducible surface pre-treatments, to achieve a sufficient surface quality for deposition of highly selective Pd-based layers on more economically viable, large media grade (~0.5 μ m) porous metal filters. The lower costs of the raw supports, coupled with the lowest possible amount of thermal treatments required is expected to reduce the costs of metallic supported Pd-Ag membranes, ultimately easing the technology's scale-up. Following these choices, several support pre-treatment techniques are introduced and thoroughly elucidated via suitable characterization techniques. The developed membranes are then employed in H₂ production applications for a first performance assessment in the membrane reactor environment.

On the approach to membrane preparation

When observing experimental sections in the literature of composite Pd-based membranes preparation, trial-and-error or One Factor At a Time (OFAT) design of experiment methods are the most implemented [60][104][79][105]. Most works propose the full characterization of a specific membrane and its specific preparation procedure. These methods offer a rapid insight on which of the multitude of parameters in membrane preparation can be influential in final performance, with a non-time-consuming design. However, this strategy implies the analysis of a sole factor or a sole level combination at the time, moving along an experimental zone which is dictated solely by the experience of the experimenter. By varying one factor at the time, it is possible to miss interactions amongst them which can also influence the outcome variables. Moreover, detection of differences in average values and characterization techniques of various steps still require a certain degree of interpretation which is left to the experience of the experimenter.

One of the main objectives of Design of Experiments (DoE) is to verify a hypothesis efficiently and cohesively, allowing the utilization of a suitable statistical technique for the data analysis to follow [106]. The ANalysis Of VAriance (ANOVA) technique, provided the data fulfills the necessary assumptions, can be used to test null hypothesis of equality of several means of several independent groups of observations having same variances

[107]. It assesses potential differences in a continuous dependent variable by one or more independent variables (factors) having one, two or more levels. The mechanism to obtain the data such that the assumptions are met, and such that the data is readily available for the application of statistical tools can be achieved with DoE. Statistical methods are often employed in membrane performance assessments, where varying membrane reactor operating conditions such as temperature, pressure, feed flow, etc. results in an outcome on membrane separation performance [108][109][110]. However, the application of statistical methods to metallic supported dense metal membranes preparation is quite rare in literature, due to their effort-intensive, time-consuming preparation procedure. In this Thesis, the integration of Design of Experiment (DoE) and statistical analysis techniques is proposed in various steps of membrane support pre-treatment, in order to analyze the preparation procedure by backing up observation with mathematical, dataset-oriented considerations aimed at setting reproducibility targets.

Outline

In **Chapter 1**, the role of membrane separation technology in lowering CO_2 emissions from industrial energy consumption is elucidated in the context of sustainable process engineering research. Thereafter, membrane reactors are proposed as intensification technology for:

- i. H₂ production via steam methane reforming.
- ii. Ammonia decomposition for efficient H₂ storage and utilization.

Pd-based membranes are introduced as core of the membrane reactor technology, briefly elucidating their H_2 transport mechanism. Finally, the main differences between ceramic and metallic supports for Palladium thin films are summarized.

In **Chapter 2**, commercial unrefined porous Hastelloy X filters with large surface roughness, wide pore size distribution, and high nominal media grade are acquired and characterised. The issue of high superficial roughness of the filters is tackled by proposing:

- i. Surface smoothening with a wet-polishing mechanism.
- ii. Deposition via dip-coating of a γ -Al₂O₃ interdiffusion barrier.

Each strategy is thoroughly characterised, evaluating the effect of relevant parameters (i.e. polishing time, γ -Al₂O₃ layer thickness, dipping-sintering route, etc.) on the final surface roughness of the filter. Finally, a Pd-Ag layer is deposited onto the prepared supports via electroless plating technique, proving that the roughness reduction allows for the deposition of Pd layers onto the selected filters.

In **Chapter 3**, the H₂ selectivity of the newly developed membranes is increased via the study of two additional preparation steps, thoroughly characterised. Specifically, the gas permeation through the polished filters is increased by chemical etching, while the superficial pore size of the filters is reduced via support filling with α -Al₂O₃ particles of decreasing size (asymmetric filling). Firstly, the asymmetric filling step is developed by analyzing a suitably defined in-pore leveling parameter (Δ) obtained via laser-optical microscopy. The parameter is then coupled with profilometry surface roughness parameters (*Ra*, *Rz*) and futher analyzed via analysis of variance, in order to evaluate the effect of *Filler size* and *extent of filling* on the supports pores morphology. Thereafter,

Capillary Flow Porometry (CFP) as a method for evaluation of supports Pore Size Distribution (PSD) is introduced, and the effect of the filler particles on the pore size distribution of the filters is elucidated. Finally, a membrane with H_2/N_2 selectivity >10 000 is fabricated via electroless Pd-Ag deposition.

In **Chapter 4**, a membrane with H_2/N_2 selectivity >10000 (500 °C, 1 bar) is selected for testing in ammonia decomposition environment. Firstly, the membrane's preparation procedure is briefly characterised via Scanning Electron Microscopy (SEM) imaging and CFP. Then, its H_2 permeation properties are studied in H_2-N_2 feed mixtures. Finally, the membrane is studied in a fixed-bed ammonia decomposition reactor with a Ru-Al₂O₃ catalyst, evaluating the main membrane reactor performance indicators and comparing them with the literature. Furthermore, a second membrane with H_2/N_2 selectivity >10000 (500 °C, 1 bar) is reproduced, and its reproduction technique is characterized via CFP. Firstly, the H_2 permeation properties of the reproduced membrane are investigated in CO-H₂ feed mixtures. Thereafter, the membrane is tested for H_2 production via steam methane reforming in a Rh-Al₂O₃ fixed-bed membrane reactor, evaluating and discussing the main membrane reactor performance indicators.

In **Chapter 5**, an additional γ -Al₂O₃ mesoporous substrate is added onto metallic supported Pd membranes. The mesoporous substrate is developed in an effort to:

- i. Improve the selectivity of defective membranes.
- ii. Promote their functionalization as catalytic membranes for ammonia cracking via deposition of Ruthenium nanoparticles.

Firstly, the development of the mesoporous layer is thoroughly characterized by investigating its effect on the membranes defect distribution and H_2/N_2 selectivity. Thereafter, the layer is functionalized with Ru by deposition-precipitation. The functionalized membrane is then exposed to pure ammonia without any catalyst bed in order to verify its catalytic activity towards ammonia decomposition.

In **Chapter 6**, the statistical analysis carried out in Chapter 3 is extended to a population of supports for more precise inference. Firstly, the optimized support pre-treatments are characterized via 3D laser-optical microscopy and CFP for illustratory purposes. Thereafter, each pre-treatment is applied on a sample batch of supports, comparing the distributions of their superficial morphology parameters and the statistical differences between each of their pore populations. The analyses are repeated for each of the illustrated support pre-treatments, elucidating their main effects between and within the support samples. Suitable targets for defined surface morphology parameters to be employed for support reproducibility are drawn from the analysis.

Finally, the conclusions of this work and the derived research outlook are summarized in **Chapter 7**.

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Chapter 2 Surface roughness modification of Hastelloy X tubular filters¹

This Chapter reports a first attempt towards a standardized preparation procedure for Pd-based membranes on rough, 0.5 μ m Media Grade (MG) Hastelloy X tubular filters. The issue of their large surface roughness is addressed, in order to allow the deposition of a uniform, delamination-free Pd–Ag layer. The surface roughness of the acquired filters is reduced via wet-polishing and addition of a γ -Al₂O₃ smoothening interdiffusion barrier layer, based on a boehmite dip-coated sol-gel dispersion.

The effect of the polishing time was assessed by studying the average support's roughness variation, its gas permeation behavior, and its ceramic coating retention. It was found that the best tradeoff between polishing extent and gas permeance of the support amounts to 6 h of residence in the polishing machine. Moreover, it was assessed that increasing the boehmite loading in the interdiffusion barrier precursor solution leads to thicker layers and larger surface roughness reduction, at the expense of solution stability. An amount of 1.2 wt.% of boehmite loading proved to be the best tradeoff between layer reproducibility and support coverage. Different dipping-sintering routes were evaluated in order to improve surface's suitability for electroless plating: a single interdiffusion layer deposition-sintering route proved the most suitable for Pd–Ag deposition. The electroless plating performed onto the treated supports resulted in a continuous, delamination-free Pd–Ag layer, proving Pd–Ag deposition to be possible on the selected filters.

¹This chapter is based on the following paper:

S. Agnolin, J. Melendez, L. Di Felice & F. Gallucci (2022). "Surface roughness improvement of Hastelloy X tubular filters for H_2 selective supported Pd–Ag alloy membranes preparation". *International Journal of Hydrogen Energy*, Volume 47, Issue 66.

2.1 Introduction

As discussed in Chapter 1, the stability of Pd layers directly deposited onto metal supports is hindered by the migration of Pd in the metallic material underneath and vice-versa, a phenomenon known as intermetallic diffusion [1]-[4]. This issue can be solved by the deposition of a ceramic layer between Pd and the metallic support, namely an interdiffusion barrier. Several ceramic materials have been investigated as possible interdiffusion barrier layer candidates, such as ZrO_2 [5][6][7], YSZ [8], Al₂O₃ [9][10], TiO₂ [11][12], CeO₂ [13][14], zeolites [15][16], or siliceous materials [17].

Moreover, low media grade metallic filters exhibit:

- i. Large average surface roughness (*Ra*).
- ii. Large superficial pore size and wide pore size distribution (PSD).

This Chapter focuses on tackling the filters surface roughness improvement issue, in order to make deposition of a continuous Pd-Ag layer possible. Generally, all metallic support types present larger *Ra* and lower gas permeance compared to the ceramic supports [18][19][20][10]. Physico-chemical treatments operated by the supplier are able to reduce surface roughness and increase gas permeance, but increase support costs [19]. The need for cheaper and more readily available metallic support options leads to the use of 0.5 μ m nominal media grade filters proposed for this work. The larger pore diameter and wide pore size distribution promote gas permeation through widely distributed large pores, rather than the narrowly distributed nanometer-sized pores of the ceramic supports, making it more difficult for the Pd-Ag layer to fully close the superficial pore mouths. Moreover, even though the pores are large, gas permeation is still hindered due to the lower porosity of the material. The surface roughness of the selected filters amounts to 6.1 μ m. A large reduction in surface roughness is therefore crucial for promoting the deposition of thin Pd-Ag layers. For this reason, the wet polishing technique was selected as most suitable candidate for roughness reduction.

In this Chapter, the interdiffusion barrier layer is employed with a double function:

- i. To prevent intermetallic diffusion.
- ii. To further reduce the surface roughness of the starting metallic support.

Bottino et al. [21] deposited a boehmite layer on stainless steel supports, selecting the ones with most suitable surface characteristics and pore size via the bubble point method.

Similarily, in this work, the deposition via dip-coating of a γ -Al₂O₃ smoothening interdiffusion layer is presented, starting from a boehmite solution precursor. The layer is deposited on an unrefined Hastelloy X filter, a material which is able to withstand temperatures up to 750 °C, allowing for a wide range of possible ceramic sintering conditions and prolonged use at high temperatures. The filters are subjected to polishing treatment for variable times, in order to reduce their large average surface roughness and to investigate the effect of pre-treatments on both bare and coated supports. No preselection of suitable surface characteristics or pore size of such filters is carried out. Three different polishing times are evaluated for interdiffusion layer deposition, as well as three ceramic loading percentages for the smoothening interdiffusion layer precursor. Different dip-coating, drying and sintering routes are assessed, aiming for an improvement of support morphology to allow a successful later Pd-Ag deposition. The supports are

characterized in terms of surface roughness via profilometry, N₂ permeance, and surface morphology via Scanning Electron Microscopy (SEM) imaging of the coated layer. A Pd-Ag layer is deposited onto the most suitable support type via electroless plating. The resulting membrane is characterized in terms of ideal H_2/N_2 selectivity and H_2 permeance.

2.2 Experimental

Porous Hastelloy X supports

Commercial, untreated, porous Hastelloy X filters with an outer diameter of 1.2 cm, average surface roughness (*Ra*) of 6.1 μ m, and 0.5 μ m nominal media grade were acquired from Hebei Golden Flame Wire Mesh Co, China. The supports were cut in samples of 10 cm length and welded to dense stainless steel (AISI316L) tubes, in order to achieve a one close end configuration.

To preliminarily reduce the surface roughness of the filters, the sample supports were polished in an industrial surface finishing machine (ERBA EVT-170) for a time varying between 1 and 12 h, in presence of water. The industrial surface finishing machine delivers polished supports via a wet polishing method: the samples are submerged in the polishing media (conical abrasive ceramic chips) in presence of a continuous stream of water. The machine is then able to vibrate for the set amount of time, allowing the polishing media to continuously slide onto and around the samples. The supports were then oxidized for 1 h at 750 °C in a furnace in static air atmosphere, in order to prevent the initial formation of oxides from disrupting the following step of ceramic layer sintering [22]. Before further treatments, the supports were thoroughly rinsed in an ultrasonic bath with ethanol and deionized water, in order to remove all impurities resulting from polishing and handling.

Interdiffusion barrier deposition

To deposit the smoothening interdiffusion barrier onto the polished supports, three consecutive steps were carried out:

- i. Aqueous boehmite-additives dispersion preparation.
- ii. Deposition via dip-coating with controlled immersion speed.
- iii. Drying and sintering.

A commercial boehmite solution, namely Alumisol 10A (Boehmite conc. 10.1 wt.%) was provided by Kawaken Co., Japan. Three sample solutions with boehmite loading 0.9 wt.%, 1.2 wt.%, and 1.8 wt.% were prepared by diluting the Alumisol 10A in distilled water and incorporating it into a water-based solution of organic additives, namely 3.5 wt.% polyvinyl alcohol (PVA) (MW 130000) and 1 wt.% polyethylene glycol (PEG) (MW 400). The boehmite dispersion was deposited onto the sample supports via dip-coating with a purpose-built automated setup. The setup consists of a pneumatic slider accommodating a membrane holder. The slider can then be programmed remotely according to the parameters listed in Table 2.1. The selected dip-coating parameters were kept constant for each sample.

Immersion speed [mm s ⁻¹]	5
Withdrawal speed [mm s ⁻¹]	5
Waiting time above solution [s]	10
Waiting time in solution [s]	5
Number of dips [s]	2

Table 2.1. Selected dip-coating parameters for interdiffusion layer deposition.

The deposited layer was dried under rotation in a climate chamber at 40 $^\circ C$ and 60% relative humidity for 1 h. The layer was then sintered for 1 h at 550 $^\circ C$ in a static air furnace.

To compare the resulting layer properties, the dip-coating and sintering route for the test supports varied according to Table 2.1. Specifically, the number of immersions is the number of times the support is submerged into the boehmite dispersion to form one layer, while the number of layers is the amount of dry layers deposited onto each other via drying-dipping-sintering route (DDS), or via sintering-dipping-sintering route (SDS).

Table 2.2. Sintering-dipping routes used for interdiffusion layer comparison.

Support type [-]	Polishing time [h]	Immersions [-]	Layers [-]
Uncoated	6	0	0
S1	6	2	1
S2	6	2	2, SDS
S3	6	2	2, DDS

Palladium-silver (Pd-Ag) deposition

Prior to plating, the support was seeded with Pd nuclei following the technique described by Tanaka et al. [23], using a chloroform-based Palladium Acetate(II) solution. Subsequently, a layer of Pd-Ag alloy was deposited onto γ -Al₂O₃ coated supports via electroless plating technique, reported in previous work [24]. The plating bath was composed of Palladium Acetate(II), AgNO₃, EDTA, NH₄OH. Hydrazine was added to the plating bath as reducing agent, in presence of the support. A water based AgNO₃ solution was continuously added to the bath with a syringe pump after a base plating of 2 h. The plating procedure was stopped after 5 h. In an effort to close leftover pores, two plating cycles of 5 h each were performed to achieve a Pd-Ag layer thickness up to 10 µm. After each plating step, the membrane was annealed at 550 °C in 10 vol.% H₂ – 90 vol.% Ar atmosphere for 4 h.

Characterization techniques

Surface morphology and N_2 permeation behavior of the modified supports were studied with the following characterization techniques:

- i. The surface morphology resulting from polishing treatments, the thickness of the deposited interdiffusion barriers, and the thickness of the plated Pd-Ag layer were observed via scanning electron microscopy (Fei-Quanta-FEG250-3D). The samples for imaging were obtained via support scoring and breakage. When observing fully plated membranes, this sample preparation procedure might result in slight detachment of the Pd-Ag layer from the smoothening interdiffusion barrier. However, this technique was employed through this Thesis to preserve the original porous structure of the metallic support, allowing for a thorough observation of the real morphology of its cross section.
- ii. The average pore diameter and the largest pore diameter of the untreated Hastelloy X filter were measured via Capillary Flow Porometry technique (CFP, Porolux 1000, Porometer). The sample filter was cut in 1 cm length and sealed to reach a one-close-end configuration.
- iii. The surface roughness of both the untreated Hastelloy X supports and the ones resulting from each polishing time were measured with a portable contact profilometer (MarSurf PS 10) and expressed in terms of:
 - Nominal average roughness (*Ra*), as the absolute value of the arithmetic average of the roughness profile's ordinates.
 - Average profile height (*Rz*), as the arithmetic average of the difference between the highest and lowest points of each profile in the evaluated length.
 - Maximum peak (*Rp*) and valley height (*Rv*), as the values of the highest and lowest points of the roughness profile, respectively.
- iv. The roughness parameters were evaluated by averaging the results obtained from 10 random positions on the 10 cm porous support tube.
- v. For uncoated Hastelloy X supports, the permeance of N₂ was evaluated in the permeation setup described in Figure 2.1 at 20 °C (room temperature) with a pressure difference of 0.2 bar. The membrane is inserted in a permeation shell, which is connected to N₂ and H₂ feed lines, whose flow is regulated via a mass flow controller (Bronkhorst). The pressure in the shell is regulated via a manual backpressure regulator at the retentate side. The permeate stream is connected to an automatic bubble flowmeter (Horiba-Stec VP3/VP4) to measure the outlet gas flow rate. The permeation setup can be heated up to 600 °C, and the temperature is indicated on three different thermocouples placed at various levels in the shell.
- vi. For coated supports, N_2 permeance was evaluated at 20 °C (room temperature) with a pressure difference of 1, 2, 4, and 6 bar.
- vii. After Pd-Ag deposition, the performance of the membrane was evaluated in terms of N₂ permeance at 20 °C with 1 bar pressure difference, as well as H_2/N_2 ideal selectivity at 400 °C.


Figure 2.1. Membrane permeation setup: (1) N₂ and H₂ feed via mass flow controllers (Bronkhorst); (2) permeation shell (AISI316 Stainless Steel, Swagelok flange connection to tubular membrane); (3) thermocouples for temperature control and indication; (4) manual backpressure regulator for trans-membrane pressure adjustment; (5) bubble flowmeters (Horiba Stec VP3/VP4) for permeating gas flow assessment.

2.3 Results and discussion

Effect of polishing time on sample filters

Figure 2.2 shows the evolution of both the average height of the roughness profile (*Rz*) and the average roughness (*Ra*) of the support with the residence time in the vibratory polishing machine. Increasing the polishing time, both parameters decrease until a plateau is reached around 7 h of polishing. Beyond this time, the variation of both parameters is less significant with respect to shorter polishing time (between 1 and 6 h). Once the plateau is reached, increasing the polishing time does not lead to significant changes in average roughness or average profile height. This behavior has been reported in previous works concerning vibratory finishing techniques [25]. In particular, two main mechanisms can be observed for this type of surface treatment: material erosion and plastic deformation. Hashimoto and DeBra measured material removal and surface finish of several workpieces, concluding that material erosion depends on the initial roughness of the workpiece and it decreases as the roughness of the material decreases [26], while in the work of Baghbanan et al. [27] plastic deformation resulting from media impact and sliding produced curvatures in aluminum alloy workpieces.

Figure 2.3 shows the evolution of both maximum peak height (Rp) and maximum valley depth (Rv) of the roughness profile of the supports with the residence time in the polishing machine. Rp decreases significantly within the first 2 h of polishing, when the initial roughness of the profile is larger, suggesting erosion of the highest profile points. Rv shows a slower decrease, suggesting valley filling due to plastic deformation from media

sliding. At longer polishing times (>7 h), the expected saturation is reached and the change in both parameters becomes less significant.



Figure 2.2. Average surface roughness (*Ra*) and average profile height (*Rz*) of the Hastelloy X supports, evaluated between 0 and 12 h of polishing time.



Figure 2.3. Maximum peak height (Rp) and maximum valley depth (Rv) of the Hastelloy X supports, evaluated between 0 and 12 h of polishing time.



Figure 2.4. Surface SEM imaging of: Hastelloy X support, unpolished; Hastelloy X support polished for 3h; Hastelloy X support polished for 6h; and Hastelloy X support polished for 9h.

Figure 2.4 shows the surface evolution of a support sample with increasing polishing time. In Figure 2.4 (0 h), it is evident the presence of potholes, protuberances, and deep valleys. Pore mouths are as large as 20 μ m. After 3 h of polishing (Figure 2.4, 3 h) the surface starts to level out. The material removal is confirmed by the presence of scratching on the sample surface, while plastic deformation presents itself with the closure of potholes: part of the surface is pushed tangentially to close the large pore mouths. At this polishing time, however, the shape of the initial structure is still visible. After 6 h of polishing (Figure 2.4, 6 h) streaks and protuberances are still visible. It is evident the presence of larger streaks, suggesting that plastic deformation is promoting the leveling of the profile peaks. After 9 h (Figure 2.4, 9 h) the surface is almost fully leveled out, and the initial structure is no longer distinguishable.

In Figure 2.5 the nitrogen permeance of supports at each polishing time is reported. The trend shows a decrease of nitrogen permeance with polishing time, suggesting superficial pore closure by plastic deformation of the surface structure [28]. Consequentially, even though smoother supports are the most suitable for Pd-Ag deposition, the gas permeation through their structure will be hindered. It is therefore necessary to select the most suitable polishing time for pre-treatment according to the best tradeoff between surface roughness reduction and gas permeance preservation.



Figure 2.5. N₂ permeance of Hastelloy X supports polished for increasing times (evaluated at a temperature of 20 $^{\circ}$ C and with 0.2 bar as trans-sample pressure).

γ-Al₂O₃ interdiffusion barrier characterization

Boehmite solutions are well-known in literature for their pseudoplastic (shear-thinning) behavior at all pH levels, possibly due to weak forces of attraction between particles (i.e. Van der Waals forces) [29]. Moreover, addition of polymers can also influence rheological behavior of the interdiffusion barrier precursors by hampering or enhancing dip-coating, improving or preventing solution stability and reusability, controlling drying stresses, and promoting or hindering coating uniformity after sintering. A crucial point for this work is the dependency of solution viscosity over time, which provides an indication of solution stability and the possibility of storage/reusability. Figure 2.6 shows the viscosity evolution with time elapsed from preparation of three sample boehmite solutions, according to their solid loading.

Increasing the amount of boehmite at constant polymer concentration, the dependency of the solution's viscosity on time increases. In particular, the solution prepared with the largest boehmite loading (1.8 wt.% boehmite) shows the highest value of viscosity, ranging between 36.6 cp and 222 cP and reaching gelation within 5 minutes from preparation. Decreasing the solid content (1.2 wt.% boehmite), the stability of solution viscosity increases, ranging from 24.5 cp to 9.5 cP within 15 minutes from preparation at constant shear rate, and reaching gelation behavior within 20 minutes. A further decrease in solid loading (0.9 wt.% boehmite) leads to the lowest viscosity, stable around 18 cP within 15 minutes from preparation, and presenting gelation after a few hours. This behavior suggests that increasing the solid loading at constant additives concentration enhances the non-Newtonian behavior of the solution, showing a rheopectic (antithixotropic) behavior previously reported in literature [30][31][32]. To achieve uniform interdiffusion layers and increase the support coverage, a tradeoff between high boehmite concentration and solution stability with time should be reached. Moreover, to reasonably compare supports performance, solution viscosity must be stable enough to ensure reproducible dip-coating conditions. For this reason, the depositions performed in this work are carried out with freshly made solutions within 5 minutes from preparation.



Figure 2.6. Viscosity evolution with time of solutions prepared with 0.9 wt.%, 1.2 wt.%, and 1.8 wt.% of boehmite and with PVA-PEG (3.5 wt.%-1 wt.%) as additive.

Table 2.3. *Ra*, *Ra* variation, and interdiffusion layer thickness measured for Hastelloy X supports prepared with 0.9 wt.%, 1.2 wt.%, and 1.8 wt.% of boehmite loading in the precursor solution.

Support treatment [-]	<i>Ra</i> [µm]	<i>Ra</i> decrease [%]	γ-Al₂O₃ layer thickness [μm]
6 h polish, uncoated	0.82	-	-
6 h polish / 0.9 wt.% boehmite	0.79	3.8	0.54
6 h polish / 1.2 wt.% boehmite	0.70	14.8	1.1
6 h polish /1.8 wt.% boehmite	0.64	21.4	1.8

Table 2.3 shows the average surface roughness and its decrease for supports polished for 6 h and coated with the three test solutions. Increasing the boehmite percentage in the precursor solution results in reduced surface roughness of modified supports after sintering, while polishing time is kept constant. This behavior is reflected by the layer thickness value for each solid loading percentage. As shown in Table 2.3, increasing the boehmite concentration in the precursor solution leads to an increased layer thickness. due both to the viscosity increase at larger solid load (and thus increased adhesion to the bare support) and to the presence of more solid itself. A thicker layer promotes support coverage, pore closure, reduction of average surface roughness and profile height. However, it might act as resistance to gas permeation through the final membrane. To assess the effect of support polishing time on ceramic layer deposition, a 1.2 wt.% boehmite solution was chosen to be deposited on supports polished for 3 h, 6 h, and 9 h, respectively. Figure 2.7 shows the nitrogen permeance behavior of each modified support. Increasing polishing time, the permeance of the support after deposition decreases. This behavior is to be expected given that a bare support polished for 3 h is more permeable than the others, according to Figure 2.5. Depositing the same ceramic precursor on the three selected supports preserves the permeance behavior of the bare supports, resulting in the same decreasing trend. All supports show positive slope of permeance with pressure in a range from 0 to 3 barg, suggesting the presence of macropores leading to viscous gas flow. The slope reduces with polishing time, indicating a pore closure effect related both to polishing extent and coating introduction.



Figure 2.7. N₂ permeance measured at a temperature of 20°C of Hastelloy X supports polished for 3, 6, and 9 h and modified with a precursor solution prepared with 1.2 wt.% of boehmite loading.

The initial roughness of a 3 h polished uncoated support is relatively higher compared to the ones polished at longer times (Table 2.4). For this reason, a large quantity of ceramic coating can be retained by its surface, resulting in a thick layer and a 26.7% reduction in *Ra* after deposition. Increasing the polishing time to 6 h leads to a support which is rough enough to retain a relatively large amount of ceramic coating, promoting an average roughness reduction of 14.8% and resulting in a uniform layer. The roughness of a 9 h polished uncoated support is relatively low if compared to the supports polished for a lesser amount of time. Given a smoother surface, less coating can be retained, resulting in a thinner layer and a reduction of average surface roughness only of 7.1%. Bottino et al. obtained similar behavior by coating porous stainless steel supports rubbed for different times with a pseudo-boehmite precursor solution [21].

Polishing time [h]	Coating composition [boehmite wt.%]	<i>Ra</i> [µm]	<i>Ra</i> decrease [%]	γ-Al₂O₃ layer thickness [μm]
3	uncoated	1.64	-	
3	1.2	1.20	26.7	1.16
6	uncoated	0.82	-	
6	1.2	0.70	14.8	1.1
9	uncoated	0.69	-	
9	1.2	0.64	7.1	0.73

Table 2.4. *Ra*, *Ra* variation, and layer thickness of Hastelloy X supports polished for 3, 6, and 9 h and coated with a precursor solutions prepared with 1.2 wt.% boehmite loading.

Once a bare support polishing time and a base precursor solution composition for the interdiffusion barrier are selected, it is possible to investigate different dip-coating–sintering routes. The main parameters evaluated for this study are the number of immersions of the metallic support into the ceramic precursor solution (namely dips), and the number of smoothening interdiffusion layers deposited on the metallic support. After

dipping for a certain amount of times in the precursor solution, each layer can be dried only (DDS) or dried and sintered (SDS) before a new dipping is performed and a new layer is deposited. Table 2.5 shows the roughness parameters and the interdiffusion layer thickness evaluation for each selected dipping-sintering route.

Support type, polishing time [-]	Layers, route [-]	<i>Ra</i> [μm]	<i>Ra</i> decrease [%]	γ-Al₂O₃ layer thickness [μm]
Bare, 6h	0	0.82	-	
S1, 6h	1	0.70	14.8	1.1
S2, 6h	2, SDS	0.61	25.3	2.3
S3, 6h	2, DDS	0.57	30.6	2

Table 2.5. *Ra*, *Ra* variation, and layer thickness of coated Hastelloy X supports prepared with different dipping-sintering routes.

The addition of a ceramic precursor layer in S1 reduces the average support roughness by 14.8% with respect to a solely polished support. Coverage of the average profile height is promoted, pushing the support's average roughness towards the one of its ceramic relatives. Pd-Ag deposition is already possible for S1, starting from a γ -Al₂O₃ layer 1.1 µm thick. The double sintering route used for S2 leads to a sensible reduction of *Ra* (25.3% with respect to a solely polished support). The double sintering route leads in fact to an average layer thickness of 2.3 µm, the highest amongst the coating procedures. Such a thick layer, however, can lead to delamination phenomena after sintering. This results in a non-uniformly smoothened profile which is detected by the profilometer. The single sintering route used for S3 is employed in order to be able to achieve a thick layer without promoting delamination after sintering. This route allows in fact the deposition of a second layer while the first one is dry but unsintered and, therefore, still in its gel form. The two layers are then sintered together at once, avoiding double thermal treatment and minimizing thermal stresses. This results in a larger reduction of average surface roughness, while presenting a thinner layer of 2 µm.

Selection of filter modification route

To be able to deposit a uniform Pd-Ag layer onto the tubular Hastelloy X filters with a universal procedure, the most suitable conditions resulting from the previously listed studies must be selected, namely:

- i. The most suitable polishing time.
- ii. The interdiffusion barrier precursor solution's boehmite loading.
- iii. The dipping-sintering route.

According to Figure 2.2, a polishing time of 6 h is close to the maximum possible smoothness given by the wet polishing treatment. Moreover, according to Table 2.4, at this polishing time the support is still able to retain enough ceramic coating while not excessively hampering the gas permeation (Figure 2.7). Considering the lowest roughness/highest permeation possible tradeoff, 6 h is chosen as standard polishing time for this work.

According to Figure 2.6, an interdiffusion barrier precursor solution prepared with 1.2 wt.% of boehmite is relatively stable within 5 minutes from preparation. The viscosity increase is not sharp and proceeds relatively slowly, while still providing a flowing viscous solution suitable for dip-coating. The increased viscosity with respect to lower solid loading promotes support coverage and thus surface roughness reduction, while still resulting in a delamination-free layer after sintering (Figure 2.8). The amount of 1.2 wt.% of boehmite is thus selected as base case solid loading for this work, acting as starting point for further studies on interdiffusion layer optimization.

To select a standard dipping-sintering combination, Pd-Ag deposition was performed for each test route mentioned in Table 2.5. Both S2 and S3 showed non-uniform Pd-Ag deposition due to delamination of the Pd-Ag layer during the plating procedure, due to the excessive smoothening layer thickness given by the two consecutive interdiffusion layers depositions (SDS, DDS routes). Even though it promotes a lower surface roughness reduction, S1 (Figure 2.8.a, Figure 2.8.b) allowed for a uniform Pd-Ag layer to be deposited (Figure 2.8.c, Figure 2.8.d). The single layer results in a lower smoothening interdiffusion barrier thickness, less prone to delamination and less harmful in terms of gas permeance reduction. For this reason, the single layer route is preferred for Pd-Ag deposition.

The strong adhesion between Hastellov X support and alumina-based layer can be observed in Figure 2.8.a and Figure 2.8.b. The smoothening layer is well-distinguishable and integrated onto the Hastelloy X support's profile, without any delamination present even after the breakage needed for sample SEM imaging. In Figure 2.8.c and Figure 2.8.d, a uniform Pd-Ag layer on a y-Al₂O₃ layer resulting from the boehmite deposition onto the Hastellov X support can be observed. The continuous Pd-Ag layer results from replating onto a support modified with the standardized base procedure. The continuous Pd-Ag layer is well attached to the alumina interdiffusion barrier, while a slight detachment from the Hastelloy X support can be observed, solely to be attributed to the breakage required for SEM imaging. Both the alumina-based laver and the Pd-Ag laver, however, follow the metallic support's profile, without any delamination present in the final membrane. Large, partially plated pores can be observed on an otherwise uniformly coated surface. These structures are difficult to close with Pd-Ag deposition and hinder membrane's selectivity. However, the base procedure proved to be able to reduce the bare support surface roughness so that a continuous Pd-Ag layer could be deposited. A thicker smoothening interdiffusion layer might improve pore closure but provide extra resistance to H_2 permeation and be more prone to delamination either during sintering or seeding procedures. Further optimization studies to improve hydrogen permeability while promoting full surface pores closure are discussed in Chapter 3.





Membrane testing

The membranes resulting from the previously described standardized base procedure (6 h of polishing, modification with one layer resulting from 1.2 wt.% boehmite precursor solution, and double 5 h Pd-Ag deposition) are preliminarily tested for nitrogen permeation at 20 °C and 1 bar. Membrane M0 was chosen for testing at high temperature due to its low value of N₂ permeance at room temperature (6.2·10⁻¹⁰ mol s⁻¹ m⁻² Pa⁻¹).

Figure 2.9.a shows the hydrogen permeating flux measured between 350 °C and 500 °C. Hydrogen permeation increases both with trans-membrane pressure increase and temperature increase, showing linear behavior for the pressure exponential factor n =0.6. This exponent deviates from the one often observed with Sievert's law (n = 0.5) for ceramic supported membranes at low pressure, indicating a contribution of the metallic support and/or the interdiffusion layer to gas transport through the membrane. This behavior has been previously observed in literature for metallic supported membranes [33][21]. The membrane's parameters are retrieved via the Arrhenius plot of the logarithm of membrane's permeance (evaluated with 1 bar trans-membrane pressure) versus the reciprocal of the temperature (Figure 2.9.b). The regressed parameters correspond to a maximized $R^2 = 0.992$: activation energy $\Delta E_a = 6.53$ kJ·mol⁻¹ and preexponential factor $P_0 = 2.96 \cdot 10^{-6}$ mol s⁻¹ m⁻² Pa^{-0.5}, both similar to values previously reported in literature for membranes of this kind [33].

Table 2.6 compares M0 with other literature works on metallic supported Pd-Ag membranes obtained via electroless plating techniques. At 400 °C, M0 shows a N₂ permeance of $3.7 \cdot 10^{-10}$ mol s⁻¹ m⁻² Pa⁻¹. Increasing the trans-membrane pressure, N₂ permeance increases with a positive slope. This trend suggests the presence of uncovered pores on the final membrane that result in viscous flow of N₂. The presence of partially closed pores is further confirmed by both SEM imaging of membrane's surface (Appendix 2A) and a helium leak test in ethanol, which highlighted the presence of a bubble flow from a few scattered pores. M0 was obtained by Pd-Ag deposition on a 0.5 µm media grade filter, one of the largest media grades to be used as membrane support. For this reason, even though the surface roughness is successfully reduced and Pd-Ag deposition achieved, the large pores of the support do not achieve full closure. Therefore, further studies on filter pre-treatments optimization, with a focus on narrowing their pore size distribution, will be discussed in Chapter 3.

The membrane's H₂ permeance at 400 °C amounts to $2 \cdot 10^{-7}$ mol s⁻¹ m⁻² Pa⁻¹. This low value might be reconducted to the resistance to gas flow caused by the introduction of a thicker, smoothening interdiffusion layer as well as the closure effect promoted by polishing on the bare metallic filter, which leads to a less permeable support. These steps, however, prove crucially necessary in order to reduce the filter's roughness and allow the deposition of Pd-Ag. Filter surface roughness reduction must in fact be promoted along with intermetallic diffusion prevention, requiring thicker ceramic layers to promote uniform Pd-Ag deposition.



Figure 2.9. (a) Linear regression performed on H₂ permeating flux vs H₂ partial pressure of M0, evaluated at 1, 2, 3, 5 and 5 bar trans-membrane pressure and at a temperature of 350, 400, 450, and 500 °C, to evaluate membrane's *n*-exponent; (b) linear regression performed on the Arrhenius plot of M0, evaluated at a temperature of 350, 400, 450, and 500 °C to determine membrane's activation energy as slope (ΔEa , in kJ mol⁻¹) and pre-exponential factor as intercept (P_0 , in mol s⁻¹ m⁻²Pa).

Membrane material, method	Layer thickness	Metallic support material	Metallic support media grade	Metallic support permeance	Barrier layer material	H₂ permeance (400-500 °C, 1 bar)	H ₂ /N ₂ selectivity	Ref.
[-]	[µm]	[-]	[µm]	[mol s⁻¹ m⁻² Pa⁻¹] ⋅10⁻⁵	[-]	[mol s ⁻¹ m ⁻² Pa ⁻¹] ·10 ⁻⁷	[-]	[-]
Pd / PVD- ELP	12	Fe-Cr alloy	-	190	YSZ	4.9	700-10 000	[34]
Pd-Ag / ELP	11	PSS 316L	0.2	-	α -Al ₂ O ₃	8.6	3770	[35]
Pd-Ag / ELP	4-5	Hastelloy X, supplier pre- treatment	0.2	3.54	YSZ, Al ₂ O ₃	10	200 000	[8]
Pd / ELP	20	PSS316L	0.1	-	Fe-Cr oxide	4.3	286	[36]
Pd-Ag / ELP	14	PSS316L	0.1	1.5	Boehmite, Al ₂ O ₃	8	100	[21]
Pd-Ag / ELP	10	Hastelloy X, 6h polish	0.5	1.25	Boehmite, Al ₂ O ₃	2	512	This work
Pd / ELP	11	PSS316L	0.5	10	Silica based	250	20.7-45	[37]

Table 2.6. Comparison of different Pd or Pd-Ag metallic supported membranes obtained via electroless plating technique reported in literature.

2.4 Conclusions

Deposition of a continuous, selective Pd-Ag layer can be achieved via surface modification of rough Hastelloy X filters and introduction of an alumina-based smoothening interdiffusion barrier. The surface of the porous Hastelloy tube can be pre-treated via wet vibratory finishing technique, leading to both material removal and plastic deformation from media action. The most suitable polishing time for a preliminary preparation procedure is selected as 6 h, as it promotes enough roughness decrease and prevents excessive gas permeation reduction. Moreover, increasing the bare support's polishing time leads to less coating retention, thinner layers, and less average surface roughness reduction with respect to supports polished for shorter amounts of time.

The supports can be further modified by introduction of a continuous, delamination-free alumina-based smoothening interdiffusion layer, starting from a boehmite dispersion. The composition of the dispersion (both in terms of additive concentration and solid load) influences its rheological properties, which eventually affect smoothening interdiffusion layer thickness, continuity, and coverage effect. Storage and reuse of boehmite based dispersions proves difficult due to their anti-thixotropic nature and gelation as early as 5 minutes from preparation for the highest solid concentration. Increasing the solutions boehmite loading leads to increased layer thickness and supports average surface reduction. 1.2 wt.% of boehmite in the dispersion is selected as tradeoff between stability and sufficient support coverage. Depositing and sintering more than one smoothening interdiffusion layer leads to delamination either after ceramic layer sintering or after Pd-Ag deposition, due to excessive layer thickness.

Membranes obtained from filters modified with the standardized procedure show the presence of partially covered pore mouths, resulting in partially open pores on the Pd-Ag layer, hindering selectivity. Moreover, the membranes exhibit low hydrogen permeance, which could be attributed to the resistance promoted by the smoothening interdiffusion barrier and the closure effect promoted by polishing. However, these pre-treatments prove themselves crucial for surface roughness improvement. Overall, boehmite based dispersions prove themselves as valuable candidates for smoothening interdiffusion layers, due to their adhesive/binding properties and ability to noticeably reduce the filter's surface roughness.

In this exploratory work, the surface roughness reduction of the unrefined Hastelloy X filters proved possible, opening to the possibility for optimization of more economically viable membrane support options. Chapter 3 will focus on filter's superficial pore size optimization, in order to both reduce defect size and increase porosity. Tuning filter pre-treatments proves in fact crucial in order to increase final membrane's H_2 permeance and, consequently, H_2 selectivity.

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Appendix A Additional considerations on support pre-treatment design

In Chapter 2, membrane M0 presented H_2/N_2 selectivity ~500 at 400 °C and 1 bar. The poor performance can be correlated to the positive slope of N_2 permeance through the membrane, which indicates the presence of large, isolated defects on the surface, as well as the low H_2 permeance given by the closure effect operated by the polishing treatment.

To further investigate the origin of the membrane's defects, the surface of samples coated with the chosen 1.2 wt.% boehmite loading was observed via SEM in Figure A.1. An uniform coating covering the surface profile of the metallic support is distinguishable. However, scattered, uncovered defects are present onto the otherwise uniform surface. The magnified view onto these defective structures confirms the presence of γ -Al₂O₃ coating collapsed into the pore neck of the metallic support structure underneath. This observation confirms that the defects onto the final Pd-Ag membranes are not given by coating failure, delamination, or cracking but rather by the coating's inability to fully fill such large porous structures, which are intrinsic of the metallic support itself and persist through the polishing procedure. Thus, this observation highlighted the necessity of further coating optimization in order to promote full superficial coverage.





The superficial coverage operated by the coating could be increased by increasing coating thickness. However, increasing coating solid loading would lead to increased solution viscosity and decreased stability. For this reason, the possibility to further tune coating thickness by designing the addition of a different concentration of plasticizer or binder was explored. The effect of plasticizer-binder concentration on rheologic behavior of boehmite coatings was studied via viscosimetry, varying the amount of PolyVynylAlcohol (PVA) at constant PolyEthylenGlycol (PEG, 1.0 wt.%) and constant boehmite loading (1.2 wt.%) in the final coating. The same assessment was repeated by varying the amount of PEG at constant PVA (3.5 wt.%) and constant boehmite loading (1.2 wt. %). All the tested coatings presented anti-thixotropic behavior, except for the solutions with the lowest loading of both polymeric components. However, the dispersion with that composition yielded to a viscosity of ~15 cP, which in turn resulted in thin, non-uniform coatings.

In Figure A.2.a, the effect of PVA addition is shown. By increasing the concentration of PVA in the final coating at constant solid loading, the average viscosity of the coating increases. However, the gelation behavior (characterized by a sharp slope increase) occurs earlier as the PVA concentration is increased. The same behavior is observed in Figure A.2.b for a constant amount of PVA and an increased amount of PEG. These observations allowed to select an intermediate concentration as a tradeoff between high viscosity (to obtain a thick, uniform, coating) and dispersion stability (retardation of the gelation curve). These results allowed to conclude that even the addition of a binder and plasticizer has an important effect on the gelation behavior of the coatings, and it plays sinergically with the solid load of boehmite. For this reason, increasing coating thickness by further tuning precursor solutions viscosity would have a detrimental effect on the resulting coatings.





Figure A.2. Viscosity evolution with time elapsed from preparation of 1.2 wt.% boehmite coatings with: (a) 2.5 wt.%, 3.0 wt.%, 3.5 wt.%, 4.0 wt.%, and 4.5 wt.% of PVA; (b) 0.5 wt.%, 1.0 wt.%, and 1.5 wt.% of PEG.

In an effort to promote defect closure without further gelation (as well as to compare the utilization of different coating materials) the addition of YSZ powder (Tosoh, Japan) to the boehmite coating was investigated. The addition of YSZ yielded to a uniform coating with the presence of dispersed, micometer-sized YSZ particles in a binding boehmite matrix (Figure A.3). In Figure A.3, the effect of YSZ/boehmite ratio in the coating on average support surface roughness is shown. The larger the YSZ/boehmite ratio in the coating, the larger the amount of peaks of the roughness profile given by particles emerging from the boehmite matrix and thus the larger the surface roughness. However, in Figure A.3.b the YSZ powder particles showed the tendency to nest into the large pore structures, reducing their superficial size, while the boehmite matrix contributed mostly to the smoothening of the surface.

Therefore, the possibility to clog the large porous structures with a filler powder of controllable size is proposed in Chapter 3, decoupling the interdiffusion barrier from the filler powder itself. In this way, the uniforming effect of boehmite based coatings is preserved, while the reduction of the defects size is operated by pore clogging.



Figure A.3.(a) SEM cross-sectional imaging of a Hastelloy X support polished for 6 h, coated with 50%-50% YSZ-Boehmite at 1.2 wt.% total solid loading; (b) SEM surface view of a Hastelloy X support polished for 6 h, coated with 50%-50% YSZ-Boehmite at 1.2 wt.% total solid loading.



Figure A.4. Average surface roughness of Hastelloy X supports polished for 6 h and coated with increasing YSZ-boehmite ratio at constant 1.2 wt.% total solid loading.

Chapter 3 | H₂ selectivity improvement of Pd–Ag membranes supported on porous metal filters²

In this Chapter, the membrane H_2 selectivity issue is tackled by studying additional support pre-treatments. Specifically, the gas permeance through the support is increased via chemical etching, while the support's superficial Pore Size Distribution (PSD) is reduced by the application of a pore filler.

The loss in gas permeance given by the polishing treatment proves fully recovered after chemical etching in aqua regia. A method to fill the large pores of the filters via insertion of a α -Al₂O₃ water-powder suspension is applied and characterized via imaging of the filled pores, statistical methods, and Capillary Flow Porometry (CFP) measurements. The most suitable filler particle size for pore size distribution reduction is identified as 18 µm, while a 5 µm filler proves optimal for further pore morphology improvement. The wide pore size distribution of the filters is thus reduced up to 200 nm by filling with α -Al₂O₃ particles of decreasing size. The γ -Al₂O₃ interdiffusion barrier proposed in Chapter 2 is deposited, achieving further surface roughness reduction. Finally, a highly H₂ selective membrane (H₂/N₂ selectivity ~ 40000 at 400 °C and 1 bar) is obtained via simultaneous Pd–Ag plating (ELP) onto the pre-treated filter.

² This chapter is based on the following paper:

S. Agnolin, F. Apostolo, L. Di Felice, J. Melendez Rey, A. Pacheko Tanaka, M. Llosa Tanco & F. Gallucci, (2023). "Development of selective Pd–Ag membranes on porous metal filters", *International Journal of Hydrogen Energy*, Volume 48, Issue 65.

3.1 Introduction

As summarized in Chapter 1, Pd-based membranes have been subjected to optimization studies, mostly in terms of their H₂ perm-selectivity performance and their suitability for integration in the reaction environment [1][2][3]. In particular, thin Pd films (<10 μ m) have been successfully deposited on tubular ceramic supports [4][5]. The deposition of Pd on an appropriate support allows in fact to reach outstanding H₂ perm-selectivity while ensuring mechanical stability of the thin films [3][6][7]. Asymmetric ceramic tubular supports prove suitable for the electroless deposition of a thin and defect-free Pd-based layer thanks to their low surface roughness, narrow pore size distribution, and low resistance to gas permeation [8][9]. On the contrary, steel-based supports display large surface roughness, large superficial potholes, and wide pore size distribution, making the preparation of Pd-based membranes with high H₂ permeation and selectivity a complex task [10] [11].

In Chapter 2, a boehmite-based layer with a dual function as interdiffusion barrier/smoothening layer was proposed. This layer, besides preventing intermetallic diffusion, if combined with a suitable polishing treatment is also able to reduce the surface roughness of the selected metallic supports [12]. However, the deposition of this barrier alone proved insufficient to close the large superficial pore mouths of the filter, resulting in membranes with low perm-selectivity [12][13], solving solely the surface roughness issue. For this reason, this Chapter focuses on the recovery of superficial porosity of polished filters via chemical etching [14] and the subsequential pore flow distribution narrowing via the introduction of a pore filler. In literature, several materials have been introduced in the metallic supports in an effort to improve their surface morphology [15]–[20]. Similarly, in the work of Kim et.al, a selective membrane obtained via pore filling method and sol-gel barrier deposition was tested for ammonia decomposition applications [21].

In this Chapter, asymmetrically layered α -Al₂O₃ inside the filter's superficial pore mouths is proposed in an effort to reduce the filter's pore size. The sequential filling is carried out with α -Al₂O₃ of decreasing particle size via vacuum assisted dip-coating. The surface roughness of the support is then lowered by the deposition of the boehmite-based barrier, covering the pores and preventing interdiffusion issues. In an effort to provide a more quantitative approach to the support filler design, the filling effect is studied on the pores population of 3 sample filters by feeding imaging parameters to a Two-way ANalysis Of VAriance (ANOVA) [22][23][24], introducing an applicable method for statistical evaluation of membrane preparation parameters. The outcomes in terms of support gas permeance, pore size distribution, surface roughness and morphology are thoroughly investigated for each pre-treatment step and, finally, the electroless deposition of a Pd-Ag layer is performed. The resulting membranes are then characterized in terms of ideal H₂/N₂ perm-selectivity.

3.2 Materials

Porous Hastelloy X supports

Commercial, untreated porous Hastelloy X filters with an outer diameter of 1.2 cm, average surface roughness (*Ra*) of 6.1 µm, and 0.5 µm nominal media grade (MG) were acquired from Hebei Golden Flame Wire Mesh Co, China. The supports were cut in samples of 10 cm length and welded to dense stainless steel (AISI316L) tubes, in order to achieve a one close end configuration. To preliminarily reduce the surface roughness of the filters, the sample supports were polished in an industrial surface finishing machine via wet-polishing mechanism (ERBA EVT-170). The chosen polishing time amounts to 6 h, as it allows for a suitable tradeoff between surface roughness reduction and gas permeation preservation, which was determined in Chapter 2 [12]. The polished supports were then etched by perpendicular immersion in Aqua Regia for 30 s and thoroughly rinsed with deionized water to remove all mordant residuals. The supports were oxidized for 1 h at 750 °C in a furnace in static air atmosphere. Before further treatments, the supports were further rinsed both in ethanol and in deionized water in an ultrasonic bath, to remove all impurities resulting from the preparation pre-treatments and handling.

α-Al₂O₃ filler

The tubular supports were submerged in a powder-water suspension, which was pulled through the superficial pores via vacuum assisted dip-coating. The immersion time was set to 60 s per cycle. Between each cycle the support was gently rinsed with distilled water and no calcination was required. The selected filler powder is α -Al₂O₃, which was evaluated in three different particle sizes (AA-1 Sumitomo 1 µm, AA-5 Sumitomo 5 µm, AA-20 Sumitomo 18 µm). The powders were 10 wt.% suspended in water with a magnetic stirrer. The suspension was improved by dropwise addition of HNO₃ (67 vol.%). First, the supports underwent several immersion cycles in order to assess both the aspiration effect and the *Filler size* effect on support's pore size distribution and surface morphology. In a second study, supports were filled asymmetrically with α -Al₂O₃ of decreasing particle size.

γ-Al₂O₃ interdiffusion layer

The smoothening interdiffusion barrier proposed in Chapter 2 was deposited to finalize the improvement of support's surface roughness and ease Pd-Ag deposition. Solutions with boehmite loading 0.9 wt.% were prepared in distilled water, incorporating a waterbased solution of organic additives, namely 3.5 wt.% polyvinyl alcohol (PVA) (MW 130000) and 1 wt.% polyethylene glycol (PEG) (MW 400). The deposited layers were dried under rotation in a climate chamber at 40 °C and 60% relative humidity for 1 h. The layers were then sintered for 1 h at 550 °C in a static air furnace. These parameters yield to a mesoporous γ -Al₂O₃ layer about 540 nm thick [12].

Pd-Ag deposition

A layer of Pd-Ag alloy was deposited onto treated supports via electroless plating technique, reported in a previous work by Tanaka et al. [4] [5]. To improve membrane selectivity, a consecutive plating procedure was carried out to achieve thicker Pd-Ag layers. After each plating step, the membrane was annealed at 550 °C in 10 vol.% $H_2 - 90$ vol.% Ar atmosphere for 4 h.

3.3 Characterizations

Capillary flow porometry

The Capillary Flow Porometry technique (CFP, or gas-liquid displacement method) relies on imposing a trans-sample pressure at which a suitable liquid is displaced from the pores of the examined sample. The displacement is detected by registering the permeating flow of a non-reactive gas through the media. In CFP tests, the sample is filled with a wetting liquid, assuming the filling of its entire accessible porosity. Pressure is applied to one side, while the other is kept at atmospheric pressure. This trans-sample pressure difference forces the wetting liquid out of the pores resulting in a permeating flow. Increasing the trans-sample pressure will promote pore clearance, increasing the permeating flow until the sample is fully cleared from the wetting liquid (Figure 3.1). Young-Laplace equation is then used to correlate the capillary pressure in the media with its pore diameter. If the capillary is assumed of cylindrical shape, Washburn equation can be applied, which is a typical assumption for indirect method CFP measurements [25][26]:

$$d = -\frac{4\gamma \cos\theta}{\Delta P} \tag{1}$$

Where ΔP is the applied trans-sample pressure, *d* is the narrowest diameter of the capillary, γ is the surface tension of the chosen wetting liquid, and θ is the contact angle between the wetting liquid and the wet surface. Assuming that the chosen liquid is able to guarantee full wettability of the porous media, the contact angle can be assumed as 0°, leading to further simplification:

$$d = -\frac{4\gamma}{\Delta P}$$
(2)

Given that the listed geometrical assumptions are to be applied to a complex porous media, it is important to remark that this technique is able to give information on an average geometry [27][28]. This averaging assumption summarizes the main flow characteristics of the media, rather than a precise pore shape. Moreover, the flow distribution proves dependent on the wetting liquid choice, the scanning speed, and the ramping method [29]. Nevertheless, given that the scope of this work was to evaluate if there is any influence of support pre-treatments on the gas permeance and flow distribution through the media, this level of accuracy is considered sufficient for quality comparisons between samples of the same nature. By measuring the permeating gas flow for each applied trans-sample pressure, the flow distribution with respect to the dry media can be used to retrieve information about its average geometry.

In particular, the cumulative flow distribution through the porous tube is:

$$C_{\text{flow}} = \frac{Q_{\text{wet}}}{Q_{\text{dry}}} \tag{3}$$

Where Q_{wet} represents the permeating flow through the wet media and Q_{dry} is the permeating flow through the dry media at the applied trans-sample pressure. From the cumulative flow distribution C_{flow} , it is then possible to retrieve the differential flow for each pore diameter D as:

$$Diff_{flow} = \frac{dC_{flow}}{dD}$$
(4)



Figure 3.1. Graphical illustration of the cumulative flow distribution evaluation through a wet sample.

To evaluate pore size distribution variations for each support pre-treatment, the 10 cm porous tubes were measured via CFP technique in a geometry-specific setup (Figure 3.2), which consists of:

- i. A tubular permeation box, which is able to withstand pressures up to 60 bar.
- An automatic mass flow controller for N₂ (Bronkhorst EL-FLOW Select F-221 M), which is chosen as inert displacement gas.
- iii. An automatic backpressure regulator at the retentate side (Bronkhorst EL-PRESS- P–502C).
- iv. An automatic three-way valve, which can switch between a low flow automatic flowmeter (Bronkhorst EL-FLOW Prestige FG-111B, range 0.004 mL min⁻¹ 0.2 L min⁻¹), and a high flow automatic flowmeter (Bronkhorst EL-FLOW Prestige FG-111B range 0.2 L min⁻¹-10 L min⁻¹).
- v. An external computer with LabVIEW software.



Figure 3.2. Illustration of the CFP setup for tubular supports/membrane samples. In red, signal streams for permeated N_2 flow measurement; in blue, signal streams for N_2 feed flow adjustment for pressure keeping in the sample chamber.

The setup was fully automated as follows:

- i. The controlling software allows the user to set a desired pressure ramp and/or step to be imposed within the permeation box.
- ii. The correct feed flow is sent to the permeation box in order to increase the pressure according to the ramp set by the user (1).
- iii. The permeating flow at each timestamp is registered at the permeate side by the flowmeter with the correct flow range, which can be automatically switched via the three-way valve (2).

Laser confocal microscopy and profilometry: statistical approach

The surface morphology of the treated filters was studied using a laser-optical confocal microscope (VKX-3000, Keyence, Osaka, Japan). Said imaging method was employed to verify and observe the presence of the selected filling particles into the superficial pore mouths of the supports. The extent of superficial pore filling was evaluated by imaging a superficial pore mouth and registering its highest point on the metal surface and its lowest point on the embedded filler. For each *Filler size* and cycles combination, 10 random pore mouths were evaluated. The result is a filling extent parameter Δ . Consequentially, a lower Δ indicates a fuller pore mouth. Δ has been employed for statistical considerations as dependent variable in a Two-way ANOVA, in order to guarantee a more quantitative approach to the filling procedure optimization [30].

The average surface roughness (Ra) and average profile height (Rz) of the treated supports were evaluated with a portable contact profilometer (MarSurf PS 10) on 10 random positions on the tubular support. These parameters were normalized on their values for an untreated support and employed as dependent variables for a Two-way ANOVA.

ANOVA allows to infer on the whole population of support pores, while observing only a representative sample amount. The factorial design allows for full observation of the outcome variable (Δ , Ra, or Rz) while variating the two selected factors *Filling cycles* and *Filler size* combinations, making it especially suitable for a comprehensive observation of the filling phenomena. The analysis was carried out through the R language. The chosen environment was RStudio. The experimental designs are summed up in Table 3.1, and additional statistical documentation is reported in Appendix 3B.

Laser-confocal microscopy (Δ)				
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	⊿ [µm]	-	
Factor 1	Independent (A)	Filling cycles [-]	10, 15, 20	
Factor 2	Independent (B)	Filler size [µm]	1.5, 5, 18	
	Average surfa	ce roughness (<i>Ra</i>)		
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	<i>Ra</i> [µm]	-	
Factor 1	Independent (A)	Filling cycles [-]	10, 15, 20	
Factor 2	Independent (B)	Filler size [µm]	1.5, 5, 18	
Average profile height (<i>Rz</i>)				
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	<i>Rz</i> [µm]	-	
Factor 1	Independent (A)	Filling cycles [-]	10, 15, 20	
Factor 2	Independent (B)	Filler size [µm]	1.5, 5, 18	

Table 3.1. Two-way ANOVA design for each dependent variable Δ , Ra, Rz.

Gas permeance

The prepared Pd-Ag membranes were tested for N₂ permeance at 20 °C and 1 bar in the permeation box described in Chapter 2 [12]. If the N₂ permeance was lower than $1 \cdot 10^{-9}$ mol m⁻² s⁻¹ Pa⁻¹ the membrane was selected for further high temperature short-term investigation. The selected membranes were activated at 400 °C with an air flow of 1 L min⁻¹ for 2 min. They were then tested at 400, 450, and 500 °C for single gas (H₂ and N₂) permeance with an imposed trans-membrane pressure difference of 1, 2, and 3 bar.

3.4 Results and discussion

Polishing and etching

The evolution of the filter's surface with the chosen pre-deposition treatments is analyzed with the laser confocal microscopy images in Figure 3.3. The untreated 0.5 μ m media grade filters are characterized by the presence of high profile peaks (red) and large surface roughness (Figure 3.3.a), in agreement with the behavior observed in Chapter 2 [12]. At this stage, the pore mouths of the support are interconnected, showing a superficial diameter larger than 50 μ m. After 6 h of polishing (Figure 3.3.b), the surface of the support is uniformly smoothened, erasing the presence of the large peaks by plastic deformation. However, the smaller superficial diameters close to 20 μ m. After etching the support for 30 s in aqua regia (Figure 3.3.c) the smoothened surface is broken down into smaller channels interconnecting the metallographic structure underneath: the surface roughness reduction achieved by polishing is preserved, while the support's valleys are uncovered. This promotes an increase in the number of superficial openings, leading to improved gas permeance after polishing, while preserving the treatment's smoothening effect.

The evolution of N₂ permeance, mean flow pore, and contact roughness parameters (Table 3.2) further confirms the behavior observed via microscopy. Firstly, the polishing treatment promotes both a gas permeance reduction of 76% and a roughness decrease of 87%. Following the chemical etching, due to the presence of a larger amount of profile valleys, *Ra* is re-increased solely with an additional 20%, while the gas permeance surpasses the untreated support's original value. This behavior is well in agreement with the work of Xu et al., who carried out similar improving pre-treatments on a disk-shaped stainless steel support, observing the same surface variations via scanning electron microscopy [14].

 ${\bf 65} \mid$ H_2 selectivity improvement of Pd-Ag membranes supported on porous metal filters



Figure 3.3. Laser confocal microscopy imaging and height distribution of a 0.5 µm Hastelloy X filter: (a)untreated; (b) polished for 6h; (c) etched 30 s in Aqua Regia.

Table 3.2. Ra, N₂ permeance, and average pore diameter of a Hastelloy X support for each pretreatment step, compared with the values for an untreated Hastelloy X filter and an α -Al₂O₃ support from Rauschert.

Pre-treatment [-]	<i>Ra</i> [µm]	N ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]·10 ⁻⁵	Avg. pore diameter [μm]
Ceramic, α-Al ₂ O ₃	0.5	8.0	0.1
Untreated Hastelloy X	6.1	5.0	1.8
Wet polishing, 6 h	0.8	1.2	1.9
Chemical etching, 30 s	1.1	8.9	1.1

a-Al₂O₃ filler design

Taking into account the mean flow pore of a ceramic support (Table 3.2), which is proven to produce supported thin and ultra-thin Pd based membranes without defects [31] [32], the size of the filter's through-pores after polishing and etching is still too large. For this reason, the introduction of the α -Al₂O₃ filler into the superficial openings of the pre-treated support is expected to prove crucial for the reduction of their size, ensuring gas tightness (and therefore H₂ selectivity) of the completed membrane. Table 3.3 shows the results of the Two-way ANOVA performed on the outcome variables listed in Table 3.1.

Lagar confeed microscopy						
Laser comocar microscopy, 2						
Factor	Factor levels	p-value	Significance			
Filling cycles [-]	10 / 15 / 20	0,581	-			
Filler size [µm]	1.5 / 5 / 18	2.3·10 ⁻⁸	***			
Interaction [-, µm]	-	0.002	**			
	Profilometry	, Ra				
Factor	Factor levels	p-value	Significance			
Filling cycles [-]	10 / 15 / 20	0.001	**			
Filler size [µm]	1.5 / 5 / 18	0.123	-			
Interaction [-, µm]	-	0.512	-			
Profilometry, <i>Rz</i>						
Factor	Factor levels	p-value	Significance			
Filling cycles [-]	10 / 15 / 20	0.001	***			
Filler size [µm]	1.5 / 5 / 18	0.025	*			
Interaction [-, µm]	-	0.782	-			

Table 3.3. ANOVA test results on outcome variables Ra, Rz, and Δ . The relevant factor effect is assumed significant if *p*-value < 0.05, with a confidence interval of 95%.

The results of the Two-way ANOVA highlight a statistically significant contribution to Δ of the interaction between the number of immersion cycles and the filler size. When an interaction is statistically significant, analyzing solely the main effects can be misleading. Therefore, the interaction effect is observed in Figure 3.4. In particular, all filler sizes underperform with the lowest number of cycles, meaning that more than 10 cycles are required for a low Δ ; at 15 cycles, the best performing size is 5 µm, while at 20 cycles the largest size (18 µm) and the smallest size (1.5 µm) also contribute to a Δ reduction. This result suggests that 5 µm is a filler that most suits the shape of the superficial pore mouths of the support, requiring less cycles to reach a performance plateau with respect to the largest and smaller filler, which will require more cycles.

This result is confirmed by the ANOVA performed on the roughness parameter Rz. For Rz a statistically significant contribution of both independent factors is observed, while the interaction effect is lost. This can be explained by the nature of the outcome variable

Rz, which averages roughness profile extremes along a measuring length, rather than purposefully imaged pore mouths, yielding to a loss of information with respect to microscopy. Nevertheless, in Figure 3.5a it is noticeable how a 5 µm filler promotes the largest reduction in Rz, independently from the number of cycles performed. However, a large number of cycles is preferred independently from the chosen filler size (Figure 3.5).

For Ra, a further loss of information is introduced within the ANOVA results. This loss is attributed to the averaging nature of Ra, which does not consider any extremes of the roughness profile, but rather averages all the deviations from the profile's mean line. A statistically significant contribution is attributed solely to the filler size, highlighting how 5 μ m is the best performing in terms of Ra reduction independently from the number of applied cycles, which, in turn, proves to be insignificant (Figure 3.6).

All three analyses conclude that a 5 μ m filler reaches a performance plateau quicker than the other sizes, making it the most suitable size for all surface morphology parameters improvement, preferably in combination with an amount of aspiration cycles greater than 15. However, microscopically, as the number of cycles grows larger, the 1.5 and 18 μ m size will contribute to the improving of the pore morphology.



Figure 3.4. Interaction effect plot of dependent variable Δ against factor *Filling cycles*, grouped by *Filler size*. The points indicate the average value for each factor levels combination.



Figure 3.5. Main independent effects plots of factor *Filling cycles* and factor *Filler size* on dependent variable *Rz*. The points indicate the average *Rz* decrease values for each independent factor level.



Figure 3.6. Sole main effect plot of factor *Filler size* on dependent variable *Ra*. The points indicate average *Ra* decrease for each level of the sole factor *Filler size*.

The evolution of surface morphology parameters is not the only phenomenon to be considered while applying a filler to the selected support. An optimal filler design should in fact guarantee sufficient support's average pore diameter reduction and pore distribution sharpening, while preserving gas permeance through the porous media.

From Figure 3.7c it is clear how an 18 µm filler sharpens the filter's pore flow distribution around an average pore diameter of about 200 nm. promoting a reduction of the mean flow pore by 80% (Figure 3.7a). This shows the filler's ability to place itself in large pore necks with respect to the smaller sizes, which only contribute to morphology improvement but require more packing to influence the pore size distribution. Similarly, as observed in Figure 3.7b, the 18 µm filler is the most influential in the decrease of permeance in the sample filter, meaning it is affecting the pore necks rather than the surface openings. This conclusion is further confirmed by the dual laser-optical confocal imaging in Figure 3.8, in which the 18 µm filler is observed to clog the largest defects, while the smaller fillers tend to assume a packed configuration, leaving larger defects open. This renders the 18 µm filler suitable for a first reduction in large support's openings, while fillers of smaller size can be layered to promote a subsequential improvement of the superficial pore morphology. These observations, paired with the results obtained by Chi et al., who observed the same behavior for α-Al₂O₃ fillers on lower media grade stainless steel tubes, allow to speculate that fillers with about half of the size of the superficial pore openings are the most suitable for pore flow distribution modification, while fillers of lower dimensions can be used for surface morphology improvement [17].



Figure 3.7. (a) Avg. pore diameter precent decrease with increasing *Filling cycles*, for each *Filler size*, measured with CFP; (b) N₂ permeance percentage decrease with increasing *Filling cycles*, for each *Filler size*; (c) pore size distribution of a filter filled 20x with 18 μm α-Al₂O₃, measured via CFP between 10% and 90% of total dry flow.



Figure 3.8. Laser-optical confocal microscopy imaging of a selected pore mouth of a Hastelloy X filer filled with 1.5 μ m α -Al₂O₃, 5 μ m α -Al₂O₃, and 18 μ m α -Al₂O₃.

For this reason, the 18 µm filler is selected as base for the asymmetric support. To then improve the morphology of the support's surface, a 5 µm and 1.5 µm filler are introduced subsequentially. The microscopy imaging in Figure 3.9 clearly highlights the presence of large α -Al₂O₃ filler underneath the smaller particles, promoting uniform leveling of the pore mouths. Figure 3.10 shows the cumulative flow distribution through the pores of a sample filter filled with the selected asymmetric design. The mean flow pore is sufficiently reduced around 100 nm, a comparable value to the one of the α -Al₂O₃ supports commonly used in ceramic membranes preparation. At this stage, most of the largest pore necks are reduced in size by the fillers. However, about 10% of the inert gas flow is still measured through pores larger than 500 nm. This pore distribution tail depends on both the initial filters themselves and any leftover large openings after pre-treatment. The control of this tail, although representing the minority of the distribution, proves in fact crucial to minimize membrane's N₂ permeation and thus selectivity, ensuring reproducibility of performance.



Figure 3.9. Laser-optical confocal microscopy imaging of a Hastelloy X filter's pore mouth asymmetrically filled with α -Al₂O₃ of decreasing size.



Figure 3.10. Cumulative percentage flow distribution through the pores of an asymmetrically filled Hastelloy X filter before and after γ-Al₂O₃ layer deposition, measured with CFP.
Pd-Ag deposition

In Figure 3.11a the surface morphology of a membrane obtained via deposition of Pd-Ag when carried out on a 0.5 μ m media grade filter solely treated with the boehmite based smoothening layer is shown. The boehmite based layer allows for uniform metal deposition on the support's surface. However, the sole presence of this layer is not enough to promote full pore closure and obtain a defect-free Pd membrane. In Figure 3.11b the same deposition is carried out on a support in which a 5 μ m α -Al₂O₃ filler has been introduced. The leveling of the pore surface promoted by the filling of the large support's mouths allows for the Pd-Ag to fully close the superficial openings, obtaining the desired defect-free dense layer even on the large superficial pore mouths. For this reason, the choice of a suitable filling procedure proves essential to impact final membrane performance and reproducibility. In Table 3.4 membranes prepared with different filling procedures are compared in terms of H₂ perm-selectivity at 400 °C.



Figure 3.11. Laser-optical confocal microscopy imaging and height distribution of a Pd-Ag layer deposited on a large superficial opening of: (a) an unfilled Hastelloy X filter; (b) a Hastelloy X filter filled with α -Al₂O₃. Both samples are coated with a 1.2 wt.% boehmite-based γ -Al₂O₃ smoothening interdiffusion layer.

Table 3.4. H₂/N₂ selectivity and H₂ permeance comparison of Pd-based membranes deposited via electroless plating onto steel-based supports pre-treated with similar methods.

Support material, media grade, and pre-treatment	Filler material and	Interdiffusion barrier material	H ₂ permeance (400-500 °C 1 bar)	H_2/N_2	Ref
[-]	[-]	[-]	[mol m ⁻² s ⁻¹ Pa ⁻¹]	[-]	[-]
Hastelloy X / 0.1 μm / pre-treated by Mott Corp.	$Al_2O_3\text{+}YSZ$ powder / -	No additional layer	1.0·10 ⁻⁶	200 000	[16]
Ceramic / - /double skin	- / -	-	4.6.10-6	26000	[3]
Inconel 600 / - / -	YSZ powder + boehmite- based sol / -	Blow coated YSZ	3.4.10-6	8050	[21]
PSS / 0.2 μm / -	CeO / 1-4 µm	No additional layer	1.2.10-6	infinite	[33]
PSS / 0.5 µm / polished and etched in alkaline sol and HCI	- / -	None	5.0·10 ⁻⁷	5000	[34]
Inconel 600 / 0.5 µm /-	YSZ / 50 nm	Blow coated YSZ	7.4.10-7	335	[35]
PSS / - / -	YSZ / 50 nm	Blow coated YSZ	3.0.10-6	240	[36]
Hastelloy X / 0.5 µm / 6 h polish	- / -	Boehmite	2.0.10-7	512	[12]
Hastelloy X / 0.5 µm / 6 h polish, 30 s aqua regia etch	α-Al ₂ O ₃ / 300 nm	Boehmite-based layer 1.2 wt.%	1.1·10 ⁻⁶	~6300	#MS, This work
Hastelloy X / 0.5 µm / 6 h polish, 30 s aqua regia etch	α-Al ₂ O ₃ / 300 nm	Boehmite-based layer 1.2 wt.%	1.1.10-6	~830	#MS2, This work
Hastelloy X / 0.5 µm / 6 h polish, 30 s aqua regia etch	α-Al ₂ O ₃ / 300 nm	Boehmite-based layer 1.2 wt.%	9.2.10 ⁻⁷	~3600	#MS3, This work
Hastelloy X / 0.5 µm / 6 h polish, 30 s aqua regia etch	α-Al ₂ O ₃ / 18 μm + 5 μm +1.5 μm	boehmite-based layer 0.9 wt.%	7.0.10-7	~43200	#MA, This work

Pd-Ag membranes prepared with a small size filler present poor selectivity compared to the membrane prepared with the asymmetric design. In particular, symmetrically filled membrane MS has been selected due to its high H₂/N₂ selectivity and its performance is compared to MA, prepared on a support filled asymmetrically. Both membranes have been characterized in terms of activation energy via linear regression through the Arrhenius plot in Figure 3.13, where MS shows an activation energy of ~6 kJ mol⁻¹ and MA of 9.3 kJ mol⁻¹. While MA is well in agreement with the activation energy range for thin Pd layer membranes, MS presents a lower value, possibly explained by the presence of scattered larger defects. The different trend (between MA and MS) of H₂ permeating flux with trans-membrane H₂ pressure is shown in Figure 3.12 at 400 °C. This fit was evaluated for all explored temperatures, allowing for the retrieval of the the *n*-exponents of each membrane, which amount to 0.71 and 0.51 for MS and MA respectively. In particular, these values of *n* suggest that MA's rate determining step for hydrogen transport is given by the Pd layer, while for MS there is an influence of the metallic support [16].

MA displays an outstanding H_2/N_2 selectivity (Figure 3.14) accounting that this membrane is prepared on a filter with 0.5 µm media grade and 50 µm large superficial pore mouths, the largest in literature obtaining membranes with selectivity >10 000. This result proves that it is indeed possible to achieve high-performing membranes using unrefined metallic filters. Pd-Ag membranes prepared with the same filler-barrier deposition technique reported in literature show promising performances on steel-based supports with larger media grades (Table 3.4). This two-step procedure therefore classifies itself as a promising standard method for Pd-based membranes on cheaper metallic support options.



Figure 3.12. H₂ permeating flux vs H₂ partial pressure evaluated at a temperature of 400 $^{\circ}$ C and a trans-membrane pressure of 1, 2, and 3 bar for both MA and MS.



Figure 3.13. Linear regression performed on the Arrhenius plot of MA and MS, evaluated at 400, 450, and 500 °C to determine membrane's activation energy as slope (ΔEa , in J·mol⁻¹) and preexponential factor as intercept to determine membrane's activation energy as slope (ΔEa , in kJ mol⁻¹) and pre-exponential factor as intercept (P_0 , in mol s⁻¹ m⁻² Pa).



Figure 3.14. Ideal H_2/N_2 selectivity of MA, evaluated right after membrane annealing at a temperature of 400, 450, and 500 °C with a trans-membrane pressure of 1, 2, and 3 bar,.

3.5 Conclusions

Hastelloy X porous filters with large media grade (0.5 μ m), 2 μ m average pore size, 50 μ m superficial pore mouths and high surface roughness (*Ra* ~6 μ m) have been successfully modified to improve their superficial characteristics to be used as support of Pd-Ag membranes with high H₂ selectivity.

Support surface roughness can be preliminarily reduced via wet polishing method, producing a decrease in the porosity and gas permeation which can be reverted by subsequential chemical etching in aqua regia. The wide pore size distribution of the filters can be reduced for the most part up to 200 nm via introduction of α -Al₂O₃ filler particles. The 18 µm filler is the most suitable to reduce the pore size distribution applying at least 20 filling cycles, while fillers of lower size (5 µm, 1.5 µm) prove more suitable for further surface morphology improvement. By combining all the studied pre-treatments, a highly selective membrane (H₂/N₂ selectivity ~40000 at 400 °C and 1 bar) was obtained on a support filled with α -Al₂O₃ particles with decreasing size.

3.6 Bibliography

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Appendix B Supplementary statistical information

In-pore behavior

The examined outcome variable (Δ) was determined as the difference between the highest peak and the lowest valley of an observed support's pore. The variable was retrieved via laser confocal microscopy by examining 10 random pores (subjects) on the surface of a support undergoing a selected filling treatment (Figure B.1). The lower the difference, the fuller the pore.



Figure B.1. Laser-optical confocal microscopy imaging of a filled pore for variable Δ observation.

The dataset was observed with boxplots in order to identify outliers and preliminary trends. The boxplots are generated by grouping the outcome variable for the respective factor level (Figure B.2). Moreover, the main descriptive statistics are summarized in Table B.1.



Figure B.2. (a) Boxplot representation of the measured variable ∆ for each level of the factor *Filler size*; (b) boxplot representation of the measured variable ∆ for each level of the factor *Filling cycles*. Median (blue), mean (red), and outliers (isolated points) are added to the graphical analysis.

Filler size								
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Max	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
1.5	6.39	11.92	15.19	15.32	17.74	26.40	5.24	0.34
5	7.49	10.50	13.71	14.87	18.02	30.18	5.40	0.36
18	5.92	11.51	13.01	14.25	15.13	30.63	5.70	0.40
				Fillin	g cycles			
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Max	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
10	11.62	15.21	18.91	19.04	21.17	30.63	5.24	0.28
15	5.92	10.09	13.33	12.89	14.98	22.79	3.58	0.28
20	6.39	9.57	11.56	12.51	14.54	30.18	4.77	0.38

Table B.1. Summary statistics of the measured variable Δ for each factor level.

By observing the boxplots and the summary statistics for each factor level, outliers were identified corresponding to Δ values close to 30 μm . These values are similar to the outcomes of measures carried out on pores of unfilled supports. Therefore, the outliers are considered representative of partially filled or unfilled pores. These values allow the detection of the treatment's efficacy, meaning one specific treatment might leave some pores unfilled. Therefore, it is chosen to keep them in the dataset to include this information in the analysis.

By analysing the coefficient of variation of Δ for each level of the factor *Filler size* and the length of the boxplot spread in Figure B.2, one can observe how, for all *Filler size*, the data is widespread. This denotes how the pores are not all filled equally with the chosen filling method. Moreover, that by increasing the *Filler size* to 18 µm, outliers are present. This suggests that increasing *Filler size* makes the homogeneous filling of the support even more difficult. Observing the boxplot of Δ for the factor *Filling cycles* (Figure B.2.b) it is denoted how the median of the box for 10 cycles is outside the boxes of 15 and 20 cycles. This notes a Δ larger at 10 cycles with respect to 15 and 20. Inferential statistics can then be implemented in order to understand if these differences are statistically significant.

In order to apply a Two-way ANOVA for the problem at hand, the assumptions of the model need to be fulfilled [1]. In particular:

- i. Homoskedasticity or equality of variances.
- ii. Randomness of sampling.
- iii. Normality of residuals.

With the original distribution of Δ , the normality of residuals is not fulfilled. Therefore, the analysis is peformed with the logarithmic transform of the dependent variable Δ . In this way, the skewness of the original distribution is reduced and the normality assumption is fulfilled (Figure B.3). To further check the validity of the model application, a Levene test for homogeneity of variances (*p*-value = 0.320) and a Shapiro-Wilk test for normality (*p*-value = 0.993) are carried out, both producing a *p*-value greater than 0.05, confirming once again that both assumptions are fulfilled. Moreover, a graphical analysis of the residuals plots confirms the validity of all the other assumptions (Figure B.4).

The ANOVA results are then evaluated via the transformed variable, while the outcome graphical observation is carried out with the original distribution for more clarity. Note that the results of the ANOVA carried out with the original distribution do not yield to a different interpretative ANOVA outcome with respect to the transformed data distribution. In fact, ANOVA has been proven to be robust to slight deviations from normality [2]. However, the variable transformation is carried out to ensure fully meeting all ANOVA assumptions for more integrity.



Figure B.3. (a) Distribution of residuals of ANOVA model obtained with original Δ distribution; (b) normal distribution of residuals of ANOVA model obtained with logarithmic transform of the dependent variable Δ .



Figure B.4. Graphical analysis of residuals for the fitted ANOVA model obtained with logarithmic transform of the outcome variable Δ .

The best fitting ANOVA model has been selected as Two-way ANOVA with interaction term by applying Akaike Information Criterion[3]. The Two-way + interaction design carried in fact 93% of the cumulative model weight (Table B.2).

Table B.2. Akaike Information Criterion table for best fitting model: Two-way ANOVA, Two-way + interaction ANOVA, One-way ANOVA are compared according to their cumulative model weight.

Model type [-]	AIC wt [-]
Two-way + interaction	0.93
One-way on Filing cycles	0.06
Two-way	0.01
One-way on Filler size	0.00

Surface roughness (Ra, Rz)

The examined outcome variables were determined as average surface roughness (Ra), and average profile height (Rz) of a filled support and their deviation from the ones of an unfilled support. In particular:

- i. *Ra* is defined as the average difference between peak and valleys over a set profile measurement length.
- ii. *Rz* is defined as the arithmetic average of the difference between the highest and lowest points of each profile in the evaluated length.

Ra and *Rz* of both a filled and unfilled support were retrieved via contact profilometry by examining 10 random points (subjects) on the surface of a support undergoing a selected treatment. The outcome variables were then calculated according to Eq. 1 and Eq. 2.

$$Ra_{var} = \frac{Ra_{filled} - Ra_{unfilled}}{Ra_{unfilled}}$$
(1)

$$Rz_{var} = \frac{Rz_{filled} - Rz_{unfilled}}{(Rz_{unfilled})}$$
(2)

The dataset was observed with boxplots in order to identify outliers and preliminary trends. The boxplots for Ra_{var} and Rz_{var} are generated by grouping the outcome variable for the respective factor level (Figure B.5, Figure B.6). Moreover, the main descriptive statistics are summarized in Table B.3.



Figure B.5.(a) Boxplot representation of the dependent variable *Ravar* for each level of the factor *Filler size*; (b) boxplot representation of the the dependent variable *Ravar* for each level of the factor *Filling cycles*. Median (blue), mean (red), and outliers (isolated points) are added to the graphical analysis.



Figure B.6.(a) Boxplot representation of the dependent variable *Rz*_{var} for each level of the factor *Filler size*; (b) boxplot representation of the the dependent variable *Rz*_{var} for each level of the factor *Filling cycles*. Median (blue), mean (red) and outliers (isolated points) are added to the graphical analysis.

			Averag	je surface ro	oughness decreas	e (<i>Ra</i>)		
	Filler size							
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Мах	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
1.5	-0.428	-0.258	-0.121	-0.125	-0.047	0.296	0.193	1.51
5	-0.470	-0.330	-0.243	-0.228	-0.110	0.057	0.130	0.57
18	-0.317	-0.204	-0.084	-0.078	0.026	0.287	0.149	1.91
				Fillin	ng cycles			
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Мах	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
10	-0.470	-0.223	-0.078	-0.096	-0.008	0.296	0.186	1.94
15	-0.422	-0.243	-0.197	-0.163	-0.079	0.109	0.135	0.83
20	-0.428	-0.282	-0.215	-0.174	-0.074	0.279	0.179	1.01
			Aver	age profile l	height decrease ((Rz)		
				Fill	ler size			
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Max	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
1.5	-0.482	-0.300	-0.142	-0.143	-0.098	0.240	0.195	1.36
5	-0.452	-0.327	-0.268	-0.142	-0.142	0.123	0.148	1.04
18	-0.371	-0.124	-0.055	-0.060	-0.037	0.300	0.172	2.87
				Fillin	ig cycles			
Levels	Min	1 st quartile	Median	Mean	3 rd quartile	Max	Standard deviation	Coefficient of variation
[-]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]	[-]
10	-0.371	-0.222	-0.070	-0.084	0.065	0.301	0.177	2.10
15	-0.428	-0.298	-0.139	-0.144	-0.032	0.211	0.171	1.20
20	-0.482	-0.335	-0.270	-0.205	-0.093	0.293	0.190	0.93

Table B.3. Summary statistics of the dependent variable Ravar, Rzvar for each factor level.

By observing the boxplots and the summary statistics for each factor level, outliers were identified corresponding to positive Ra_{var} and Rz_{var} values. The presence of positive values indicates an increase of surface roughness after a filling procedure. This could both signify that a spot with higher surface roughness with respect to an unfilled support has been measured or that the treatment created surface disturbances. To retain this information, the outliers are kept in the dataset. By analyzing the coefficient of variation of Ra_{var} and Rz_{var} for each level of both the factor *Filler size* and *Filling cycles* the length of the boxplot spreads in Figure B.5 a and b and Figure B.6 a and b, data variability is quite significant, especially at low *Filling cycles*. This is intrinsical of the nature of the Ra measurements, which can significantly variate for each point of the supports, especially when it is partially unfilled. Moreover, a seemingly linear decrease in Rz_{var} with increasing *Filling cycles* can be noticed. Inferential statistics can then be applied to detect any statistically significant variations for both variables.

In order to apply a Two-way ANOVA for the selected design on Ra_{var} and Rz_{var} , the assumptions for ANOVA must be fulfilled. To check their validity, a graphical analysis of the residuals plots has been carried out and is summarized in Figure B.8. Morover, the normality of the data can be observed in the model residuals histogram in Figure B.7, with a slight skew to the left in case of Ra_{var} . A Shapiro-Wilk test for normality with a *p*-value of 0.7 for Ra_{var} and 0.68 for Rz_{var} confirms the data normality within confidence range, while a Levene test with a *p*-value of 0.186 for Ra_{var} and 0.999 for Rz_{var} confirms homogeneity of variances. Therefore, no data tranformation has been operated for this analysis.



Figure B.7 Distribution of residuals of the ANOVA model obtained with original *Ra*_{var} and *Rz*_{var} distribution.



Figure B.8. Graphical analysis of the residuals for the fitted ANOVA model.

A Two-way ANOVA has been executed for the selected design, with outcome variable Ra_{var} . The insignificacy of the factor *Filling cycles* and interaction term led to the selection of a One-way ANOVA on the Factor *Filler size* as best fitting model by applying Akaike Information Criterion. The one-way design carried in fact 50% of the cumulative model weight (Table B.4). A Tukey pairwise comparison has been then performed as post hoc test to futher understand differences in factor levels (Table B.5). The results of the analysis suggest that the only contributing factor to a change in average surface roughness of the support is the *Filler size*. A Two-way ANOVA has been executed for the selected design on Rz_{var} . This model carried in fact 83% of the cumulative model weight according to the Akaike Information Criterion(Table B.6). Both factors *Filler size* and

Filling cycles are significant as main effects on Rz_{var} , while the interaction term is insignificant. Therefore, a Tukey pairwise comparison has been then performed as post hoc test to futher undestand differences in factor levels (Table B.7).

Table B.4. Akaike Information Criterion table for best fitting model: Two-way ANOVA, Two-way + interaction ANOVA, and One way ANOVA are compared according to their cumulative model weight.

Model type [-]	AIC wt [-]
Two way + interaction	0.02
One way on Filing Cycles	0.00
Two way	0.48
One way on Filler Size	0.50

Table B.5. Tukey pairwise comparison performed on the One-way ANOVA for the Filler size factor.

Cycles [-]			
Levels	p-value	Significance	
5-1.5	0.0373	*	
18-1.5	0.4872	-	
18-5	0.0013	**	

Table B.6. Akaike Information Criterion table for best fitting model: Two-way ANOVA, Two-way + interaction ANOVA, and One way ANOVA are compared according to their cumulative model weight.

Model type [-]	AIC wt [-]
Two way + interaction	0.02
One way on Filing Cycles	0.00
Two way	0.83
One way on Filler Size	0.15

Table B.7. Tukey pairwise comparison performed on the One-way ANOVA for the Filler size factor.

	Filling Cycles [-]	
Levels	p-value	Significance
5-1.5	0.10800	-
18-1.5	0.14000	-
18-5	0.00045	***
	Filler size [µm]	
Levels	p-value	Significance
10-15	0.3450	-
10-20	0.0165	*
15-20	0.3380	-

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Chapter 4 Metallic supported Pd-Ag membranes for Ammonia Decomposition³ and Methane Steam Reforming⁴ in membrane reactors

In this Chapter, an investigation on the applicability of the novel Hastelloy X supported H₂ selective Pd-Ag membranes for integration in fixed-bed membrane reactors for Ammonia Decomposition (AD) and Methane Steam Reforming (SMR) is proposed. Two Pd-Ag membranes (M1 and M2) are prepared on an untreated, 0.5 µm media grade, porous Hastelloy X tubular filter modified with α -Al₂O₃ filler particles and equipped with a γ -Al₂O₃ interdiffusion barrier to reach the desired surface quality and prevent intermetallic diffusion, according to the procedure developed in Chapter 3. The fabricated membranes show the ability to, respectively:

- i. Promote >99% NH₃ conversion above 475 °C with H₂ feed recovery >60% for ammonia decomposition.
- ii. Overcome thermodynamic conversion for conventional methane steam reforming at each of the selected operating conditions with 99.3% permeated H_2 purity.

Both cases are completed by the characterization of the membrane preparation procedure, ideal selectivity, and permeation behavior in presence of binary gas mixtures (N₂-H₂ for NH₃ decomposition and CO-H₂ for SMR, respectively). Both membranes display ideal H₂/N₂ selectivity >10000, while concentration polarization/inhibition effects prove relevant in both analyzed cases.

This chapter is based on the following papers:

³ V. Cechetto[†], S. Agnolin[†], L. Di Felice, A. Pacheco Tanaka, M. Llosa Tanco & F. Gallucci (2023). "Metallic Supported Pd-Ag Membranes for Simultaneous Ammonia Decomposition and H₂ Separation in a Membrane Reactor: Experimental Proof of Concept". *Catalysts*, 13, 920.

⁴ S. Agnolin, L. Di Felice, A. Pacheco Tanaka, M. Llosa Tanco, W. J. R. Ververs, F. Gallucci (2024). "Intensification of Hydrogen Production: Pd–Ag Membrane on Tailored Hastelloy-X Filter for Membrane-Assisted Steam Methane Reforming". *Processes*, 12, 40.

4.1 Introduction

Membrane assisted ammonia decomposition

NH₃ has been gaining increasing interest as potential H₂ carrier. In particular, its endothermic decomposition into N₂ and H₂ and consequent H₂ production have been extensively reviewed in recent years [1]–[4]. Given the advantages in terms of continuous H₂ removal from the reaction zone, H₂ production via Membrane Assisted Ammonia Decomposition (MA-AD) proves itself as an attractive intensification technology. As such, membrane assisted ammonia cracking has been experimentally investigated in several works available in literature, demonstrating that the membrane reactor configuration is expected to significantly enhance ammonia conversion with respect to a conventional packed-bed reactor [5]–[9]. Outstanding performance in terms of NH₃ conversion, hydrogen recovery and purity of hydrogen produced have been obtained when using a Ru-based catalyst and ultra-thin ceramic supported "double skin" Pd-based membranes for hydrogen separation [10][11]. As discussed in previous Chapters, the smooth surface of the ceramic support (with accurate control on porosity and narrow pore size distribution up to a few nanometers) facilitates the deposition of ultra-thin and defect-free palladium layers [12][13].

However, the difficulties in membrane sealing and coupling to stainless-steel reactor modules are still a relevant challenge for the industrial scale up of membrane reactors for ammonia decomposition [14]. These challenges could be overcome by using metallic supported Pd-based membranes, particularily favoring low-cost support options.

In this Chapter, the promising preparation procedure developed in Chapter 3 is employed for the fabrication of Pd-Ag membranes on low-cost, rough, porous Hastelloy X filters. An untreated Hastelloy X filter is filled with α -Al₂O₃ of decreasing size, and equipped with a boehmite-based coating, yielding to a γ -Al₂O₃ interdiffusion barrier. The membrane is completed with electroless plating of a 6-8 µm thick Pd-Ag layer and employed for ammonia decomposition in a Packed-Bed Membrane Reactor (PBMR) configuration. In order to study the performance of the newly developed membrane, its permeation properties are studied both in ideal H₂/N₂ permeation conditions and H₂-N₂ mixture conditions. Finally, to elucidate on the applicability of the membrane in ammonia decomposition reactor equipped with a Ru-Al₂O₃ packed catalyst bed, exploring realistic operating conditions.

Membrane assisted steam methane reforming

The potential of the Membrane Assisted Steam Methane Reforming (MA-SMR) technology for H₂ production, previously discussed in Chapter 1, favored the investigation of possible membrane candidates, such as ceramic-based membranes (i.e. silica [15][16], silica supported on γ -Al₂O₃ [17]) and dense metal membranes, both self-standing and supported. Among them, Pd-based membranes are the most suitable candidates for a membrane reactor for steam methane reforming due to their extensively discussed perm-selectivity to hydrogen. Similarly to ammonia decomposition membranes [18][10], ceramic supported Pd-based membranes are the most widely investigated for this type of application, yielding outstanding hydrogen purity especially if equipped with additional ceramic protective layers [11]; [19]–[22]. However, once again, the drawbacks related to their reactor integration and gas tightness of their sealings remain challenges to overcome, making the investigation of metallic supported membranes of interest also for this application [23][14].

Porous metal filters with controlled surface characteristics at competitive prices for industrial scale-up are scarce on the market. For this reason, the acquisition and modification of cheaper support options would represent a valuable contribution to the scale-up of the technology. Therefore, it is imperative to develop suitable pre-treatments to bring these unrefined, large media grade filters to sufficient surface quality for Pd-Ag deposition in a reproducible way [24]–[27]. In this Chapter, a feasibility study on the integration of the newly developed Pd-Ag membranes (supported on cheap Hastelloy X filters) in a MA-SMR reactor is reported.

The conditioning of a Hastelloy X filter with 0.5 µm media grade and 4.32 µm surface roughness to support a 6-8 µm thick Pd-Ag membrane is proposed. The filter is asymmetrically filled with α -Al₂O₃ of decreasing size, reproducing the procedure that was followed for ammonia decomposition applications [28]. Particular focus is posed on the reproduction of the pore size distribution of the asymmetrically filled support of the ammonia decomposition membrane. Specifically, a reproduction by target method (with the target being the pore size distribution) is characterized via Capillary Flow Porometry (CFP) and surface morphology evolution analysis (via laser-optical confocal microscopy), filling the new support until the desired pore size distribution target is reached. The support is equipped with a y-Al₂O₃ interdiffusion barrier to prevent Pd-support interdiffusion [29]-[36] and the membrane is completed with the Pd-Ag layer via electroless plating. Subsequently, the permeation properties of the membrane are studied in ideal permeation conditions (H₂ and N₂) and CO-H₂ mixture permeation conditions. Finally, the methane steam reforming reaction is performed in a fixed-bed membrane reactor equipped with a Rh-Al₂O₃ packed catalyst bed at different temperatures and pressures, providing insightful information on the behavior of these newly developed membranes during short-term operation.

4.2 Experimental

Membrane preparation and characterization

Two commercial unrefined porous Hastelloy X filters with an outer diameter of 1.2 cm and $0.5 \mu \text{m}$ nominal media grade (MG) were acquired from Hebei Golden Flame Wire Mesh Co, China. The filters were cut to 10 cm length and welded to dense stainless-steel (AISI316L) tubes, to achieve a dead-end configuration (Figure 4.1).

The surface of the filters was modified according to the procedure studied in Chapter 3 and illustrated in Figure 4.2:

- i. The rough filters were polished in an industrial surface finishing machine (ERBA EVT-170) via wet-polishing mechanism for 6 h, delivering a suitable tradeoff between surface roughness reduction and gas permeation preservation [24]. The polished supports were then vertically submerged in Aqua Regia for 30 s, to recover the lost superficial porosity. After the acid attack, the filters were thoroughly rinsed with deionized water to remove all mordant residuals. An oxidation in static air atmosphere was then performed in a furnace for 1 h at 750 °C, with a heating rate of 2 °C min⁻¹.
- ii. The superficial pore size of the supports was improved by filling asymmetrically with α -Al₂O₃ of decreasing particle size by immersion in a magnetically stirred α -Al₂O₃/H₂O suspension improved by dropwise addition of HNO₃ (67 vol.%). The filler was pulled through the superficial pores via vacuum-assisted dip coating, with a lower wait time of 60 s per immersion cycle. Between each cycle, the support was gently rinsed with distilled water. For M1, tested in the ammonia decomposition environment, 20 aspiration cycles were performed with alumina 18 µm (AA-18, Sumitomo), 10 aspiration cycles with alumina 5 µm (AA-5, Sumitomo) and 10 with alumina 1.5 µm (AA-1, Sumitomo). For M2, tested in the methane steam reforming environment, the procedure was slightly modified. In order to reproduce support M1, its superficial pore diameter distribution peak (~100 nm) was set as target. M2 was then reproduced by filling the support up until the target was reached. To achieve overlapping distributions, 30 aspiration cycles were performed with alumina 18 µm (AA-18, Sumitomo), 20 aspiration cycles with alumina 5 µm (AA-5, Sumitomo) and 10 with alumina 1.5 µm (AA-1, Sumitomo).
- iii. Finally, a mesoporous smoothening interdiffusion barrier was deposited on both supports to complete the improvement of their surface uniformity. A solution with boehmite loading 0.9 wt.% was prepared in distilled water, incorporating a water-based solution of organic additives, namely 3.5 wt.% PolyVinyl Alcohol (PVA) (MW 130000) and 1 wt.% PolyEthylene Glycol (PEG) (MW 400). The deposited layer was dried under rotation in a climate chamber at 40 °C and 60% relative humidity for 1 h and sintered for 1 h at 550 °C in a static air furnace.
- iv. A layer of Pd-Åg alloy was deposited onto the treated supports with a 5 h electroless plating procedure (which was reported in previous works by Tanaka et al. [37][38]) up to a 6-8 μ m thick Pd-Åg layer. The membranes were then annealed in 10 vol.% H₂ in Ar at 550 °C for 4 h with a heating rate of 1 °C min⁻¹ under pure Ar atmosphere, to avoid the fragilization of the Pd-Åg layer below 300 °C [39].

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Figure 4.1. Hastelloy X filter welded to a dense, open-end SS316L tube (permeate exit) and to a closed SS316L cap (one-close-end configuration).



Figure 4.2. Illustration of support pre-treatments: the polishing + etching treatment promotes surface smoothening and gas permeation; the asymmetric filling reduces the size of the superficial openings; the mesoporous interdiffusion barrier deposition prevents Pd-support interaction while improving the support's surface morphology.

The preparation procedure of both membranes was analyzed with the following characterization techniques:

- i. The surface roughness of the untreated and pre-treated filters was measured via contact profilometry (MarSurf PS 10). The media grade and elemental composition of the supports was provided by the supplier.
- ii. The N₂ permeance of the untreated and pre-treated filters was measured in a gas permeation setup, described in Chapter 2 [24].
- iii. The presence of α-Al₂O₃ filler particles embedded in the treated filters was verified via Scanning Electron Microscopy and Energy Dispersive X-Ray analysis (SEM-EDX, Phenom Pro, ThermoFisher) of a twin filled filter's cross section. To preserve the metallographic structure of the porous metal, the samples were prepared via scoring and breakage of the tube and observed as is.
- iv. The pore size distribution evolution of M2's support during the reproduction procedure was measured via Capillary Flow Porometry (CFP) in the tailor-made setup described in Chapter 3.
- v. The superficial morphology of the filters was observed via laser-optical confocal microscopy (VKX-3000, Keyence), both before and after interdiffusion layer deposition.
- vi. The thickness of the Pd-Ag layer was measured on a twin membrane, prepared with the same electroless plating procedure, via SEM imaging with a Fei-Quanta-FEG250-3D.

Membrane assisted ammonia decomposition tests

Ammonia decomposition tests were performed in a stainless-steel tubular membrane reactor (internal diameter = 4.5 cm, length = 28 cm) by fully submerging M1 in a packedbed of catalyst (250 g, commercial 2 wt.% Ru/Al₂O₃, 3 mm pellets, Alfa Aesar).

Heat is supplied to the reactor by an electrical split oven with three independently controlled heating sections. A porous stainless-steel plate at the bottom of the reactor is used to ensure uniform gas distribution at the reactor inlet. The feed gases (NH₃, H₂, and N₂) are controlled by mass flow controllers (Bronkhorst) and the pressure of the system is controlled by a backpressure regulator (Bronkhorst) at the retentate side. The permeate side of the membrane is connected to a film-flowmeter (Horiba Stec VP3/VP4) to determine the permeation flowrate. The retentate side of the membrane, after passing through a gas filter which aims at protecting the downstream equipment from fine particles, is sent to a micro-GC (Varian CP-4900) to measure its composition. The retentate and permeate lines are subsequently mixed and sent to a water absorption unit in which possible traces of NH₃ are absorbed, preventing their release in atmosphere. A schematic representation of the setup is shown in Figure 4.3.



Figure 4.3. Ammonia decomposition setup: (1) mass flow controllers (Bronkhorst) for NH_3 , H_2 , and N_2 gas feed; (2) packed-bed membrane reactor with oven temperature control and indication; (3) analysis zone with micro-GC (Varian) and bubble flowmeter (Horiba); (4) NH_3 absorption in water.

Before its integration in the reactor, M1 was sealed with graphite tape and pressed in a stainless steel ring (internal diameter = 1.3 cm) in order to exclude any possible leaks from the welding cord at the dead-end cap. The membrane was then tested in helium/ethanol in order to verify the absence of undesired leakages from both the sealing and Pd-Ag surface. The reactor was heated up to 500 °C at a heating rate of 2 °C min⁻¹ in N₂ atmosphere and activated with 1 L min⁻¹ of H₂ until stable permeation. Subsequently, single gas (H₂/N₂) and binary mixture (H₂-N₂) permeation tests were performed, followed

by permeation tests under reactive conditions. The explored operating conditions are summarized in Table 4.1.

Single gas permeation tests			
Investigated gases [-]	H ₂ , N ₂		
Temperature [°C]	400, 425, 450, 475, 500		
Retentate pressure [bar]	2, 3, 4, 5, 6		
Permeate pressure [bar]	1		
Binary mixture permeation tests			
Binary mixture [-]	H ₂ -N ₂		
Temperature [°C]	400, 425, 450, 475, 500		
Retentate pressure [bar]	2, 3, 4, 5, 6		
Permeate pressure [bar]	1		
N ₂ in feed [vol.%]	5, 10, 15, 30, 50		
Ammonia decomposition			
Temperature [°C]	425, 450, 475, 500		
Retentate pressure [bar]	3, 4, 5, 6		
Permeate pressure [bar]	1		
NH ₃ feed flow rate [L _N min ⁻¹]	0.5		

Table 4.1. Overview of the experimental conditions investigated in this work.

The reaction performance was monitored until steady state operation was observed. The permeate flowrate and the composition of the retentate stream were measured 5 times. NH₃ conversion (X_{NH3}) (Eq. 1) and H₂ recovery (*HRF*) (Eq. 2) were then calculated as the ratio between consumed ammonia and fed ammonia, and the ratio between the permeating H₂ and the maximum amount of H₂ producible at full conversion, respectively.

$$X_{\rm NH_3} = \frac{\rm NH_{3,in} - \rm NH_{3,out}}{\rm NH_{3,in}}$$
(1)

$$H_{2,recovery} = \frac{H_{2,permeate}}{1.5 \text{ NH}_{3,in}}$$
(2)

Membrane assisted methane steam reforming tests

Methane steam reforming tests were performed in a stainless-steel tubular membrane reactor (internal diameter = 4.5 cm, length = 28 cm) where the Pd-Ag membrane (M2) was immersed in a packed-bed of catalyst (300 g, commercial 2 wt.% Rh/Al₂O₃, 1 mm spheres, Jonson Matthey).

The reactor temperature is controlled by an external oven via three thermocouples placed at three different heights. The reaction temperature is monitored with three thermocouples inside of the reactor. The reactor is equipped with a porous stainless-steel gas distributor in order to ensure uniform reactant gas feeding. The feedstock gases (CH₄ and N_2) are fed via mass flow controllers (Bronkhorst), while steam is fed through a controlled evaporation system (Bronkhorst). Note that N_2 was fed as an internal standard to verify the correctness of the experimental mass balance. The reaction products are rid of steam with downstream water coolers both at the retentate and permeate side, while the gases are sent to a micro-GC (Interscience, Compact GC 4.0, 3 channels) for analysis. Moreover, the permeate and retentate streams flow through a bubble flowmeter (Horiba Stec VP3/VP1) to fully characterize the outlet flowrates. The permeate stream tube can be closed to perform standard methane steam reforming experiments, opened to have the permeate stream at atmospheric pressure, or connected to a vacuum pump for H₂ to increase the permeating flow, if necessary. The reaction pressure is controlled with a backpressure regulator (Bronkhorst) at the retentate side. A schematic representation of the setup is given in Figure 4.4.



 Figure 4.4. Steam methane reforming setup: (1) gas feeding system (CO, N₂, H₂, CH₄, and Air via Bronkhorst mass flow controllers); (2) controlled evaporation system for steam feed; (3)
membrane reactor with oven temperature control and indication; (4) steam condensation system; (5) analysis zone (micro-GC and Horiba bubble flowmeters). Before the integration in the reactor, membrane M2 was sealed with graphite tape, pressed into a stainless-steel ring (internal diameter = 1.3 cm). A helium leak test was performed by introducing He at 1 bar through the bore of the membrane and bubbling it through ethanol to detect any possible leakages. As no leakages were observed, the membrane was connected to the reactor flange via Swagelok fittings. The reactor was heated to 500 °C under N₂ flow with a 2 °C min⁻¹ heating ramp. The membrane was then activated in a H₂ flow of 1 L min⁻¹ until stable permeation. Subsequently, single gas (H₂ and N₂) and binary mixture (CO-H₂) gas permeation tests were performed. The reactor was cooled down with a 1 °C min⁻¹ rate, and M2 was submerged in the catalyst bed. The heating and activation were performed once again, reaching 400 °C. The procedure followed with permeation tests in reactive conditions. During methane steam reforming operation, vacuum was applied to the permeate side to maximize H₂ permeance. The explored operating conditions are summarized in Table 4.2.

Single gas permeation tests				
Investigated gases [-]	H ₂ , N ₂			
Temperature [°C]	400, 450, 5	500		
Retentate pressure [bar]	2, 3, 4			
Permeate pressure [bar]	1			
Binary mixture permeation tests				
Binary mixture [-]	CO-H ₂			
Temperature [°C]	400, 450, 500			
Retentate pressure [bar]	2, 3, 4			
Permeate pressure [bar]	1			
CO in feed [vol.%]	5, 10, 15			
Metha	ane steam reforming			
	Membrane assisted	Conventional		
Temperature [°C]	400, 450, 500	400, 450, 500		
Retentate pressure [bar]	2, 3, 4, 5	4		
Permeate pressure [-]	Vacuum	-		
CH₄ in feed [vol.%]	24	24		
Steam to Carbon ratio [-]	3:1	3:1		

Table 4.2. Explored experimental conditions for single gas permeation tests, binary mixture permeation tests, and M2- assisted SMR reaction tests. For SMR, a reference case without membrane was investigated at 4 bar (retentate side) for each examined temperature.

Single gas permeation tests were performed at three different temperatures (400, 450, and 500 $^{\circ}$ C) and pressures (1, 2, and 3 barg), to fully characterize H₂ permeance and ideal H₂/N₂ selectivity.

Following the ideal conditions, CO-H₂ mixture tests were performed to assess the effect of CO on the H₂ permeance of the membrane. Specifically, the explored concentrations of CO ranged between 5 to 15%, since a highly selective membrane would not allow > 15% of CO to permeate through. For each explored concentration, hydrogen permeation flux was evaluated at 400, 450, and 500 °C and 2, 3, and 4 bar at the retentate side.

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Methane steam reforming tests were performed at 400, 450, and 500 °C to study realistic membrane operation temperature. For each temperature, a conventional methane steam reforming reaction was carried out at the reference pressure of 4 bar (retentate side) by closing the permeate stream. Once the reference case was assessed, the permeate stream was restored and the membrane-assisted methane steam reforming was performed in the specified pressure range (Table 4.2). For all the cases, the reaction performance was monitored until steady operation. The composition and flowrates of both permeate and retentate streams were measured 5 times, as well as both outlet flowrates. CH₄ conversion (X_{CH4}) was calculated as the consumed methane over the total methane inlet (Eq. 3); H₂ recovery factor (*HRF*) as the permeated hydrogen over the maximum amount of hydrogen producible at full conversion (Eq. 4), hydrogen separation factor (*SF*) as the permeating hydrogen over the total hydrogen produced by the current reaction (Eq. 5), and hydrogen purity (*HP*) as the percentage of H₂ detected in the permeate stream.

$$X_{CH_4} = \frac{CH_{4,in} - CH_{4,out}}{CH_{4,in}}$$
(3)

$$H_{2,recovery} = \frac{H_{2,permeate}}{_{3} \cdot CH_{4,in}}$$
(4)

$$H_{2,separation} = \frac{H_{2,permeate}}{H_{2,produced}}$$
(5)

4.3 Results and discussion

Membrane preparation

The surface of the acquired porous Hastelloy X filters presents large average surface roughness (*Ra*). Therefore, before the tailored support filling procedure, both Hastelloy X filters (M1's support and M2's support) were polished, reducing their initial surface roughness (*Ra*) from 6.23 μ m (M1) and 4.32 μ m (M2) to 1.1 μ m (M1) and 0.9 μ m (M2). For elucidatory purposes, the surface evolution with each pre-treatment of a twin support is shown via SEM imaging in Figure 4.5. The untreated filter presented superficial pore mouths larger than 50 μ m, which were partially closed during the wet-polishing treatment (Figure 4.5.a, Figure 4.5.b). The loss in superficial porosity due to the polishing procedure was then recovered with the chemical etching, as confirmed by the superficial cracks in Figure 4.5.c. These cracks promote gas permeation while preserving the smoothening and closing effect of the polishing treatment (increase in N₂ permeance from ~1×10⁻⁵ mol m² s⁻¹ Pa⁻¹ to ~ 5×10⁻⁵ mol m² s⁻¹ Pa⁻¹ at 1 bar trans-sample pressure for both filters). However, some of the largest pore mouths remained untouched by the selected pre-treatments.

The depth of these valleys was filled with α -Al₂O₃ of decreasing size, promoting both surface leveling and pore size distribution reduction (Figure 4.5.c). The presence of the alumina filler in the support's structure is further confirmed in Figure 4.6 by SEM examination of the twin support's cross section, which confirms the presence of the filler not only onto the superficial pore openings, but also well inside the pore necks, guaranteeing a reduction of the average pore diameter and thus avoiding the collapse of the palladium film inside the pore during electroless plating deposition.

In Figure 4.7, the surface morphology of a superficial pore mouth after filling and interdiffusion barrier deposition is shown in laser-optical view and height distribution. In Figure 4.7a, the presence of the asymmetrical filling configuration is clearly distinguishable, with filler of lower dimension (5 and 1.5 µm) laying onto larger alumina particles (18 µm), clogging a pore of the metallic filter. In the height distribution view (right), the highest and lowest points of the surface can be observed in red and blue, respectively. The filler particles can be observed in green, while the presence of blue zones indicates that the large pore structure has been reduced into relatively smaller (<50 um) scattered pores. In Figure 4.7b, the leveling effect and the further reduction of the size of superficial openings thanks to the y-Al₂O₃ interdiffusion barrier deposition is clearly observable in the laser-optical imaging. In the height distribution view, a reduction in the diameter of blue zones (lowest height points, corresponding to superficial openings) can be observed. Furthermore, the height distribution is more symmetrically centered around 0 (green) with respect to Figure 4.7a, indicating a more uniform surface. In Figure 4.8, the cumulative flow distribution through M1's support, obtained via CFP after each modification step, is shown. After the polishing and etching pre-treatments, the filter presented wide pore size distribution and high gas permeance. However, after asymmetrically filling with α -Al₂O₃, the detected average pore diameter was ~150 nm. The deposition of the interdiffusion barrier promoted further sharpening of the pore size distribution towards pores of ~60 nm. This value proved comparable to the target of 100 nm, representing the average pore diameter of a ceramic support for highly selective Pd-Ag membranes [13] for ammonia decomposition. In Figure 4.9, the pore size distribution

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evolution of M2 after successive fillings with a-Al₂O₃ 18, 5, and 1.5 µm is shown. In particular, the pore size distribution peak of filled M1's support [28] was taken as reference for support reproduction, while the filling procedure was repeated on M2 until its distribution peak was comparable to the < 100 nm target imposed by M1. The pore size distribution shifted towards smaller sizes as smaller particles were introduced in the pores (decreasing with each batch of fillings of alumina 18 µm and 5 µm and reaching the target distribution after the last 10 fillings with alumina 1.5 µm). Specifically, as elucidated in Chapter 3 [25], the 18 µm particles clog the largest pores of the filter, while by adding 5 µm and 1.5 µm particles an asymmetric structure is formed similarly to the case of asymmetric ceramic supports. By proceeding step by step, the reproduction by target of M1's support proved successful, resulting in a final support with average pore size ~60-90 nm. In Figure 4.10, the cross section of a twin Pd-Ag layer produced with the chosen plating parameters is shown. In particular, the metallic support, the interdiffusion barrier, and the double plated Pd-Ag layer (average thickness = 6-8 µm) can be clearly distinguished. The same average layer thickness is taken as reference for the M1 and M2 membrane. Moreover, in Figure 4.11, the surface of M1 is observed via confocal laser and optical microscopy. Particularly, the selected superficial section is fully closed by the deposited Pd-Ag layer. This is possible due to the filter pre-treatments and two-step modification, which guarantee the formation of the fully dense Pd-Ag layer.



Figure 4.5. Surface SEM imaging of: (a) an untreated Hastelloy X filter; (b) the Hastelloy X filter after 6 h of wet-polishing treatment; (c) the Hastelloy X filter after etching and filling with α-Al₂O₃ of decreasing particle size, magnified to 10000x on a filled superficial pore mouth.



Figure 4.6. Cross sectional SEM of a twin porous Hastelloy X support filled asymmetrically with α -Al₂O₃ of decreasing particle size.



Figure 4.7. Surface morphology imaging and height distribution view obtained via laser-optical confocal microscopy of: (a) a superficial pore mouth on the M2 support, asymmetrically filled with α -Al₂O₃ of decreasing particle size; (b) a superficial pore mouth on the M2 support, asymmetrically filled with α -Al₂O₃ of decreasing particle size and equipped with a γ -Al₂O₃ interdiffusion barrier.



Figure 4.8. Cumulative flow distribution curves obtained via CFP of the M1 support: cumulative percentage of N₂ flow through the wet sample over the N₂ flow through the dry sample as a function of the correlated pore diameter. The measurements are repeated after each pre-treatment on the Hastelloy X filter.



Figure 4.9. Pore diameter distribution shift, retrieved via CFP, of the M2 support after multiple filling cycles with α -Al₂O₃ particles of 18, 5, and 1.5 μ m, compared with the reference target of M1 support [28].



Figure 4.10. Cross-sectional SEM imaging of a 6-8 μm thick Pd-Ag layer, obtained via double 5-h electroless plating procedure on a Hastelloy X support equipped with a γ -Al_2O_3 interdiffusion barrier.



Figure 4.11. Laser-optical confocal imaging and height distribution view of M1 Pd-Ag layer, deposited after the selected pre-treatments.

M1-assisted ammonia decomposition

The measured hydrogen and nitrogen permeances at 400, 450, and 500 °C and 1 bar pressure difference across M1 are listed in Table 4.3, with the corresponding ideal selectivity. The experimental results show that the H₂ permeance significantly increases with increasing temperature, whereas N₂ permeance is less affected by the temperature variation. This results in increasing H₂/N₂ ideal selectivity when increasing temperature.

Temperature [°C]	H ₂ permeance [mol/s/m ² /Pa]	N ₂ permeance [mol/s/m ² /Pa]	H₂/N₂ selectivity [-]
400	5.8·10 ⁻⁷	1.1·10 ⁻¹⁰	5287
450	6.6·10 ⁻⁷	1.1·10 ⁻¹⁰	5892
500	7.3·10 ⁻⁷	1.9·10 ⁻¹¹	38839

Table 4.3. H_2 permeance, N_2 permeance, and ideal H_2/N_2 selectivity of M1 at 400, 450, and 500 $^\circ C$ and 1 bar trans-membrane pressure.

In Figure 4.12, the hydrogen flux through M1 at different temperatures is represented as a function of the trans-membrane pressure. The best fit for the hydrogen fluxes and the hydrogen partial pressure difference across the membrane is found for a *n*-exponent value of 0.69. In Pd-based membranes, the pressure exponent is 0.5 when the rate limiting step is diffusion through the bulk of palladium. A value of *n* deviating from 0.5 may indicate the presence of a contribution of the metallic support to the H₂ transport mechanism, external mass transfer limitations, or limitations in the surface reactions [40] [41].



Figure 4.12. Linear regression performed on H₂ permeating flux vs H₂ partial pressure under pure gas permeation tests of M1, evaluated at 1, 2, and 3 bar trans-membrane pressure and at a temperature of 400, 425, 450, 475 and 500 °C, to retrieve the characteristic *n*-exponent of the membrane.
From the Arrhenius plot of hydrogen fluxes through the membrane, measured in the temperature range between 400 °C, and 500 °C, the activation energy for hydrogen permeation through the membrane is estimated as 9.1 kJ mol⁻¹. This value is well in agreement with previously reported values of apparent activation energy for Pd-based membranes [31][24][42]. The calculated value for activation energy lumps the activation energy required for hydrogen permeation through the selective layer of the membrane and the activation energy required for hydrogen to permeate through the membrane support. In Figure 4.13 the effect on the separation performance of M1 of different nitrogen concentration in the feed is shown. Specifically, the hydrogen permeation flux through the membrane is represented as a function of the hydrogen partial pressure difference across the membrane for a H_2-N_2 feed mixture containing nitrogen between 5 vol.% and 50 vol.%. The results of the single gas hydrogen permeation tests are also reported and used as benchmark for comparison. The membrane separation performance is different compared to the case in which the pure hydrogen permeation test was performed. When the N₂ concentration in the feed mixture increases, a lower amount of hydrogen is available for separation and therefore, at constant pressure difference across the membrane, the hydrogen permeation flux decreases. Moreover, a lower hydrogen partial pressure in the feed mixture results in lower driving force for hydrogen separation, which in turn leads to lower hydrogen permeation. This discrepancy in the results arises from a a mass transfer limitation phenomena known as concentration polarization. In line with literature, mass transfer limitations become more remarkable when the hydrogen concentration in the feed mixture decreases as well as when the pressure difference across the membrane increases [43][44]. As a result of concentration polarization, a lower amount of hydrogen is recovered at constant hydrogen partial pressure difference across the membrane. Moreover, H₂ permeation across Pd-based membranes being an activated process, the hydrogen flux across Pdbased membranes increases with temperature. Therefore, the higher the temperature, the higher the amount of hydrogen that permeates, and thus the higher the concentration polarization effect.



Figure 4.13. H₂ permeation flux under N₂/H₂ binary mixture test conditions, evaluated at a temperature of 450 °C with 5, 10, 15, 30, and 50 vol.% of N₂ in the feed flow and compared with pure H₂ permeation flux evaluated at the same conditions. The effect of temperature and pressure on ammonia conversion and hydrogen recovery is shown in Table 4.4 and Table 4.5, respectively.

Temperature [°C]	Thermodynamic equilibrium conversion [%]	NH₃ conversion [%]	H₂ recovery [%]	
425	97.0	84.2	37.6	
450	97.8	98.2	55.5	
475	98.3	99.2	60.7	
500	98.7	99.3	62.9	
Read	Reaction pressure = 5 bar, NH_3 feed flow rate = 0.5 L _N min ⁻¹			

Table 4.4. NH_3 conversion and H_2 recovery evaluated at 425, 450, 475, and 500 $^\circ C$ with 4 bar trans-membrane pressure.

Table 4.5. NH₃ conversion and H₂ recovery aevaluated at a temperature of 475 °C and a transmembrane pressure of 2, 3, 4, and 5 bar.

Pressure [bar]	Thermodynamic equilibrium conversion [%]	NH₃ conversion [%]	H₂ recovery [%]	
3	99.0	99.2	42.7	
4	98.7	99.2	51.9	
5	98.3	99.2	60.7	
6	98.0	99.1	66.1	
Rea	Reaction temperature = 475 °C, NH ₃ feed flow rate = $0.5 L_N$ min ⁻¹			

As shown in Table 4.4, the increase in temperature results in higher ammonia conversion as well as in higher hydrogen recovery. The increase in ammonia conversion can be ascribed to the more favorable kinetics and thermodynamics of reaction when operating the reactor at high temperature, whereas the improved hydrogen recovery results from the higher hydrogen partial pressure in the reactor, which in turn leads to higher driving force for hydrogen separation. Moreover, as shown in Table 4.4 and Figure 4.14, NH_3 conversion in the membrane reactor is higher than the calculated thermodynamic equilibrium conversion of the conventional reactor (without H_2 separation membrane) for temperatures above 450 °C. Overall, these results are well in agreement with other literature studies [5]–[7]; [9]; [45].



Figure 4.14. NH₃ conversion achieved in the membrane reactor fed with 0.5 L_N min⁻¹ of pure NH₃ at a temperature of 425, 450, 475, and 500 °C and with a retentate pressure of 5 bar, compared to the thermodynamic equilibrium conversion of the conventional system evaluated at the same operating conditions.

More specifically, in Table 4.6 a comparison with the results of Cechetto et al. [45], obtained under similar operating conditions, in the same equipment, and using a ceramic supported membrane, is presented. The lower H₂ permeance and length of the M1 membrane used in this work (10 cm, due to ease of preparation and handling) result in a decreased H₂ recovery and NH₃ conversion (the latter being particularly evident at the lowest temperature of 425 °C, while reaching >99% at T >475 °C). Highly selective metallic supported membranes display in fact lower H₂ permeance compared to the ceramic supported equivalents. This difference is to be attributed to the intrinsic difference in the support's porosity, the necessity for a filler to reduce the metallic support interaction phenomena [29][25].

Hydrogen recovery can be improved by increasing the reactor operating pressure, which means increasing the driving force for hydrogen separation (Table 4.5). It is worth noticing that, while in a conventional system a pressure increase has a significantly negative impact on NH_3 conversion, in a membrane reactor, in the investigated pressure

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range, the decrease in NH₃ conversion due to increasing pressure is rather minor. The decrease in NH₃ conversion that is expected at high pressure according to the Le Châtelier's principle is thus counterbalanced by the fact that a pressure increase improves the hydrogen removal from the reaction zone, resulting in shifted equilibrium which in turn enhances ammonia conversion. In view of these results, despite the need to scale-up membrane length and optimize membrane's H₂ permeation properties, the proposed pre-treated metallic supports are a suitable alternative to ceramic ones for the fabrication of Pd-based, H₂ selective membranes to be used in ammonia decomposition membrane reactors.

This work	Cechetto et al. [45]
Supported tubular Pd- based membrane	Supported tubular Pd-based membrane with a porous Al ₂ O ₃ -YSZ protective layer
Metallic (Hastelloy X)	Ceramic (Al ₂ O ₃)
Pd-Ag	Pd-Ag
~ 6-8	~ 6-8
90	195
6.6·10 ⁻⁷	1.2·10 ⁻⁶
5890	68960
NH₃ conversion* [%]	
84.2 98.2 99.2 99.3	96.5 99.7 99.8 99.8
H₂ recovery [*] [%]	
37.6	79.5
55.5	87.5
60.7	88.9
62.9	88.9
	This work Supported tubular Pd-based membrane Metallic (Hastelloy X) Pd-Ag ~ 6-8 90 6.6·10 ⁻⁷ 5890 NH ₃ C 84.2 98.2 99.3 H2 I 37.6 55.5 60.7 62.9 g feed flow rate = 0.5 Ln min

Table 4.6. Comparison between the experimental results achieved in this work and in the work of
Cechetto et al. [45].

M2-assisted methane steam reforming

 H_2 and N_2 permeance and ideal H_2/N_2 selectivity of M2 are shown in Table 4.7. The H_2 permeance exhibits the typical behavior for Pd-Ag films, showing an increased value at higher temperatures due to the activated nature of the solution diffusion mechanism for hydrogen permeation through Pd membranes. Meanwhile, the N₂ permeance decreases with increasing temperature, exhibiting the presence of Knudsen-type of transport of N_2 through possible isolated defects in the membrane and/or its welding parts between porous and dense metals. However, since the N_2 permeance is still extremely low, the increase in H₂ permeance with temperature prevails, resulting in increasing H_2/N_2 selectivity at high temperatures.

Temperature [°C]	H ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	N ₂ permeance [mol m ⁻² s ⁻¹ Pa ⁻¹]	H ₂ /N ₂ selectivity [-]
400	6.3·10 ⁻⁷	5.5·10 ⁻¹¹	11454
450	6.4·10 ⁻⁷	3.8·10 ⁻¹¹	16842
500	7.5·10 ⁻⁷	3.7·10 ⁻¹¹	20270

Table 4.7. H₂ permeance, N₂ permeance, and ideal H₂ selectivity of M2 at 400, 450, and 500 °C and 1 bar trans-membrane pressure.



Figure 4.15. Linear regression performed on H_2 permeating flux vs H_2 partial pressure under pure gas permeation tests of M2, evaluated at 1, 2, and 3 bar trans-membrane pressure and at a temperature of 400, 450, and 500 °C, to retrieve the characteristic *n*-exponent of the membrane.

The linear regression performed on the H_2 permeation flux across the membrane as a function of temperature resulted in an *n*-exponent of 0.53 with an average R_{sq} of 0.999 for all considered temperatures (Figure 4.15). This value slightly deviates from the 0.5 exponent of a purely Sieverts-driven transport mechanism, highlighting the possible effect of the support (i.e.: interdiffusion barrier and/or filler) on the hydrogen transport **113** | Metallic supported Pd-Ag membranes for Ammonia Decomposition and Methane Steam Reforming in membrane reactors

mechanism. The activation energy for this membrane amounts to 9.3 kJ mol⁻¹, a value in the same order of magnitude as the typical ones for metallic supported membranes [31][24][42]. This value entails the activation energy contributions of hydrogen transport through the Pd-Ag layer, through the interdiffusion barrier (mesoporous, which implies a lower activation energy value given by Knudsen-type transport), through the filler, and the porous metal support (both likely contributing with viscous flow type of transport) [21][29].

Following the single gas tests, a CO-H₂ binary mixture was fed to the membrane and analyzed to simulate the main permeating species during the steam methane reforming reaction. In Figure 4.16, the permeation flux of hydrogen is shown as a function of CO partial pressure in the feed. CO is well known to inhibit the Pd surface, occupying active sites for hydrogen splitting, significantly reducing the H₂ permeation flux [46][47]. Furthermore, concentration polarization effects can occur and both effects can synergically lower H₂ flux across the membrane [19][43][48]. In this case, a mass transfer limitation effect is observed with decreasing H₂ partial pressure and therefore increased CO concentration in the feed, with a progressively reduced H₂ flux compared to the pure H₂ permeation case. In the case of a H₂ and CO mixture in the feed, the flow reduction with respect to the pure H₂ at 1 bar, 5% of CO in the feed, and 450 °C amounts to 64.6%. This value implies a significant reduction that cannot solely be explained by mass transfer limitation effects.

Firstly, the behavior of the hydrogen flux in presence of CO was studied by fitting the CO- H_2 binary mixture tests with the model equation proposed by Barbieri et al. [46]:

$$H_2 \text{ permeance} = (1 - \alpha(T) \frac{K_{CO} P_{CO}}{1 + K_{CO} P_{CO}}) \pi_0 e^{-\frac{E_a}{RT}}$$
(7)

By assessing H₂ permeance at two different CO partial pressures, it is possible to retrieve the α reduction factor and the Langmuir affinity K_{CO}. However, since M2 is a very thin membrane (6-8 µm), mass transfer limitation effects are expected, which should be considered together with the depletion effect. To better decouple mass transfer limitation and CO inhibition contributions, a model which predicts external mass transfer limitation effects (via a Sherwood correlation) and the depletion effect was developed. The effect of CO inhibition was then quantified by fitting the Langmuir-Sieverts equation with the developed model. Moreover, the use of the model allowed to calculate the Langmuir parameters for CO inhibition, resulting in values of $\alpha = 0.56$ and K_{CO} = $5.7 \cdot 10^{-5} \text{ Pa}^{-1}$ (values that are in line with literature values for similar types of membranes [46]).

The resulting CO inhibition curve (Figure 4.17a, red) initially shows a sharp reduction in H_2 permeance with respect to pure H_2 right after the introduction of 5% CO (CO partial pressure 10 kPa), with a less pronounced decrease in H_2 permeance for CO partial pressures larger than ~10 kPa. This behavior suggests that for feed CO concentrations above 5% the membrane surface is progressively saturated with CO, making the H_2 flow reduction due to CO inhibition less pronounced. On the other hand, by increasing the CO partial pressure, the mass transfer limitation effect proportionally increases (Figure 4.17a, blue). This has been already reported also for thicker membranes and explained with DFT calculations by Gallucci et al. [49]. These behaviors can be further observed in Figure 4.17b, where both contributions to H_2 flow reduction are quantified. At the highest CO partial pressure (30 kPa, corresponding to 15% CO in the feed), the H_2 permeance reduction due to CO inhibition corresponds to 59% with respect to the pure H_2 gas, while

the contribution due to mass transfer limitation effect is 48%. Even though the CO inhibition contribution prevails, at larger CO partial pressures it increases with a lower slope with respect to the mass transfer limitation contribution. On the other hand, the mass transfer limitation contribution to H₂ flow reduction keeps proportionally increasing with a larger slope when CO partial pressure in the feed increases. This behavior further confirms the membrane's progressive surface saturation with CO gas.



Figure 4.16. H₂ permeation flux under CO-H₂ binary mixture test conditions, evaluated at a temperature of 450 °C with 5, 10, and 15 vol.% of CO in the feed flow and compared with the pure H₂ permeation flux evaluated at the same conditions.





Eq. 7 of the Sieverts-Langmuir model by Barbieri et al. (black, dashed); (2) predictive mass transfer limitation model by Ververs et al. (blue, dashed); (3) sole CO inhibition contribution (red, dashed); (b) H₂ permeatin flux reduction given by CO inhibition (red) and mass transfer limitations (blue).

While performing CO-H₂ binary mixture tests the presence of methane was detected in the permeating flow, without any CO detection. In Figure 4.18, the presence of methane in the permeating flow is shown as a function of CO concentration in the feed flow. The CH₄ in the permeating flow reached values close to 275 ppm at 500 °C and at higher trans-membrane pressure. This behavior is in accordance with methanation reaction thermodynamics:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O, \ \Delta H^0 = -206 \text{ kJ mol}^{-1}$$
 (8)

Which is favored at high pressure and at low temperature (exothermic), with an almost complete CO conversion below 450 °C. The permeation of CO, which turns into CH₄ in the permeate stream in presence of H_2 , might indicate the presence of defects on the membrane surface which expose the Nickel-Iron of the metallic support, which in turn could catalyze the methanation reaction (Methane presence was not previously detected with ceramic supported membranes tested in the same equipment, excluding possible catalytic activities of the stainless-steel reactor and Swagelok stainless-steel connections) [50]. The catalytic activity of the steel-based supports towards methanation was previously verified by Medrano et al. [23] by testing a bare, porous metallic support similar to the one employed in this work, without any Pd-Ag layer. In their work, hydrogen conversion through the metallic support was detected. However, the direct presence of methane in the examined flow was not verified [23]. The presence of CH₄ as pollutant in the permeate stream is much less detrimental with respect to the poisoning effect of CO to most fuel cells and catalysts. Thus, the removal of CO from H₂ stream in the permeate side of the membrane reactor is a further advantage resulting from the use of these metallic membrane supports.



Figure 4.18. CH₄ concentration in the permeate stream evaluated at a temperature of 500 °C and 1, 2, and 3 bar trans-membrane pressure, with 5, 10, and 15 vol.% of CO in the feed flow.

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In Table 4.8 and Table 4.9, the results of M2-assisted SMR studies are shown. In particular, the effect of operating temperature and pressure on methane conversion, hydrogen recovery and separation factor are listed. The methane conversion increases with temperature as expected for typical methane steam reforming processes. With the selected catalyst, at the selected operating parameters, the thermodynamic equilibrium conversion is reached without the membrane (conventional process). Upon membrane installation, the thermodynamic equilibrium conversion of the conventional process is overcome for each of the investigated temperatures, with the highest CH₄ conversion at 500 °C. Ath this temperature, the hydrogen flux across the membrane is higher and the reaction rates are faster. Similarly to the previously investigated ammonia decomposition membrane reactor [28], the methane conversion increases when increasing the transmembrane pressure. This behavior is in contrast with what is expected from the conventional process, in which methane conversion decreases with increasing pressure due to thermodynamic constraints. However, in the case of a membrane reactor, the membrane's presence counterbalances the detrimental pressure effect, which is instead beneficial for H₂ permeation and increases the H₂ removal contribution owing to le Chatelier's principle [51].

Hydrogen recovery and separation factors are strictly correlated to membrane performance. However, it is important to consider that the low achievable conversion at the selected operating conditions has a direct influence on the hydrogen recovery and separation factor, as well as the low membrane surface area considered in this study. Both hydrogen recovery factor and separation factor increase when the operating transmembrane pressure is increased, due to the increased H_2 permeation flux through the membrane. At the highest temperature and pressure (500 °C and 5 bar) 42.2% of the produced hydrogen passes through the membrane to the permeate side. This parameter can give more indication on effective membrane performance as it accounts solely for the hydrogen produced by the process with its actual methane conversion. The lower H₂ permeance of the metallic supported membrane with respect to the one of the ceramic relatives directly influences the separation factor. Optimization on gas permeance increase across the membrane surface and/or installed membrane area increase will contribute to a large improvement of the separation factor and, in turn, hydrogen recovery and achievable CH₄ conversion. Moreover, the presence of competing gases in the reaction zone and along the membrane surface (e.g., CO, CH₄, H₂O, CO₂, N₂) might significantly enhance mass transfer limitation effects, decreasing the H₂ permeating flux across the membrane [48]. All these parameters can be fine-tuned by means of dedicated membrane and reactor modelling, as well as design studies which were beyond the scope of this work. Nevertheless, it can be affirmed that with the current membrane design the thermodynamic conversion of the conventional process (without membrane) is surpassed (upon membrane installation) for each of the explored reaction operating conditions, setting a starting point for further metallic supported membranes optimization studies (Figure 4.19).

In Table 4.10, a comparison between this work and the work of Medrano et al. [23] (carried out in the same setup) is reported. In [23], the focus was on investigating the high temperature stability of a metallic supported membrane in fluidized-bed conditions. In this work, similar operating parameters were chosen to be able to produce comparable experimental results for highly selective M2 membrane in fixed-bed conditions at 500 °C. While most outcome reaction parameters result very similar (HRF and SF due to low permeance of metallic supported membranes), the conversion increase given by the

investigated reactor configuration is slightly higher, probably due to the different type of catalyst in packed-bed configuration compared to the fluidized-bed configuration of Medrano et al. However, the most remarkable difference is the permeate stream composition, which accounts for 99.3% of H₂ in case of a highly selective membrane versus 97.6% for a low selectivity membrane. This difference can become relevant when the downstream application requires high purity hydrogen (i.e., semiconductor manufacturing, fuel cells, aerospace industry [52]), which can be achieved with improved membrane selectivity. Thus, these results highlight the importance of membrane optimization, which in the case of metallic supported membranes for methane steam reforming calls for increase in H₂ permeance without H₂ selectivity expenditures.

	Calculated	Conventional	Membrane reactor		tor
Т [°С]	Thermodynamic equilibrium conversion [%]	CH₄ conversion [%]	CH₄ conversion [%]	H₂ recovery [%]	Separation factor [%]
400	11.8	10.1	15.3	1.5	8.8
450	18.2	18.2	31.8	10.7	31.6
500	26.7	26.7	42.1	13.9	32.5

Table 4.8. CH₄ conversion, HRF, and SF evaluated at 4 bar trans-membrane pressure and at a temperature of 400, 450, and 500 $^\circ$ C both for conventional and M2- assisted SMR.

Table 4.9. CH4 conversion, HRF, and SF evaluated at a temperature of 500 °C and 1, 2, 3, and 4 bar trans-membrane pressure both for conventional and M2-assisted SMR.

	Calculated	Conventional	Membrane reactor		
P [bar]	Thermodynamic equilibrium conversion [%]	CH₄ conversion [%]	CH₄ conversion [%]	H₂ recovery [%]	Separation factor [%]
2	34.4	-	39.0	10.4	19.4
3	29.7	-	39.9	12.6	26.2
4	26.7	26.7	42.1	13.9	32.5
5	24.6	-	52.4	15.4	42.2



Figure 4.19. CH₄ conversion of the M2-assisted SMR compared with the conventional SMR experimental campaign and the calculated thermodynamic equilibrium conversion, evaluated at a temperature of 400, 450, and 500 °C and at reference pressure conditions (4 bar).

	This work	Medrano et al. [23]
Reactor configuration [-]	Fixed bed	Fluidized bed
Catalyst [-]	2 wt.% Rh/Al ₂ O ₃ , 300 g	NiO/CaAl ₂ O ₄ , 300 g
Ghsv [L min ⁻¹ g _{cat} -1]	0.012	0.012 - 0.017
Membrane configuration [-]	Supported tubular Pd- based membrane	Supported tubular Pd-based membrane
Support [-]	Metallic (Hastelloy X, 0.5 µm MG)	Metallic (Hastelloy X, 0.1 µm MG, pre-treated)
Selective layer composition [-]	Pd-Ag	Pd-Ag
Selective layer thickness [µm]	~6-8	~6-8*
Length [mm]	90	137
H₂ permeance before SMR (at 450 °C and 1 barg) [mol m⁻² s⁻¹ Pa⁻¹]	6.4·10 ⁻⁷	8.6·10 ⁻⁷
H₂/N₂ selectivity before SMR (at 450 °C and 1 barg) [-]	16842	574
CH₄ conversion increase (500 °C, 4 bar) [%]	58	46**
H₂ recovery factor (500 °C, 4 bar) [%]	14	17**
H₂ separation factor (500 °C, 4 bar) [%]	33	35**
H₂ in permeate side (500 °C, 4 bar) [%]	99.3	97.6

Table 4.10. Comparison between the main reaction performance indicators of the M2-assisted SMR in fixed-bed configuration reported in this work and the membrane-assisted SMR in fluidized-bed configuration reported in previous work.

*Derived from SEM imaging in the manuscript. **Derived from manuscript's plots analysis.

4.4 Conclusions

The modification of rough metallic filters (0.5 μ m media grade, 50 μ m pore mouths) by polishing, etching and filling with asymmetric deposition of particles of α -Al₂O₃ reported in Chapter 3 has been successfully replicated in this work.

The selected pre-treatments proved suitable to achieve a support with superficial pore size ~60-90 nm, resulting in a Pd-Ag membrane with H₂/N₂ ideal selectivity at 500 °C and 1 bar of ~38000 (M1). H₂-N₂ mixture permeation tests on the prepared M1 membrane showed an effect of concentration polarization on the H₂ permeation, resulting in lower H₂ fluxes when N₂ concentration in the feed is increased. Tests for M1-assisted ammonia decomposition showed the overcoming of the conventional thermodynamic conversion of NH₃, reaching NH₃ conversions >99% for temperatures including and above 475 °C. The hydrogen recovered from the feed was >60% for the same temperature range, considering the membrane being solely 10 cm long.

Furthermore, a membrane reproduction procedure was tuned by setting a suitable support pore size distribution peak target to ~100 nm, based on M1's support. In this way, a second support was successfully reproduced and employed for the preparation of another highly selective Pd-Ag membrane (M2) (H_2/N_2 selectivity ~20200 at 500 °C and 1 bar). H₂-CO mixture permeation tests on the prepared M2 membrane showed an inhibition effect due to the presence of CO. A reduction in H₂ permeance with respect to pure H₂ gas feed was observed and successfully elucidated by applying a predictive mass transfer limitation model. Moreover, the presence of CH₄ was detected in the permeate stream, confirming the membrane's support catalytic activity towards methanation reaction and thus the support's ability to remove CO traces from the permeate stream (avoiding possible downstream fuel cell poisoning). The tests for M2-assisted SMR showed the ability of the membrane reactor to overcome the conventional thermodynamic conversion of CH₄ for all the explored operating conditions, promoting an increase of methane conversion with respect to a conventional process up to 58% at 500 °C and 4 bar, while guaranteeing at least 99.3% of hydrogen purity.

Overall, the selected membrane preparation procedure and membrane reproduction method proved suitable for further optimization and utilization in both ammonia decomposition and methane steam reforming membrane reactors, paving the way towards cheaper and easily scalable metallic support options.

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Appendix C | Supplementary information

Membrane stability during ammonia decomposition test campaign

In order to show the impact of membrane exposure at high temperature as well as the ammonia decomposition reaction on the membrane separation performance, the ideal H_2/N_2 selectivity of M1 at 450 °C and 4 bar is shown as a function of time in Figure C.1. The ideal H_2/N_2 selectivity decreases over time, indicating that during the experimental campaign defects have formed on the membrane surface or on the sealings, resulting in permeation of a higher amount of impurities (N₂) through the membrane walls. Specifically, over a time of 360 h the H_2/N_2 ideal selectivity decreased from 4807 to 3017, due to an increase in N₂ permeance. This increase could be attributed to welding cord failure after prolonged high temperature operation. However, further long-term studies of the proposed membranes are necessary to draw conclusions on the magnitude and causes of the membrane's selectivity decrease.



Figure C.1. Stability test of the membrane performance at 450 °C, and 4 bar.

Additional elemental analysis of embedded alumina filler

In Figure C.2, the SEM-EDX examination of porous Hastelloy X filter filled asymmetrically with α -Al₂O₃ shows the presence of larger and smaller alumina particles (in yellow) inside a cross-sectional pore structure, surrounded by all the characteristic elements of oxidized Hastelloy X alloy (Fe, Cr, Mo, Ni, O).



Figure C.2. Cross sectional SEM-EDX of a porous Hastelloy X support filled asymmetrically with α -Al₂O₃ of decreasing particle size. In yellow, the elemental map of Al.

Membrane permeation model principles

The model used to characterize the H_2 permeation flux behavior of M2 membrane in CO-H₂ mixture conditions is based on Richardson's equation, which is used to describe the solution-diffusion transport mechanism through the dense Pd-Ag selective layer:

$$J_{H_2} = P_{H_2}^0 e^{-E_a/_{RT}} \frac{(P_{H_2,ret}^n - P_{H_2,perm}^n)}{\delta}$$
(1)

Where J_{H_2} is the H₂ permeation flux, $P^{0}_{H_2}$ is the characteristic pre-exponential factor of M2, E_a is the activation energy of M2, R is the universal gas constant, T is the temperature of the system, δ is the membrane thickness, n is the characteristic exponent of M2, and $P_{H_2,perm}$ are the partial pressure of H₂ at the retentate and permeate side, respectively. E_a , and $P^{0}_{H_2}$ are evaluated by fitting the Arrhenius plot of M2 at different temperatures, while n is retrieved by fitting the H₂ permeation flux through M2 under pure H₂ permeation conditions, as discussed in Chapter 4 and shown in Figure 4.15.

To account for the effect of the H_2 depletion, which is defined as a loss of H_2 permeating flux across the length of the membrane, a basic plug-flow model was used. The retentate volume around the membrane was discretized in its axial direction (*z*-axis), resulting in the mole balances of H_2 and non-permeating species reported below:

$$0 = F_{H_{2},z} + F_{H_{2},z+\Delta z} - J_{H_{2},z} dA$$
(2)

$$0 = F_{i,z} - F_{i,z+\Delta z} , \text{ for } i \neq H_2$$
(3)

Where $F_{H_{2,Z}}$ is the H₂ flow at the *z* position of the membrane's length, $F_{H_{2,Z}+\Delta z}$ is the hydrogen flow in the *z*+ Δz position of the membrane's length, $J_{H_{2,Z}}$ is the H₂ permeating

flux across the membrane, dA is the discretized membrane area, and *i* is the *i*-th nonpermeating component of the examined mixture. Additionally, the contribution to the H₂ permeating flux given by the *external mass transfer* phenomena was modelled using the film-layer model according to Eq. 4, where *k* is the mass transfer coefficient, ρ is the gas density, *x*_{H2,memb} is the concentration of H₂ at the membrane surface and *x*_{H2,bulk} is the concentration of H₂ in the bulk. The mass transfer coefficient was calculated from Eq. 5, where *d_h* is the hydraulic diameter, and D_{H2,mix} is the diffusivity of H₂ in the examined mixture. The Sherwood number (*Sh*) was calculated by using the empirical correlation in Eq. 6 (which aims to adjust the more generalized Graetz-Lévêque equation). The parameters of said correlation (Graetz number (*Gz*) adjustment = 1.846 and exponent = 0.6) were derived through extensive experimental tests on similar Pd-Ag membrane systems.

$$J_{H_2} = k \rho \ln \left(\frac{1 \cdot x_{H_{2,memb}}}{1 \cdot x_{H_{2,bulk}}} \right)$$
(4)

$$Sh = \frac{k d_h}{D_{H_2,mix}}$$
(5)

$$Sh = 1.846 \text{ Gz}^{0.60}$$
 (6)

Finally, the *CO* inhibition parameters (K_{co} and α) which are included in the Langmuir adsorption model discussed in Chapter 4, Eq 7. were fitted from the H₂-CO binary mixture experimental data by adding the CO inhibition contribution to the mass transfer and depletion contribution described by the membrane permeation model. In this way, all the contributions to the H₂ permeating flux across M2 membrane in CO-H₂ environment could be differenciated and represented in Chapter 4, Figure 4.17.

Chapter 5 Porous γ -Al₂O₃ substrate for metallic supported Ru/ γ -Al₂O₃/Pd-Ag catalytic membranes

In this Chapter, the development of a γ -Al₂O₃ mesoporous substrate to be deposited onto metallic supported Pd-Ag membranes is proposed with a dual function:

- i. To improve H₂/N₂ selectivity of defective membranes.
- ii. To be further functionalized as catalytic Ru-based layer for ammonia cracking, to employ the Ru/γ-Al₂O₃/Pd-Ag membranes as catalytic membranes for a novel catalytic membrane reactor (CMR) configuration.

Boehmite-PVA-PEG coatings, previously developed in Chapter 2, are deposited onto two modified Pd-Ag membranes and sintered into γ -Al₂O₃ mesoporous substrates in N₂ and air atmosphere, respectively. The mesoporous layer is observed via Scanning Electron Microscopy (SEM) and laser-optical microscopy, while the effects of N₂ and air sintering atmospheres on the Pd-Ag layer underneath, as well as the polymeric degradation of the coating, are characterized.

Three defective metallic supported Pd-Ag membranes are characterized via Capillary Flow Porometry (CFP) before and after mesoporous substrate deposition, showing average defect's diameter reduction after the layer deposition, as well as H₂/N₂ selectivity increase. A highly selective (H₂/N₂ selectivity > 10000 at 500 °C, 1 bar) metallic supported Pd-Ag membrane is prepared and equipped with the γ -Al₂O₃ mesoporous substrate, which is further functionalized with Ru nanoparticles via deposition-precipitation method. The prepared metallic supported Ru/ γ -Al₂O₃/Pd-Ag membrane showed catalytic activity for ammonia cracking under a 100 mln/min NH₃ flow, promoting 65.8% NH₃ conversion at 500 °C.

5.1 Introduction

Both in Chapter 1 and Chapter 4, extensive discussions have been presented regarding the feasibility of integrating ammonia decomposition and hydrogen separation into a single unit through the utilization of membrane reactor technology. By means of a membrane reactor, the produced hydrogen can be immediately separated from the reaction zone, resulting in an increase in ammonia conversion owing to le Chatelier's principle. This convenient property has been proven to contribute to the reduction of the operating temperature and pressure of the process, increasing the overall energy efficiency and compactness of the system [1]–[9]. To prove that the proposed metallic supported membranes can also be employed as core of this technology, in Chapter 4 a highly selective metallic supported membrane was tested for ammonia decomposition in a membrane reactor, equipped with a packed bed of Ru-based catalyst, reaching >60% H₂ recovery and overcoming thermodynamic equilibrium conversion for temperatures above 450 °C [10]. A membrane reactor (MR), consists of a reaction vessel which accommodates one or multiple membranes submerged in a suitable catalyst. As downstream separation and purification units are avoided, the intensification of the system is already achieved. However, compactness of the system can be further increased by reducing the reactor's catalyst loading, increasing productivity by employing a lesser amount of catalyst as well as reducing external mass transfer limitations (concentration polarization) and decreasing the membrane area required. For this purpose, most literature works focused on the integration of Ru directly into the Pd-Ag layer via electroless deposition [11]-[16].

Zhang et al. [17] proposed a Catalytic Membrane Reactor (CMR) configuration, in which the Ru catalyst is suitably accomodated into the porous YSZ tube used to support the Pd membrane layer. Following this work, Sitar et al [18] packed a Ru-based catalyst in the lumen of the Ru-YSZ membrane support, employing the more compact catalytic membrane reactor configuration for ammonia cracking, reaching nominally complete conversion and > 80% recovery. The close contact between catalyst and membrane reduced operating temperature, catalyst loading, and enhanced H₂ productivity compared to similar Packed-Bed Membrane Reactor (PBMR) configurations. In Chapter 4, the works of Cechetto et al [19] were reported, for which best performances for ammonia decomposition were obtained with a Ru-based packed-bed of catalyst accommodating a ceramic supported Pd-based membrane, which was equipped with a mesoporous YSZ-Al₂O₃ protective laver. In Chapter 2, it was discussed how, in the case of Pd-based membranes supported on large media grade metallic filters, the main cause of defect formation and thus H₂ selectivity loss is the missed closure of superficial large pore mouths via Pd electroless plating. Given these considerations, the addition of a mesoporous layer onto the Pd-Ag layer is expected to promote the reduction in defect's dimension and thus increase H₂ selectivity in defective membranes.

Consequentially, an alumina substrate is designed based on the interdiffusion barrier studied in Chapter 2. The porous substrate is deposited onto the Pd-Ag membranes with a dual aim:

- i. In the presence of defects, enhance the Pd-Ag membrane's selectivity by narrowing the membrane's defect distribution.
- ii. As support for Ru nanoparticles functionalize the membrane for ammonia decomposition in a catalytic membrane reactor.

 $131\,|$ Porous $\gamma\text{-}Al_2O_3$ substrate for metallic supported $Ru/\gamma\text{-}Al_2O_3/Pd\text{-}Ag$ catalytic membranes

The Ru nanoparticles are deposited via deposition-precipitation method directly onto the mesoporous alumina substrate, attached to the Pd membrane surface. Firstly, the porous ceramic substrate is thoroughly characterized, investigating its ability to enhance membrane's hydrogen selectivity onto defective metallic supported Pd-Ag membranes. Subsequently, a highly selective metallic supported Pd-Ag membrane is prepared following the procedure described in Chapter 3 and equipped with the Ru/ γ -Al₂O₃ catalytic substrate. The membrane is finally tested for ammonia decomposition in a catalytic membrane reactor (without any catalyst bed) in order to preliminary assess the catalytic activity of the newly functionalized porous substrate.

5.2 Experimental

Preparation of sample membranes

Commercial, untreated, porous Hastelloy X filters (outer diameter 1.2 cm, average surface roughness (*Ra*) 6.1 µm, 0.5 µm nominal media grade (MG)) were acquired from Hebei Golden Flame Wire Mesh Co, China. The filters were cut in samples of 10 cm length and welded to dense stainless steel (AISI316L) tubes, to achieve a one close end configuration. The supports were then polished in an industrial surface finishing machine via a wet-polishing mechanism (ERBA EVT-170) for 6 h [20]. 2 of the 5 polished supports were etched by perpendicular immersion in aqua regia for 30 s and thoroughly rinsed with deionized water to remove all mordant residuals. All samples were then oxidized in a static air furnace for 1 h at 750 °C. Before further treatments, the supports were rinsed both in ethanol and in deionized water in an ultrasonic bath, to remove all possible residuals. The supports were then filled with α -Al₂O₃ of different particle sizes, as summarized in Table 5.1.

A boehmite-based γ -Al₂O₃ interdiffusion barrier was deposited onto each sample support, following the procedure summarized in Chapter 2 [21]. The supports were then seeded with palladium nuclei by subsequent immersion in a 0.6 vol.% solution of Pd acetate in chloroform and reduction in hydrazine 0.2 M. The Pd-Ag membranes were formed on the samples via electroless plating co-deposition of both Pd and Ag for 5 h. The membranes are annealed at 550 °C for 4 h in Ar – 10 vol.% H₂ atmosphere.

All membranes were sealed at the welding cords by pressing in stainless steel rings of internal diameter 1.3 cm with graphene tape, to exclude any welding defect from the analyses. After membrane testing, a mesoporous γ -Al₂O₃ substrate was deposited onto the Pd-Ag surface. The layer was prepared with 1.2 wt.% or 0.9 wt.% boehmite in 3.5 wt.% PVA-1 wt.% PEG water-based solution. The layer was deposited via vacuum assisted dip-coating in the custom dip-coating machine discussed in previous Chapters. The membranes were then dried under rotation in a climate chamber at 60% Rh and 40 °C. Finally, the layer was sintered in inert atmosphere (N₂) for 2 h at 550 °C, with heating rate 1 °C min⁻¹ to preserve the metallic supported Pd-Ag layer. Solely for ML7, the substrate was sintered in air atmosphere, in order to compare the different sintering environments.

Membrane code [-]	Support pre- treatments [-]	Filler material and size [-]	Interdiffusion barrier precursor [-]	Porous substrate precursor and sintering atmosphere [-]
ML1	6 h polish	α-Al ₂ O ₃ , 300 nm	1.2 wt.% boehmite	0.9 wt.% boehmite, N ₂
ML2	6 h polish	YSZ, 1 µm	1.2 wt.% boehmite	0.9 wt.% boehmite. N2
ML4	6 h polish, 30 s etch	α-Al ₂ O ₃ , 300 nm	0.9 wt.% boehmite	0.9 wt.% boehmite, N ₂
ML5	6h polish	α-Al ₂ O ₃ , 300 nm	0.9 wt.% boehmite	1.2 wt.% boehmite, N ₂
ML6	6 h polish, 30 s etch	α-Al ₂ O ₃ , asymmetric [22]	0.9 wt.% boehmite	0.9 wt.% boehmite, N ₂
ML7	6 h polish	YSZ, 1 µm	0.9 wt% boehmite	1.2 wt.% boehmite, Air

Table 5.1. Test membranes preparation conditions.

The deposition of Ru onto the mesoporous γ -Al₂O₃ layer was carried out on ML6 through the deposition-precipitation method [23][24][25] with urea as the precipitating agent [26]. RuCl₃ \cdot nH₂O was used as precursor salt and it was dispersed in a 0.1 M solution of HCl. The alumina-coated Pd/Ag membrane was immersed in the urea solution and the precursor solution was slowly added. The molar ratio Ru:HCl:urea was 2:10:100. Once all precursor solution was dropped, the temperature was increased to 80 °C, vigorously stirring for 5 h. The solution was then brought back to room temperature under stirring.

The functionalized membrane was washed with distilled water and ethanol, dried at 100 $^{\circ}$ C in Ar atmosphere and annealed at 500 $^{\circ}$ C under N₂ flow for 6 h, directly in the ammonia decomposition reactor shell.

Characterizations

The mesoporous substrate was investigated with the following characterization techniques:

- i. The defects distribution of the membranes was measured before and after the deposition of the substrate via capillary flow porometry technique, in the geometry specific setup described in Chapter 3.
- ii. The average pore size and surface area of the γ -Al₂O₃ layer were measured via Brunauer-Emmett-Teller analysis (BET, Triflex, Micromeritics). A thin layer was cast in a petri dish and dried at 40 °C, 60% Rh in a climate chamber and sintered at 550 °C (with the same conditions as the fabricated membranes). It was then peeled and crushed into a powder for analysis.
- iii. The weight variation of the porous substrate during the sintering procedure in both N₂ and Air atmosphere was observed via ThermoGravimetric Analysis (TGA). A twin layer was cast in a petri dish and dried at 40 °C, 60% Rh in the climate chamber with the fabricated membranes. It was then peeled, cut to size,

and employed for the analysis prior to sintering. The analysis was carried out in the setup illustrated in Figure 5.1, using air and N₂ as feed gases. The balance is connected to a porous basket made of alumina (40 μ m pores) through an Ir wire. A robotic lift is used to bring the basket outside the reactor to load it with the sample. The temperature in the shell is controlled using a thermocouple positioned close to the sample to ensure stable conditions, while the temperature of the balance head is kept constant.



Figure 5.1. Thermogravimetric analysis setup.

- iv. The porous substrate was observed on ML5 via Scanning Electron Microscopy (SEM, Fei-Quanta-FEG250-3D) imaging of the membrane's cross section obtained via scoring and breakage.
- v. The porous substrate was further observed onto the Pd-Ag surface of ML5 via laser-optical confocal microscopy (VKX-3000, Keyence, Osaka, Japan).
- vi. The effect of the sintering atmosphere on the Pd-Ag layer's composition was assessed by X-ray diffraction analysis (XRD) (Rigaku Miniflex 600, Ni β -filtered Cu-K α radiant, 40 kV, 30 mA, 0.05 ° min⁻¹) and X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha, ThermoFisher) of ML7 and ML5. In both cases, the Pd-Ag/ γ -Al₂O₃ layers were peeled off the support surface and cut to size. To allow for investigation below the surface of the γ -Al₂O₃ layer, XPS depth profiling was performed by etching the γ -Al₂O₃ under ultrahigh vacuum. An Ar ion beam (2000 V, etching rate 0.37 nm s⁻¹) was used with repeated 60 s cycles, while wide-range survey spectra and high-resolution core level spectra were taken after every etching cycle with the detector in scan mode. Peak fitting was carried out with a Shirley background subtraction, following the procedure in [27]. The chosen post-processing software was CasaXPS.
- vii. The presence of Ru in the mesoporous layer was qualified via post-mortem XPS surface scan of ML6 Ru/γ-Al₂O₃/Pd-Ag layer, peeled off and cut to size.

- viii. The weight of the mesoporous gamma alumina layer deposited onto ML6 was quantified by weighing ML6 before and after gamma alumina deposition and sintering.
- ix. The presence of Ru in the mesoporous layer was qualified and preliminarily quantified in atomic wt.% via post-mortem XPS surface scan of ML6 Ru/γ-Al₂O₃/Pd-Ag layer, peeled off and cut to size. The wt.% of Ru in the sample was then calculated as:

$$Wt_{i} = \frac{At.wt_{i}Mw_{i}}{\sum_{i=1}^{i=n}At.wt_{i}Mw_{i}}, \quad i = 1, _, n$$
(1)

Where At.wt is the atomic weight percentage, Mw is molecular weight, Wt is the weight percentage and *i* is the *i*-th component of the analysis, which can vary between 1 and *n* analyzed elements. The amount of Ru in the membrane layer was then quantified as:

$$g_{Ru,layer} = Wt_{Ru} g_{Al_2O_3}$$
(2)

Where $g_{Ru,layer}$ is the weight of Ru in the γ -Al₂O₃ layer, Wt_{Ru} is the calculated weight percentage of Ru and $g_{Al_2O_3}$ is the weight of the deposited γ -Al₂O₃ layer.

Single gas permeation tests

To evaluate the influence of the mesoporous layer on membrane selectivity, the prepared Pd-Ag membranes were tested before and after layer deposition. For each test, the prepared Pd-Ag membranes were activated at 400 °C with an air flow of 1 L min⁻¹ for 2 minutes. They were then tested at 400, 450 and 500 °C for single-gas H₂ and N₂ permeance with an imposed pressure difference of 1, 2, 3, and 5 bar. The setup description is provided in Chapter 2.

Ammonia decomposition tests

Ammonia decomposition tests have been performed in a stainless-steel tubular membrane reactor (internal diameter = 4.5 cm, length = 28 cm) in the setup summarized in Chapter 4, with the modifications shown in Figure 5.2. The membrane ML6 was simply connected to the reactor's flange with Swagelok fittings, without any catalytic bed. Heat was supplied to the reactor by an electrical split oven with three independently controlled heating sections. The pressure was controlled with a backpressure regulator (Bronkhorst). The permeate was equipped with a vacuum pump for H_2 . Both the retentate and permeate sides of the membrane were sent to a micro-GC (Varian CP-4900) to measure their composition. Due to limitations of both the GC equipment and the flowmeters for NH₃ detection, dilution of both streams with an inert internal standard gas was required. He gas was used as dilutant and detected in the Ar carried molecular sieve channel of the micro-GC. The dilutant was fed via manual mass flow controllers (Bronkhorst), directly connected to the He line. The dilutant was then used to quantify both permeate and retentate flow, as well as to prevent the corrosion of the GC equipment with large concentrations of NH₃. The retentate and permeate lines were subsequently mixed and sent to a water absorption unit in which possible traces of NH₃ are absorbed preventing their release in atmosphere.





The reactor was heated up to 500 °C at a heating rate of 2 °C min⁻¹ in N₂ atmosphere and kept in temperature for 6 h in order to anneal the Ru/ γ -Al₂O₃ layer. Afterwards, the membrane was activated at 400 °C with 1 L min⁻¹ of pure H₂ until stable permeation, while the catalyst was reduced thanks to the H₂ atmosphere. After reduction, permeation tests

under reactive conditions were performed. The temperature history and the explored operating conditions are summarized in Figure 5.3 and Table 5.2.



Figure 5.3. NH₃ decomposition tests, temperature history.

Table 5.2. Explored operating conditions for the NH₃ decomposition tests.

Ammonia decomposition with CMR		
Temperature [°C]	400, 450, 500	
Retentate pressure [bar]	4	
Permeate pressure [bar]	Vacuum	
NH ₃ feed flow rate [L _N min ⁻¹] 0.100		

The reaction performance was monitored until steady state operation was observed. The permeate flow rate and the composition of the retentate stream were measured 15 times. NH₃ conversion (X_{NH3}) (Eq. 3), H₂ Recovery Factor (*HRF*) (Eq. 4), Separation Factor (*SF*) (Eq. 5), and Hydrogen PRoductivity (*HPR*) (Eq. 6) were then calculated as the ratio between consumed ammonia and fed ammonia, the ratio between the permeating H₂ and fed H₂, the ratio between permeated H₂ and produced H₂, and the produced mmol of hydrogen over the quantified grams of Ru, respectively.

$$X_{\rm NH_3} = \frac{\rm NH_{3,in} - \rm NH_{3,out}}{\rm NH_{3,in}}$$
(3)

$$H_{2,recovery} = \frac{H_{2,permeate}}{1.5 \text{ NH}_{3,in}}$$
(4)

$$H_{2,separation} = \frac{H_{2,permeate}}{H_{2,produced}}$$
(5)

$$H_{2,productivity} = \frac{H_{2,produced}}{g_{Ru,layer}}$$
(6)

5.3 Results and discussion

Porous substrate characterization

The presence of the mesoporous substrate onto ML5 is verified via SEM imaging in Figure 5.4, where a 3 µm thick layer (well in agreement with the selected boehmite concentration in the precursor solution [21]) is clearly distinguishable on a 6 µm thick Pd-Ag layer. Part of the interdiffusion barrier is also distinguishable as a interlayer between the Pd-Ag and the large media grade Hastelloy X filter. The average pore size of the mesoporous substrate measured via BET amounts to ~6 nm, with a surface area of area 311 m² g⁻¹. It is important to remark that the total surface area available for the layer's functionalization with Ru nanoparticles is expected to be way less than 311 m² g⁻¹, as the substrate is deposited onto the Pd-Ag layer and it is not crushed in powder form.

In case of a mesoporous substrate sintered in air atmosphere, the high temperatures and the oxygen penetration are expected to favour the oxidation of Pd from Pd metallic (Pd⁰) to Pd oxide (Pd²⁺). The change of structure of Pd⁰ to Pd²⁺ is expected to modify the structure of the selective layer, with detrimental effects on the H₂ transport mechanism through the layer and possibly promoting the opening of defects. However, if the protective layer is sintered in inert atmosphere, both chemical and structural changes in the dense selective layer would be avoided. The presence of Pd oxide on the air sintered sample was firstly observed macroscopically as the blue color onto the sample surface after sintering procedure (Figure 5.5). To further verify the presence of PdO, the XRD pattern of a the mesoporous layer sintered in N_2 and air is shown in Figure 5.6. The air sintered sample pattern presents extra peaks compared to the N_2 sintered sample's pattern. The extra peaks at 33.5° and 55° are clearly relatable to XRD patterns of literature works exploring the evolution from Pd metallic to PdO [28][29][30]. These peaks are not present in the case of the N₂ sintered sample, which solely presents Pd-Ag alloy face centered cubic structure peaks [31]. However, the low intensity peaks at 60° and 70.5° cannot be clearly attributed to the presence of PdO.

Therefore, the presence of PdO onto the air sintered sample is further investigated with the XPS characterization in Figure 5.7, where the fitting of high resolution peaks taken below etched γ -Al₂O₃ mesoporous substrate are reported for both samples. A fit for a single 3d_{5/2} peak (signal located at 335.27 eV) and a single 3d_{3/2} peak (signal located at 340.68 eV) was enough to fully describe the signal of the nitrogen sintered sample (Figure 5.7a), while in the case of the air sintered sample a significant binding energy contribution of Pd 3d_{5/2} was needed compared to bulk Pd, as already observed in oxidized Pd-Ag membrane layers[31] as well as a binding energy contribution to Pd 3d_{3/2} (Figure 5.7b). Moreover, a slight shoulder for Pd 3d_{5/2} and Pd 3d_{3/2} at 336.94 eV and 342.19 eV was detected, ascribable to a uniform layer of PdO [32][33] (Figure 5.7c).

Given the delicate nature of the Pd-Ag layer structure, which is essential to guarantee membrane selectivity and continuous permeation of H_2 , elemental composition and possible structural modifications of the layer should be avoided whenever possible. For this reason, N_2 sintering atmosphere would be the preferred choice for the functionalized layer whether it would allow for polymeric loss of the coating.



Figure 5.4. Cross-sectional SEM imaging of ML5 after mesoporous γ -Al₂O₃ substrate deposition.



Figure 5.5. Side by side comparison of: peeled-off ML5 Pd-Ag layer after mesoporous γ -Al₂O₃ substrate deposition and sintering in N₂ atmosphere; peeled-off ML6 Pd-Ag layer after γ -Al₂O₃ mesoporous substrate deposition and sintering in air atmosphere.



Figure 5.6. XRD patterns of peeled-off ML5 and peeled-off ML6 γ-Al₂O₃/Pd-Ag layers.



 $139\,|$ Porous $\gamma\text{-}Al_2O_3$ substrate for metallic supported Ru/ $\gamma\text{-}Al_2O_3/Pd\text{-}Ag$ catalytic membranes

Figure 5.7. XPS depth profile of Pd-Ag layer beneath etched γ-Al₂O₃ porous substrate: (a) comparison between sample sintered in air and nitrogen atmposphere. Highlighted (arrow) the signal shoulders corresponding to the binding energies related to PdO by literature; (b) peak fitting of air sintered sample; (c) peak fitting of nitrogen sintered sample.

To observe the coating's evolution during sintering procedure, TGA of a boehmite-PVA-PEG layer is shown in Figure 5.8 for both sintering atmospheres. In particular, a first weight loss is observed at ~ 80 °C, which can be attributed to loss of physically bound water of the samples. After that, between 250 °C and 500 °C, most of the weight is lost by both samples. At about 400 °C, the phase change from boehmite to γ -Al₂O₃ is expected, which, however, is masked by the weight loss given by polymers decomposition [34][35]. At about 450 °C, the final weight loss is observed. However, more weight is retained by the nitrogen sintered sample. This weight retention could be attributed both to polymeric residuals and a greater content of boehmite. To better study the polymeric retention of both samples, the same TGA analysis on solely a PVA-PEG layer in Figure 5.9 is shown for both sintering atmospheres. Both sintering atmospheres promote a significant sample weight loss between 200 °C and 450 °C. This loss is attributed to the evolution of volatile compounds from the pyrolysis of the polymers [35][36]. In this phase, both samples degrade in a similar way, whether oxidized by the presence of air (evolving into CO₂, ethylene oxide, acetone, acetic acid, ethanol, etc.) or pyrolized in inert atmosphere (evolving into aromatics such as benzene, toluene, isoxylene, etc.) However, above 450 °C the air sintered sample loses all carbon residuals (and/or additional volatiles) which are evolved as CO₂, while the inert sintered sample solely evolves the additional volatiles, producing char [37]. Sintering in inert atmosphere implies a \sim 7% of remaining weight in comparison with the air sintered sample. This means that leftover char given by high temperature carbonization in nitrogen might reside in the mesoporous substrate. However, as most of the polymer is degraded during the inert sintering procedure, this atmosphere is preferred in order to preserve the original structure of Pd⁰ beneath the mesoporous substrate. The \sim 7% of carbon leftovers is expected to either reside in the pores of the mesoporous substrate, partially occupying the sites for Ru deposition, or to further contribute to the porosity of the layer (similarly to a carbonized precursor for a carbon membrane structure) or to evolve with time as CH₄ during H₂ exposure of the membrane. For these reasons, it is suggested that the same procedure could be followed for the production of double skin membranes, as the ones employed in the work of Cechetto et al [19].

In Figure 5.10, the laser-optical view of a closed porous structure in the Pd-Ag layer is shown. In particular, in Figure 5.10a, the γ -Al₂O₃ mesoporous substrate is deposited onto the analyzed membrane (ML5). Compared to the bare Pd-Ag layer in Figure 5.10b, the porous substrate can be observed as a transparent, refractive layer which fully covers the Pd-Ag surface, adhering to the closed pore mouth. The adhesion to these potential defect sources is driven by the selected vacuum deposition technique. In this way, the mesoporous alumina layer is expected to reduce the defects size and, therefore, increase membrane selectivity by reducing other species leakage, leading to possible recovery and/or improvement of defective membranes.

In Figure 5.11, the defects distribution of the leaking Pd-Ag membranes before and after mesoporous layer deposition are reported. ML1 and ML2 present defects in the range of 150 to 600 nm. After the deposition of the mesoporous layer, the defects distribution is sharpened towards average pores diameters of about 30 nm. In case of ML4, the starting defects distribution is located between 30 and 150 nm. After the mesoporous layer deposition, solely the defects between 50 and 150 nm are successfully reduced in size, promoting a smaller shift in defect size distribution. This is to be attributed to the comparable size between the pores of the alumina layer and the defects themselves. Thanks to this observation, it is possible to speculate that the mesoporous layer is best employed to cover defects larger than 50 nm, outside the mesoporous range.

141 | Porous γ -Al₂O₃ substrate for metallic supported Ru/ γ -Al₂O₃/Pd-Ag catalytic membranes



Figure 5.8. TGA of a dried (40 °C, 60% Rh) boehmite-PVA-PEG precursor for mesoporous γ -Al₂O₃ substrate. The analysis reproduces the selected sintering conditions (heating rate = 2 °C min⁻¹, 550 °C for 2 h) in both nitrogen and air atmosphere.



Figure 5.9. TGA of a dried (40 °C, 60% Rh) PVA-PEG polymeric binder for the boehmite coating precursor of the mesoporous γ-Al₂O₃ substrate. The analysis reproduces the selected sintering conditions (heating rate = 2 °C min⁻¹, 550 °C for 2 h) in both nitrogen and air atmosphere.



Figure 5.10. Laser-optical imaging of: (a) a large pore mouth closed by Pd-Ag on the surface of ML5, covered by γ -Al₂O₃ transparent porous substrate; (b) the surface of a large pore mouth closed by a bare Pd-Ag layer.



Figure 5.11. Defects size distribution of ML1, ML2, and ML4 before and after γ -Al₂O₃ mesoporous substrate deposition, evaluated via CFP.

 $143\,|$ Porous $\gamma\text{-}Al_2O_3$ substrate for metallic supported Ru/ $\gamma\text{-}Al_2O_3/Pd\text{-}Ag$ catalytic membranes

Membrane permeation properties

In Figure 5.12 the increase in selectivity for all 3 defective membranes after mesoporous layer deposition is shown. The selectivity of both ML1 and ML2 is more than doubled after mesoporous layer deposition, while ML4 presents a selectivity increase of about 50%. These results are to be correlated to the defects distributions shown in Figure 5.11, where the more pronounced left skewed shift in defects distribution of ML1 and ML2 compared to ML4 is clearly shown. The analysis therefore represents a further confirmation of the defects dimension reduction effect promoted by the selected mesoporous layer.



Figure 5.12. Ideal H_2/N_2 selectivity of defective membranes ML1, ML2, and ML4 before and after mesoporous substrate deposition, evaluated at a temperature of 500 °C and 1 bar transmembrane pressure.

In Figure 5.13, the increase in selectivity on ML6 after mesoporous substrate deposition is shown. The membrane was fabricated with high selectivity, which significantly improved after the addition of the layer especially at 1-2 bar trans-membrane pressure. The increase in selectivity at lower pressures is attributed to the coverage of smaller defects promoted by the deposition of the mesoporous substrate. However, as shown in Figure 5.14, the N₂ permeance of the membrane increases with pressure with a positive slope, highlighting the presence of Knudsen-type/viscous flow contribution to gas transport, meaning that the presence of large defects is still relevant. Given the low N₂ permeance and the deposition of a mesoporous layer, it is highly likely that this positive slope is given by sealing failure, whose contribution is particularly evident at higher pressures by observing the selectivity behavior in Figure 5.13. The reduction in slope of the linear fit of N_2 permeance with pressure highlights a reduction in N_2 permeance through defects contributing to the Knudsen/viscous type gas transport. However, the preservation of the slope's positivity highlights that the same contribution of viscous-Knudsen type of defects is still present. Given the extremely low values of N_2 permeance, these contributions are likely confirmed to come from the membrane's welding cord sealings. More information on membrane defects distribution, however, could not be retrieved due to the average dimension of the defects (below 20 nm) which represented the detection limit of the CFP setup.
In Figure 5.15, the H₂ permeation flux is fitted at different temperatures before and after mesoporous layer deposition. Firstly, a decrease in H₂ permeation flux after mesoporous substrate is observed, given by the additional resistance to gas permeation promoted by the mesoporous layer. However, no changes in the membrane characteristic exponent *n*, which amounted to *n* = 0.50 both before and after mesoporous layer deposition (with an average R² = 0.999, and 0.997, respectively) were detected, attributing most of the resistance to H₂ permeation to the Pd-Ag layer. The membrane's activation energy before and after mesoporous layer deposition was retrieved and amounted to 9.6 kJ mol⁻¹ and 12.9 kJ mol⁻¹, respectively.



Figure 5.13. H₂/N₂ selectivity of ML6 evaluated at a temperature of 500 °C and 1, 2, 3, and 5 bar trans-membrane pressure before and after mesoporous substrate deposition.



Figure 5.14. N2 permeance at at a temperature of 500 °C and 1, 2, 3, and 5 bar trans-membrane pressure for ML6 before and after mesoporous substrate deposition.

 $145\,|$ Porous $\gamma\text{-Al}_2O_3$ substrate for metallic supported Ru/ $\gamma\text{-Al}_2O_3/Pd\text{-Ag}$ catalytic membranes



Figure 5.15. Linear regression performed on H₂ permeating flux vs H₂ partial pressure of ML6, evaluated at 1, 2, 3, and 5 bar trans-membrane pressure and at a temperature of 400, 450, and 500 °C, to evaluate the characteristic *n*-exponent of the membrane before and after deposition of the mesoporous substrate.

Catalytic Ru/γ-Al₂O₃ layer

The presence of Ru onto the functionalized v-Al₂O₃ layer of ML6 was verified via postmortem XPS surface scan, shown in Figure 5.16. From the XPS signal, a clear peak of Ru 3s is distinguishable at 586.08 eV, certifying the presence of the active metal. Clear peaks for AI 2s and O 1s at 119.08 eV and 531.08 eV are identified, ascribable to the y-Al₂O₃ mesoporous layer. A C 1s signal at 285 eV is present, due to the residual char promoted by the chosen N₂ sintering atmosphere and/or sample contamination. Weak signals for Pd and Ag at 43.08 eV and 54.08 eV are also visible, as the scan weakly detected the Pd-Ag layer beneath the mesoporous layer. The atomic weight percentage of Ru in the analyzed sample amounts to 4.22%, which corresponds to 18 Ru wt.%, according to Eq.1. Following Eq. 2, the total amount of Ru in the mesoporous gamma alumina layer was characterized as 5.94 mg. However, it is important to remark that this value is employed to preliminarily assess the productivity of the examined CMR configuration and it is considered merely as an initial indication of Ru loading. Further analyses are needed to fully and precisely quantify the amount of Ru both onto and wellinside the mesoporous layer. (i.e. XPS analysis of multiple samples to precisely assess the wt.% across the whole membrane, in different positions), as well as quantifying its particle size for a more precise analysis of the Ru/y-Al₂O₃ layer's efficiency as a catalyst.



Figure 5.16. Post-mortem XPS surface scan of ML6 peeled-off Ru/γ-Al₂O₃/Pd-Ag layer.

 $147\,|$ Porous $\gamma\text{-}Al_2O_3$ substrate for metallic supported $Ru/\gamma\text{-}Al_2O_3/Pd\text{-}Ag$ catalytic membranes

In Table 5.3, ammonia conversion, hydrogen recovery factor, separation factor, and hydrogen productivity promoted by the functionalized metallic supported Ru/y-Al₂O₃/Pd-Ag membrane ML6 at different temperatures and 4 bar pressure are shown. The ammonia conversion follows the expected thermodynamic behavior. As the cracking reaction is endothermic, the ammonia conversion increases with increasing temperature. This influences the amount of hydrogen produced, which in turn influences the separation performance of the membrane. Both hydrogen separation factor and hydrogen recovery factor increase in fact with increasing temperature thanks to the larger amount of hydrogen produced but also thanks to the increased activation of the hydrogen diffusion through the Pd-Ag film. The separation factor indicates that at least 83% of the produced hydrogen permeates through the Pd-Ag layer in the permeate stream. However, given the very low flows of reaction products, vacuum at the permeate side is needed and it is therefore impossible to affirm that all the hydrogen is produced through the functionalized membrane, and thus impossible to fully exclude any catalytic activity of the reactor environment itself. Specifically, in Figure 5.17 the ammonia conversion of the catalytic membrane reactor configuration, equipped with the functionalized metallic supported Ru/γ -Al₂O₃/Pd-Ag membrane at different temperatures and 4 bar pressure is shown and compared to:

- i. The corresponding calculated thermodynamic equilibrium conversion.
- ii. The conversion achieved in the same equipment with a packed bed of 300 g of a commercial Ru/Al_2O_3 catalyst at 4 bar pressure [6].

In the packed-bed reactor configuration the thermodynamic equilibrium conversion is reached at 500 °C, while in the catalytic membrane reactor configuration the thermodynamic conversion is far from reached. However, the presence of ammonia conversion at each temperature in the catalytic membrane reactor configuration confirms a catalytic activity towards ammonia decomposition.

The ammonia conversion promoted by the catalytic membrane reactor configuration can be attributed (without the possibility to discriminate) either to:

- i. The amount of Ru onto the mesoporous substrate, its particle size, and/or its physical accessibility as active catalytic site.
- ii. The possible catalytic activity of Ni or Fe in the reactor, in the defects of the membrane's surface, and/or in the membrane's sealings.

A fairer comparison between both catalytic configurations can be given by the hydrogen productivity, which is normalized on the amount of active metal present. However, the difficulty in the exact quantification of Ru onto the catalytic membrane layer allows solely for a preliminarily qualitative comparison. In particular, the productivity of the newly explored catalytic membrane reactor configuration amounts to 48.39 mmol min⁻¹ g_{Ru} ⁻¹ at 400 °C and 4 bar, very similar to the catalytic membrane reactor explored by Zhang et al [17], whose productivity amounted to 53.53 mmol min⁻¹ g_{Ru} ⁻¹ at the same temperature and trans-membrane pressure. Moreover, comparing the hydrogen productivity of the explored catalytic membrane reactor configuration (123.45 mmol min⁻¹ g_{Ru} ⁻¹ at 450 °C, 4 bar) with the productivity of the packed-bed membrane reactor configuration of Cechetto et. al. [6] (6.5 mmol min⁻¹ g_{Ru} ⁻¹ at 450 °C, 6 bar), it is possible to preliminarily observe that the CMR configuration promotes the production of 20 times the amount of H₂ produced by a packed-bed membrane reactor. However, taking into account the promising results and their limitations, further characterizations are to be performed in

order to surely confirm the increased hydrogen productivity of the Ru/ γ -Al₂O₃ layer, particularly: XPS depth profiling to quantify the exact amount of Ru deposited onto the mesoporous substrate, coupled with Inductively Coupled Plasma (ICP) analysis of dissolved membrane layers (which proved challenging given the resistance to dissolution of γ -Al₂O₃ in most media); TEM to assess the exact size of the Ru nanoparticles, XRD to confirm their presence and/or structure, and chemisorption to investigate the active sites of the functionalized layer. Moreover, a blank test without membrane and with non-functionalized membrane needs to be performed in the same ammonia decomposition conditions to exclude the possible activity of stainless-steel parts towards ammonia cracking. At that point, it would be possible to exactly quantify the ammonia converted over the quantity of active metal present in the layer, net of any eventual catalytic activity of the reaction environment, shifting from preliminary quantification to precise quantification. Finally, tests at higher ammonia conversions should be carried out for a more precise comparison in terms of catalytic activity.

Regardless, it is possible to affirm that deposition of a mesoporous substrate for Ru deposition can be easily achieved onto highly selective metallic supported Pd-Ag membranes and that catalytic activity towards ammonia cracking is detected for each explored temperature, opening the possibility for additional functionalization of the Pd-based membranes, which may lead to further intensification of the membrane reactor concept. For this reason, additional works are in progress based on the concepts reported in this Chapter.



Figure 5.17. NH₃ thermodynamic equilibrium conversion, NH₃ conversion in in a PBR [6], and NH₃ conversion in the examined CMR at 4 bar retentate pressure and at a temperature of 400, 450, and 500 °C.

 $149\,|$ Porous $\gamma\text{-}Al_2O_3$ substrate for metallic supported $Ru/\gamma\text{-}Al_2O_3/Pd\text{-}Ag$ catalytic membranes

Table 5.3. NH₃ conversion, H₂ recovery factor, separation factor, and H₂ production rate at 4 bar and at a temperature of 400, 450, and 500 °C of the proposed Ru/ γ -Al₂O₃/Pd-Ag CMR configuration.

Temperature [°C]	<i>Х_{NH3}</i> [%]	SF [%]	HRF [%]	<i>HPR</i> [mmol min ⁻¹ g _{Ru} ⁻¹]
400	7.7	83.2	7.6	48.39
450	22.7	90.8	20.4	123.45
500	65.8	95.2	64.4	349.2

5.4 Conclusions

Boehmite-PVA-PEG coatings have been successfully deposited onto two modified metallic supported Pd-Ag membranes and sintered into γ -Al₂O₃ mesoporous substrates in N₂ and air atmosphere, respectively. The presence of a continuous γ -Al₂O₃ layer was confirmed via SEM and laser-optical microscopy. XRD and XPS characterizations showed the presence of PdO on the surface of the air sintered sample, which could hinder the structure of the H₂ selective Pd-Ag layer. The polymeric degradation of the coating was studied via TGA, showing complete polymeric degradation in air atmosphere and almost full polymeric pyrolysis in N₂ atmosphere, with ~7% char formation.

Three defective metallic supported Pd-Ag membranes were characterized via CFP before and after mesoporous substrate deposition, showing average defect's diameter distribution shift from 150-600 nm to 30-100 nm after v-Al₂O₃ laver deposition. The consequential selectivity increase of the defective membranes was ~50% to ~120%. Finally, a highly selective metallic supported Pd-Ag membrane was prepared and equipped with the v-Al₂O₃ mesoporous substrate, increasing its selectivity to \sim 65000 at 500 °C and 1 bar. The analysis of the permeation properties of the membrane before and after mesoporous layer deposition highlighted most N_2 leakage from the welding cord's sealing failure, as well as a H_2 permeation flux reduction after mesoporous laver deposition. Finally, the v-Al₂O₃ layer was further functionalized with Ru nanoparticles via deposition-precipitation method. The resulting metallic supported Ru/y-Al₂O₃/Pd-Ag membrane system showed catalytic activity when integrated in the setup for ammonia cracking under a 100 mL_N min⁻¹ NH₃ flow, promoting 65.8% NH₃ conversion at 500 °C. The presence of Ru in the mesoporous layer was qualified via post-mortem XPS survey scan of the laver. Although further investigations are needed to fully quantify and compare the effective catalytic activity of the functionalized mesoporous layer, the promising results show the conceptual possibility for further function lization of Pd-Ag membranes to be employed as self-standing catalytic membrane reactors.

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Appendix D Additional characterizations of embedded Ru

Prior to the functionalization with Ru of the γ -Al₂O₃/Pd-Ag layer of highly selective membrane ML6 presented in Chapter 5, a twin Ru/ γ -Al₂O₃/Pd-Ag layer was prepared onto defective membrane ML1. The following characterizations were carried out on ML1 to qualify the presence of Ru before deposition precipitation onto highly selective Ru/ γ -Al₂O₃/Pd-Ag membrane ML6.

In Figure D.1, SEM-EDX mapping of ML1 Ru/ γ -Al₂O₃/Pd-Ag layer, qualifying the presence of well dispersed bulk Ru in the layer matrix. Al and O are also present, further confirming the presence of γ -Al₂O₃. Additionally, Pd and Ag are detected from the selective Pd-Ag layer beneath. In Figure D.2, XRD characterization of ML1 Ru/ γ -Al₂O₃/Pd-Ag layer. The XRD patterns show clear presence of Pd-Ag alloy, which is the most present pattern, partially overlapping the other layer elements. However, weak peaks at 33.5° and 37° are detected, particularly, the weak peak at 37° could be ascribed to XRD patterns for samples with multiple layers prove insufficient to properly characterize the presence of an element of interest. In Figure D.3, Ru 3p XPS spectra of twin ML6 layer, further confirming the presence of a 3p_{3/2} metallic Ru peak at ~462 eV [4].



Figure D.1. SEM-EDX elemental mapping of Ru/γ-Al₂O₃/Pd-Ag layer peeled off from defective ML1 membrane, surface view at 1500x.



Figure D.2. XRD pattern of Ru/ γ -Al₂O₃/Pd-Ag layer peeled off from defective ML1 membrane.



Figure D.3. Ru 3p XPS spectra and corresponding peak fitting of Ru/ γ -Al₂O₃/Pd-Ag layer peeled off from defective ML1 membrane.

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Chapter 6 Metallic supports reproducibility considerations with a statistical approach⁵

In this Chapter, a hybrid observational-statistical approach is applied to elucidate on the reproducibility of the Hastelloy X supports pre-treatment procedure proposed in Chapter 3, considering a representative sample of multiple supports. Each pre-treatment step has been thoroughly characterized and observed with ANalysis of Variance (ANOVA) as statistical tool, introducing a new approach to composite Pd membranes preparation.

The analysis allowed to set average surface roughness (*Ra*) <0.8 µm, average profile height (*Rz*) <7 µm, in-pore leveling (Δ) <6 µm, as targets for support morphology reproducibility. The target average pore diameter after asymmetric filling was identified as 100-500 nm, and the target average pore diameter after interdiffusion barrier deposition was <=100 nm. The most effective particle size for in-pore leveling was identified as <=5 µm and the most effective particle size for average pore diameter reduction was confirmed as 18 µm.

⁵ This chapter is based on the following paper:

S. Agnolin and F. Gallucci (2024), "Unravelling the effects of surface modification pretreatments on porous hastelloy X supports for H_2 selective Pd-based membranes preparation with a statistical approach," *J. Memb. Sci.*, vol. 700, p. 122690.

6.1 Introduction

Both in Chapter 1 and Chapter 4, it was extensively discussed how Pd-based membranes find their collocation for most applications in which H₂ is the desired product (membrane assisted steam methane reforming [1][2][3], membrane assisted ammonia decomposition [4][5][6] and even membrane assisted dehydrogenation applications [7][8]). Moreover, through this Thesis, the use of supported thin Pd films for these applications is a recurring topic. Emphasis was posed on the differences between ceramic supported Pd films and metallic supported Pd films. The ease of deposition given by the easily tailorable superficial characteristics of the ceramic supports (i.e., low surface roughness, average pore size ~100 nm) [9][10][11] plays a pivotal role in membrane performance reproducibility. Particularly important is their average pore diameter (~100 nm) and narrowness of pore size distribution, which guarantees ease of pore closure via electroless Pd plating. In the case of metallic supported Pd membranes, however, the deposition of Pd films on steel-based supports requires additional steps due to:

- i. Insufficient support surface quality (i.e., high surface roughness, large superficial pore size ~20μm) [12][13].
- ii. Strong support-Pd interaction known as metallic interdiffusion [14][15][16].

It is therefore necessary to investigate suitable support pre-treatments to ease the deposition of Pd-based films [17][18], posing consequential difficulties to their ease of reproducibility. Contrary to ceramic supports, the large average pore size and the width of the distribution naturally prevent ease of closure with electroless Pd deposition. Moreover, even when all the pre-treatments previously discussed in this Thesis are applied, the reproducibility of final membrane performance cannot be achieved with a fixed procedure, but rather with target setting. In Chapter 4, a reproduction by target method was proposed to reproduce a support yielding to a highly selective Pd-Ag membrane via electroless plating. However, this target was chosen based on a sole support sample, which was fabricated via the preparation procedure discussed in Chapter 3. The preparation procedure development was carried out by studying the support's surface morphology with a statistical method [19]. Therefore, with the aim to provide more precise targets for supports reproducibility, a full statistical analysis on a representative supports sample is proposed in this Chapter.

Statistical methods are often employed in membrane's performance assessment, where varying membrane reactor operating conditions such as temperature, pressure, feed flow, etc. results in an outcome on membrane separation performance [20][21][22]. Moreover, they are often applied whenever the selected type of membrane allows for a non time consuming preparation, when keeping all non-analyzed preparation parameters constant is easily achievable or when solely a few parameters are expected to influence membrane performance (i.e. with polymer casting) [23][24][25]. However, when observing experimental sections in the literature of Pd-based/composite membranes preparation, trial-and-error or one factor at a time (OFAT) design of experiment methods are the most implemented, mostly due to their complex, time-intensive preparation procedure [26][27][11][28]. These methods offer in fact a rapid insight on which of the multitude of parameters in membrane preparation can be influential in final performance, with a non-time-consuming design. However, this strategy implies the analysis of a sole factor or a sole level combination at the time, moving along an experimental zone which is dictated solely by the experience of the experimenter. This approach implies that

oftentimes solely the best performing membranes (resulting from the best combination of investigated factors) are presented [16]; [29]—[35]. However, a multitude of parameters can hinder the reproducibility of best results, especially if the applied preparation procedure includes intrinsically random steps (i.e. large differences between support surface characteristics, wide support pore size distributions, the filling procedure proposed in Chapter 3, etc.). Moreover, detection of differences in average values and characterization techniques of various preparation steps still require a certain degree of interpretation which is left to the experience of the experimenter.

To analyze membrane preparation steps without observational bias, backing up observation with mathematical considerations, Design of Experiment (DoE) and statistical analysis techniques can be employed. One of the main objectives of DoE is to verify a hypothesis efficiently and cohesively, allowing the utilization of a suitable statistical technique for the data analysis to follow [36]. The Analysis Of Variance (ANOVA) technique, provided the data fulfills the necessary assumptions, can be used to test null hypothesis of equality of several means of several independent groups of observations having same variances [37]. It assesses potential differences in a continuous dependent variable by one or more independent variables (factors) having two or more levels.

In this Chapter, the characterization of the surface modification techniques that were proposed through this Thesis, aimed at rendering highly rough Hastelloy X filters with large pore diameter suitable for Pd deposition via electroless plating, is carried out with a hybrid observational-statistical approach. The filters are modified by polishing, etching, filling with α-Al₂O₃ particles of decreasing size and deposition of a γ-Al₂O₃ interdiffusion barrier. Subsequently, an elucidatory study of the main variables involved in surface modification of metallic supports for Pd-based membranes is carried out. Such variables and their evolution are investigated for each of the chosen support pre-treatments via suitable DoE, coupled with ANOVA as analysis tool. The pre-treatments are operated on a suitable sample of 20 support filters, drawn from a population of supplied supports. Onto each support, a sample representative of a population of pores is drawn. The measurement and repetition of the same for morphological variables involved in each pretreatment guarantees for the first time to study the effect of support pre-treatment steps on several equal samples, allowing for the correlation between the studied outcome variables and support reproducibility considerations, completed by setting suitable targets to ensure final supports with similar surface characteristics.

6.2 Materials

Four 50 cm long porous sintered Hastelloy X filters have been acquired from Hebei Golden Flame Wire Mesh Co, China. The filters were cut in samples of 10 cm and welded to dense stainless-steel caps to achieve a one close end configuration, while the other side was welded to a dense stainless-steel tube, as per previous procedures. The samples were then introduced in a vibratory polishing machine for a total amount of 6 h. They were then rinsed with deionized water and dried in a tubular furnace at 120 °C for 2 h. The dry samples were then submerged in fresh Rey water for 30 s each. They were once again thoroughly rinsed inside and out with deionized water immediately after submersion to prevent the etching process from continuing. Finally, the physicochemical pre-treatments were completed with an oxidation process in a static air furnace at 750 °C for 1 h, with a heating ramp rate of 3 °C min⁻¹.

The filters were filled via dip-coating with a 10 wt.% dispersion of α -Al₂O₃ of different particle sizes (18 µm, 5 µm) and for a different number of cycles (20, 30), according to the DoE described in the following sections. Finally, 5 selected supports were asymmetrically filled with spherical α -Al₂O₃ of decreasing size (18 µm, 5 µm, 1.5 µm). Onto these supports, a γ -Al₂O₃ interdiffusion barrier was deposited by vacuum assisted dip-coating of a 1.2 wt.% boehmite-PVA-PEG solution, rotary drying at 60% relative humidity and 40 °C, and sintering in air atmosphere at 550 °C for 1h, as per previous Chapters [12]. The pre-treatments were thoroughly characterized for each of the 20 sample supports with the characterization techniques discussed in the next section.

Finally, membrane MR was prepared via electroless plating of Pd. The membrane was fabricated onto a support presenting average surface roughness (Ra), average profile heigh (Rz), average in-pore filling (Δ), and average pore diameter (d) below the targets set with this work. The plating bath was composed of Pd(II)Acetate, EDTA, NH₄OH 1M, and AgNO₃.The modified support was seeded with Pd nuclei in 0.6 vol.% Pd(II)Acetate in chloroform and reduced in hydrazine 1M. Thereafter, the substrate was submerged in the plating bath for 2 h in presence of hydrazine. Subsequently, a 0.113 mmol/L AgNO₃ solution was added to the bath with an addition rate of 0.04 ml/min. After 5 h the membrane was removed from the plating bath, thoroughly rinsed with demi water inside and out, and annealed at 550 °C in Ar/H₂ atmosphere for 4 h, with a heating ramp of 1 °C/min in sole Ar.

6.3 Methods

In Chapter 3 [19], a balanced design of in-pore measurements (via laser-optical confocal microscopy) on a population of support pores using solely 3 supports was proposed as starting point for considerations about the effects of support filler size and amount of filling cycles employed. In this work, the aim is to expand the analyses to a population of different supports, rather than solely different pores. This allows for more precise inference on the effects that each support pre-treatment has on the following one. 20 supports have been prepared and 5 random pores (or positions, in case of contact profilometry) are analyzed, expanding the power of the analysis. The use of different supports allows the measurement of each support's pore diameter distribution (PSD) after each pre-treatment, adding the support's average pore diameter as outcome variable to the analysis.

The use of a sample of 20 prepared supports is considered representative of a population of different supports, each independent from another and each containing a population of pores. The representativeness of the sample is ensured by the randomness of supports choice, which are drawn from supplied 50 cm supports randomly cut and mixed into a batch of 10 cm supports. Meanwhile, the population of pores on each support is analyzed with a sample of 5 observed images (or positions) for each support. The imaging is carried out as randomly as possible, positioning the microscope lens (or the profilometer) onto different locations of the examined support, avoiding selection bias as much as possible. However, due to experimental effort, solely 5 pores and positions are examined for each support. Even though ANOVA is considered robust for small sample sizes when the design is balanced and the data respects variance homogeneity [38]-[41], the small imaging sample size is to be taken into account during the observation of statistical inference by coupling the results with the observation of descriptive statistics (i.e. density plots, boxplots, average values) or eventual previous analyses (i.e. the inference carried out in our previous works [19]). Even though exploratory, considering its limitations, this design opens the possibility for a cohesive analysis of the changes occurring with each support pre-treatment and how these changes may influence the next preparation steps within a whole production population, ultimately giving precious insight on the actual, factual reproducibility of the membrane supports and, in turn, the membranes themselves. Moreover, it represents a starting point for similar, additional statistical studies which can ultimately increase the sampling size, yielding to a greater amount of information and a greater inferential precision.

For this analysis, the seeding and plating procedures have been excluded from the evaluation, as they do not represent critical reproducibility steps. Both plating and seeding procedures are in fact optimized for ceramic supports within the targeted surface characteristics and are not expected to fail once a support is properly tuned to the desired performance.

Outcome variables evaluation: characterization techniques

For each support modification treatment, the following characterization techniques were employed:

i. The pore morphology was analyzed via laser-optical confocal microscopy (laser-optical confocal microscope, Keyence, Osaka, Japan) by imaging 5 random pores on each support's surface, yielding to the *outcome variable* Δ , to be intended as the difference between the highest and lowest point of the imaged pore's height distribution (Figure 6.1);



Figure 6.1. Laser-optical confocal imaging, height distribution view and Δ definition.

- ii. The surface roughness of the supports was analyzed via contact profilometry (MarSurf PS 10, Mahr) on 5 random positions of the selected support, yielding to *outcome variables Ra (Avg. surface roughness) and Rz (Avg. roughness profile's height),* characteristic roughness profile parameters.
- iii. The pore size distribution of the supports was measured via Capillary Flow Porometry (CFP) in a specifically designed setup described in Chapter 3 [19]. The *average pore diameter (Mean flow pore)* was kept as outcome variable.

Design of Experiment (DoE)

The analysis proposed in this work was carried out for the following treatment stages, with the following considerations:

- i. <u>Untreated filters</u> (Appendix E, Table E.1): The sample of untreated supports was considered representative of a population of supports provided by the supplier, as well as supports which might be employed by any membrane preparation operator who intends to reproduce a highly selective Hastelloy X supported Pd-based membrane. For this reason, 14 supports were characterized with the aim to assess the outcome variables variability within each of the supports and between different supports. A One-way ANOVA was then used to compare the outcome variables between supports.
- ii. <u>Polished and etched filters</u> (Appendix E, Table E.2): After undergoing polishing and etching pre-treatments, the supports presented morphological changes. The design was balanced by adding 6 supports, increasing the sample size to 20. In particular, any statistical changes caused by the treatment were compared with their untreated version. A One-way ANOVA was used to compare the outcome variables between supports.

- iii. <u>Symmetrically filled filters</u> (Appendix E, Table E.3, Table E.4): Each etched and polished support was filled with α-Al₂O₃ of two different sizes, for different amounts of times. For each *Filling cycles-Filler size* combination, 5 repetitions for all outcome variables were carried out. For this analysis, all outcome variables were normalized on their corresponding unfilled values from the previous step. A Two-way ANOVA was then employed to assess whether the variation of either factor (filling size or *Filling cycles*) or their interaction (*Filling cycles-Filler size*) generated any statistically significant changes in the selected outcome variables.
- iv. <u>Asymmetrically filled filters</u> (Appendix E, Table E.5): 5 symmetrically filled supports were selected for asymmetric filling design, based on the results of the previous analyses (discussed in the next sections). The supports were completed by the addition of α -Al₂O₃ particles with average diameter of 5 µm and 1.5 µm, for an amount of 30 cycles per size, as per preparation procedure. Each outcome variable was evaluated, and a One-way ANOVA was performed to assess differences between supports. The results were then compared with previous pre-treatments.
- v. <u>Filters equipped with interdiffusion barrier</u> (Appendix E, Table E.5): The 5 supports were completed with the interdiffusion barrier, which was deposited via vacuum-assisted dip-coating with constant parameters as per preparation procedure. Each outcome variable was evaluated once again and a One-way ANOVA was performed to assess differences between supports. The results were compared with previous pre-treatments.

Analysis of variance

The two main aims of classical ANOVA [37] are:

- i. To examine the relative contribution of different sources of variation (i.e., factors or combination of factors, predictors, independent variables) to the total amount of variation in the response variable (i.e., dependent variable, influenced outcome variable).
- ii. To test the null hypothesis (H₀), specifically:
 - a. H₀: The means of the independent groups of observations are not statistically different (*p*-value > 0.05).
 - b. H₁: There is at least one statistically different mean among the independent groups (*p*-value < 0.05).

Considering the sum of squares (SS) and the degrees of freedom (df) between examined groups (B):

$$SS_{B} = \sum n_{k} (\overline{Y}_{k} - \overline{Y})^{2}$$
⁽¹⁾

$$df_{\rm B} = k - 1 \tag{2}$$

And within groups (*W*):

$$SS_W = \sum (Y_i - \overline{Y_k})^2 \tag{3}$$

$$df_W = N - k \tag{4}$$

Where n_k is the number of cases in a sample, \overline{Y}_k the mean of the group, \overline{Y} is the overall mean (grand mean), k is the total number of groups, Y_i is the individual score in a group, and N is the number of observations. The *F*-ratio is then calculated as the ratio between the mean sum of squares between groups and within groups:

$$F - ratio = \frac{SS_B/df_B}{SS_W/df_W}$$
(5)

Therefore, the higher the *F*-ratio the larger the variation between groups of observations rather than the variation within groups of observations. To a larger *F*-ratio corresponds a lower *p*-value, which allows for the rejection of the null hypothesis if < 0.05.

One-way ANOVA is used to analyze the means of independent groups of observations for an outcome variable influenced solely by one independent factor (with multiple levels). In this work, the factor is the support code, and the tool is used to analyze if the average of the outcome variables is statistically different between each support.

Two-Way ANOVA + interaction refers to an ANOVA using two independent variables (two factors are involved). It can be used to examine the interaction between the two independent variables. Interactions indicate that differences are not uniform across all levels of the independent variables, meaning the factors cannot be considered independent from each other in their contribution to the variance of the selected outcome variable. A Two-way ANOVA allows to assess a combination of multiple levels of two factors on a response variable with a balanced design, the experiment is designed in such a way that an equal number of observations is performed for each combination of the levels, guaranteeing the most precise outcome possible for the testing of the selected null hypothesis. Each ANOVA analysis relies on three pillar assumptions:

- i. The population from which samples are drawn is normally distributed (normality).
- ii. The samples are independent and random with respect to each other (randomness of sampling).
- iii. The variances among the groups are approximately equal (homogeneity of variances or homoskedasticity).

The assumptions are verified for each analysis by observing:

- i. The normal probability plot paired with a Shapiro-Wilk test for normality [42]; whether the data did not assume a normal distribution, a Log transform or sqrt transform are performed on the dataset, according to the skewness of the data distribution.
- ii. Residual vs order plot for randomness of sampling.
- iii. Residual vs fit plot paired with a Levene test for homogeneity of variances [43].

The null hypothesis for ANOVA is accepted if p-value > 0.05. Moreover, if ANOVA is paired with an appropriate post-hoc test, it is possible to assess which of the analyzed groups express statistically different means. For this work, a Tukey pairwise comparison was employed. All analyses are carried out with R language and the chosen environments were Rscript and Rstudio [44].

6.4 Results and discussion

Characterization of support pre-treatments

Filter E14 was selected from the support's batch for illustrative purposes. In Figure 6.2. the surface evolution of filter E14 undergoing the selected pre-treatments is shown in 3D view. In Figure 6.2a, the untreated filter's surface is imaged. Specifically, a large superficial pothole with superficial diameter ~45 µm is noticeable on the untreated filter's surface, as well as high profile peaks and deep valleys. In Figure 6.2b, the surface of the support after polishing and etching is shown. After polishing, the high-profile peaks are lowered and the surface is leveled. However, porous structures are covered by plastic deformation of the peaks being pushed into the profile valleys, reducing the gas permeation through the support. The porous structure under the polished layer is then uncovered via chemical etching, which results in valley veins interconnecting larger superficial potholes and surrounding the smoothened superficial islands, as shown in the 3D view. These veins contribute to the re-increase of the gas permeance through the support. In Figure 6.2c, the 3D view of a support's large pothole both empty and filled with α -Al₂O₃ of decreasing size is shown. 18 µm α -Al₂O₃ is layered first with the aim of clogging the large pore necks and reducing the filter's average pore size. 5 µm and 1.5 μ um α -Al₂O₃ are then subsequently layered to improve the leveling of the pore mouth. In this way, the asymmetrical filler operates a progressive closure of the pothole, reducing its average diameter. In Figure 6.3, the reduction in average pore diameter of the filter is monitored by analyzing the pore flow distribution of the filter after each pre-treatment via CFP coupled with height distribution by laser-optical imaging analysis. When the support is solely polished and etched it presents large pore mouths (blue) interconnected by valley veins (green), with a large height difference and an average pore diameter of ~ 1.5 um (Figure 6.3a). When the support is asymmetrically filled, the closure and leveling effect on the pore mouth is observed by the shift of the height distribution, the presence of the filler in the pore mouth (green) and the average pore diameter shift to ~500 nm (Figure 6.3b). After the addition of the interdiffusion barrier, the height distribution imaging shows an even more pronounced leveling effect: a layer covering the pore mouth (green), reducing the pore valleys size (red), and pushing the average pore diameter below 100 nm can be clearly distinguished (Figure 6.3c). The gualitative characterization of E14 confirms the conceptual reproducibility of the procedures proposed through this Thesis.



Figure 6.2. 3D laser-optical imaging of: (a) untreated E14 filter's surface; (b) polished, etched E14 filter's surface; (c) E14 filter's surface asymmetrically filled with α -Al₂O₃ 18 µm, 5 µm, and 1.5 µm, each imaged in surface view; (d) E14 filter's surface equipped with γ - Al₂O₃ interdiffusion barrier.



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Figure 6.3. Cumulative flow percent distribution (evaluated with CFP) and height distribution view (evaluated via laser-optical microscopy) of: (a) polished and etched E14 support; (b) E14 support asymmetrically filled with α -Al₂O₃ 18 µm, 5 µm, and 1.5 µm; (c) E14 support equipped with a γ -Al₂O₃ interdiffusion barrier.

Statistical analysis of support pre-treatments

Untreated filters

In Figure 6.4, the boxplot representation of in-pore morphology (Δ), average surface roughness (Ra), and average profile height (Rz) of completely untreated filters is shown. The length of the box and the whiskers for each sample denote a large variability within the repetitions for each support, meaning that the examined variables can significantly change with respect to the randomly chosen measured pore/position. The average values of the outcome variables correspond to Δ = 26.9 µm, Ra = 4.3 µm, and Rz = 25 um. These values of surface roughness are well in agreement with bare PSS substrates previously investigated in literature for the preparation of metallic supported Pd-based membranes. In particular, high surface roughness and large pore mouths have been observed via SEM imaging in several membrane preparation studies, for Porous Stainless Steel (PSS) and Hastelloy X [18] supports ranging between 0.1 µm and 0.5 µm media grade both in tubular and disk form [34], [45]-[48]. Ryi et al. [49] utilized 3D renders of acquired 0.5 µm PSS substrates and evaluated their height distribution, observing a height difference (similarly to the Δ variable analyzed in this work) of ~10 µm. Such height difference, associated with high surface roughness (topographically observed or measured via contact profilometry/atomic force microscopy/laser-optical microscopy, etc.) is thought to impede the deposition of defect-free Pd thin films, requiring support modification steps to achieve acceptable support's surface characteristics.

The results of the One-way ANOVA between supports for each outcome variable is reported in Table 6.1. The average values of Δ and Rz are not statistically different in a significant way between each of the prepared sample supports. This result denotes how at this stage, right after the supports are supplied, cut, and welded, each of them can be considered quite similar to one another. The morphological characteristics of each filter are variable within each one of them, but if they are compared to one another they do not significantly differ. The only variable that presented a significant difference corresponds to Ra. By applying the Tukey pairwise comparison, each pair of average Ra between supports are compared, allowing to understand which sample supports present Ra that are statistically different from each other. In the selected supports batch, the Tukey pairwise comparison highlighted a statistical difference solely between average Ra of sample D and sample F. This result allows to speculate that, if the examined support batch is representative of a population of supplied supports, at least 2 in 20 supplied samples might significantly differ from each other in terms of average surface roughness.

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Figure 6.4. Boxplot of (a) Δ , (b) *Ra*, and (c) *Rz* for each untreated support of the chosen sample batch.

In-pore morphology (Δ) [μm]					
Factor F-value P-value Significance					
Support code	1.503	0.145	no		
Avg. profile surface roughness (<i>Ra</i>) [μm]					
Factor F-value P-value Significan			Significance		
Support code	1.919	0.047	*		
Tukey pairwise comparison: D-F					
Avg. profile height (<i>Rz</i>) [μm]					
Factor	F-value	P-value	Significance		
	i vuiuc	i valao	eiginneanee		

Table 6.1. Results of One-way ANOVA on Δ , Ra, and Rz of fully untreated filters. The relevant factor effect is assumed significant if *p*-value < 0.05, with a confidence interval of 95%.

Polished and etched filters

Once physicochemical support pre-treatments are operated, a variability increase within the dataset can be noticed in terms of visual differences between each filter, as large numbers of boxes fall outside of each other for each outcome variable (Figure 6.5).

The results of the One-way ANOVA on each outcome variable are reported in Table 6.2. A very strong statistically significant difference is confirmed between each support for all the examined outcome parameters. The Tukey pairwise comparison highlights differences between 4 pairs of supports with respect to Δ , 43 with respect to Ra, and 27 with respect to Rz. These results highlight the random effect of the operated physicochemical pre-treatments: even though the initial batch is of non-statistically different supports, the pre-treatments increase the morphological differences between each filter. These differences imply an intrinsic difficulty in controlling the process around a desired average value for all the observed outcome parameters, particularly in terms of average surface roughness, with the highest observed number of statistically different filter pairs. This increased differences between supports proves inconvenient in terms of reproducibility, as these differences can propagate to the following filling procedure.

In Figure 6.6, the data distribution for each outcome variable before and after the physicochemical pre-treatments are compared. A shift towards lower Δ , Ra and Rz values can be observed, with average $\Delta = 19.62 \ \mu m$, $Ra = 1.28 \ \mu m$, and $Rz = 10.35 \ \mu m$. This confirms the effectiveness of the chosen treatments in terms of shift of morphological characteristics towards a smoother, more even surface. Moreover, in Figure 6.6a, a higher distribution spread with respect to the untreated morphological data distribution for Δ of the untreated supports can be observed. This behavior indicates the introduction of morphological differences within the in-pore behavior of the support itself, as the randomly chosen measurement points yield to more variable results after the pretreatments. This might suggest that, at this stage, the distance between pore valleys and superficial peaks is quite variable along each support. In Figure 6.6b and Figure 6.6c little

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variation of the distribution spread is observed, indicating that the variability of *Ra* and *Rz* stays the same after the support physicochemical pre-treatments, denoting a variable surface roughness profile but an overall smoother surface. In several literature works, as-supplied PSS and Hastelloy X supports are treated via surface polishing in order to reduce their original surface roughness. Generally, all the examined literature works confirm the effectiveness of this pre-treatment by observing morphological surface changes via SEM imaging of a treated sample [18], [19], [46], [49], [50]. The proposed analysis of a larger batch of supports and the observation of the surface roughness variables evolution within the batch confirmed the average smoothening effect of this strategy but highlighted its random nature, emphasizing the need for a quality check on each support, on different points of the surface.



Figure 6.5. Boxplot representation of (a) Δ , (b) Ra, and (c) Rz for each filter of the sample batch after the polishing and etching pre-treatments.



Figure 6.6. Comparison of density plots of (a) Δ , (b) *Ra*, and (c) *Rz* between the sample batch of polished and etched supports (red), and the sample batch of fully untreated supports (blue).

Table 6.2. Results of One-way ANOVA on Δ , Ra, and Rz of polished and etched filters. The relevant factor effect is assumed significant if *p*-value < 0.05, with a confidence interval of 95%.

In-pore morphology (Δ) [μm]					
Factor F-value P-value Significance					
Support code	3.11	2.11.10-4	***		
Tukey pairwise	comparison	: 4 statisticall	y different pairs		
Avg. profile surface roughness (<i>Ra</i>) [μm]					
Factor	F-value	P-value	Significance		
Support code	9.05	4.15.10			
Tukey pairwise	Tukey pairwise comparison: 43 statistically different pairs				
Avg. profile height (<i>Rz</i>) [μm]					
Factor	F-value	P-value	Significance		
Support code	5.98	5.02·10 ⁻⁹	***		

Tukey pairwise comparison: 25 statistically different pairs

Symmetrically filled filters

For the optimization of the filling procedure, it is crucial to understand the morphological changes that occur when fillers of different sizes are applied to the chosen supports. . In the work of Macedo et al. [31], several dimensions of Ceria particles have been evaluated to find the most appropriate size for membrane interlayer fabrication. Similarly, Xu et al. [13] coated a PSS substrate with alumina powder of different particle size suspended in water. In Chapter 3 [19], the morphology of three different supports consecutively filled with alumina 18 µm. 5 µm, and 1.5 µm for an increasing number of times (10, 15, and 20) was studied. The ANOVA then allowed to infer on a population of pores with a sample drawn from three supports. It was then assumed that the outcome of the analysis could be applied to different supports from different batches of the same supplier. While this speculation can be considered reasonable as hypothesis, it would still be unverified by objective experimental data, unless more membranes are prepared with the same procedure as the three considered supports. This was the case of membrane M2 of Chapter 4. for which a target of reproducibility was derived from the analysis carried out in Chapter 3 [19]. However, to be able to confirm that the behavior of the filler particles is extendible to a population of supports, the analysis must be expanded on pores coming from a representative support sample. For this purpose, the results of the extended Twoway ANOVA are listed in Table 6.3.

In-pore morphology (Δ _{reduction}) [%]					
Factor	F-value	P-value	Significance		
Filler size	2.67	0.1060	No		
Filling cycles	0.51	0.4770	No		
Filler size:Filling cycles	13.54	0.0004	***		
Avg. profile surface roughness (<i>Ra_{reduction}</i>) [%]					
Factor	F-value	P-value	Significance		
Filler size	1.03	0.31	No		
Filling cycles	2.23	0.14	No		
Filler size:Filling cycles	1.36	0.25	No		
Avg. profile height (<i>Rz</i> _{reduction}) [%]					
Factor	F-value	P-value	Significance		
Filler size	0.02	0.88	No		
Filling cycles	1.96	0.16	No		
Filler size:Filling cycles	2.63	0.11	No		
Avg. pore diameter (D _{reduction}) [%]					
Factor	F-value	P-value	Significance		
Filler size	2.28	0.17	*		
Filling cycles	6.55	0.03	No		
Filler size: Filling cycles	0.82	0.39	No		

Table 6.3. Two-way ANOVA + interaction results for Δ reduction, *Ra* reduction, *Rz* reduction, and average pore diameter reduction promoted by the factors *Filler size* and *Filling cycles*. The relevant factor effect is assumed significant if *p*-value < 0.05, with a confidence interval of 95%.



Figure 6.7. (a) Interaction plot of Δ reduction for the factors *Filler size* and *Filling cycles*; (b) main effect plot of average pore diameter reduction for the factor *Filler size*.

The Two-way ANOVA results for the reduction of Δ confirm the in-pore behavior observed in our previous work [19]: as the interaction contribution is statistically significant, it is not possible to decouple the effects of solely Filling cycles or Filler size on the observed supports. A 5 µm filler improves the superficial morphology of the supports with less filling cycles with respect to the filler of larger size, which requires a larger number of cycles (Figure 6.7a). However, when the analysis is extended to a batch of supports there is no detectable statistical difference between the average values of Ra and Rz between supports filled in different ways. These findings indicate that the selected filler sizes and cycle count do not exhibit a noticeable impact on the surface roughness parameters of the profile. Rather, their influence appears to be confined solely to the behavior within the pores. However, the acceptance of ANOVA's null hypothesis for outcome variables Ra and Rz could also be reconducted to a Type II error (wrongly accepting a null hypothesis), due to the combined effect of high variability of the surface profilometry data and the small sample size for each support. In our previous analysis, in fact, the examined Filler size and *Filling cycles* sorted an effect on profile roughness parameters when a larger sample of pores (on solely three supports) was observed [19].

This conclusion suggests that:

- i. The expansion of the analysis to a larger sample of support pores (e.g. 30 repetitions for each support), although time-consuming, would exclude the possibility of neglecting statistically significant differences between outcome profile roughness parameters, which are intrinsically more variable.
- ii. If Type II errors may be excluded, to sort a sensible effect also on profile roughness parameters, the analysis should be expanded to different *Filling cycles-Filler size* combinations. More specifically, as the filler of 5 μ m seem to sort the greatest effect on in-pore leveling, their combination with a larger number of *Filling cycles* (i.e., 50x, 60x) could be explored and the effect on profile roughness parameters assessed. Moreover, filler particles between 5 and 18 μ m (i.e. ~10 μ m, 8 μ m) could be added to the analysis, allowing to select an optimized combination and to infer on a greater plethora of possibilities to find an optimal filler.

Concerning the average pore diameter of the support, the results in Table 6.3 confirm that even for a population of supports, the size of the filler is the dominating factor (main and sole statistically significant effect) that will promote a reduction in the average pore diameter. Similarly, in [31], the supports prepared with an interlayer particle size best matching the diameter of the chosen PSS substrate (medium Ceria particles – 0.1 μ m media grade PSS) led to the highest H₂ permeance and the best observed surface morphology amongst the presented samples, suggesting an effect of the filler size on a sensitive variable, which was identified in this work as the average pore diameter of the supports. As observed in Figure 6.7b, the 18 μ m filler promotes a statistically significant decrease in average pore diameter with respect to the smaller filler, completing purely observational results obtained in [19] with statistical meaning.

Given these results, the development of an asymmetrical filling configuration is backed up by mathematical considerations on the gathered datasets. In particular:

- i. The variability increase given by the polishing and etching pre-treatments needs to be resolved by the following filling design and/or interdiffusion barrier deposition.
- ii. Fillers of largest size promote a statistically significant decrease in the average pore diameter of the supports.
- iii. Fillers of largest size require a larger number of cycles to operate in-pore morphological changes, while fillers of smaller sizes can require less.

Asymmetrically filled filters

Given the considerations in the previous analysis, five supports filled with 18 μ m α -Al₂O₃ particles were chosen as starting point for the asymmetrical filling evaluation. They were then completed with 5 µm and 1.5 µm particles and analyzed as-is. The results of the One-way ANOVA are listed in Table 6.4. By analyzing the effect on Δ of the asymmetric filling design, no statistically significant differences between the selected supports are detected. This result proves that the chosen asymmetric filling design reduces the differences between in-pore behavior of different supports, eliminating the differentiating effect sorted by the polishing and etching treatment. In Figure 6.8a, all the Δ distributions for the examined supports overlap around a similar average value, while their spreads still differ from each other. This result denotes guite some variability within the pores of the supports themselves. Specifically support E1, given the larger spread of its morphological distribution. At this stage, the variability within the pores of filled supports is inevitable, but such a spread for an isolated sample could be due to the intrinsic difficulty in controlling the filling procedure in the lab. Hence why the fabrication, monitoring and characterization of twin supports is so crucial to ensure membrane replicability. Particularly, given the spread of its in-pore characteristics, E1 support has a higher chance of resulting in a membrane with defects, making it harder to control its pore closure. Concerning the outcome variables Ra and Rz, the ANOVA results highlight statistical differences. Specifically, support E14 presents a strongly different Ra with respect to the others, while Rz differs generally for supports E14 and E12. These results indicate once more the difficulty in controlling profile surface roughness parameters solely by introducing a pore filler in the support. In Figure 6.8b and Figure 6.8c, the differences between the distributions can be distinguished in the density plots, where E14 is clearly shifted towards the left, differentiating its average value from the other supports.

In Figure 6.9, a clear distribution shift towards lower average pore diameters after the introduction of the asymmetric filler is observed. However, the distribution spread increases, meaning that after filling the average pore diameter is quite different amongst different supports. At this stage, it is important to properly design the amount of filling cycles to reach a target pore size, as demonstrated in Chapter 4 for steam methane reforming. In our previous work, 100 nm was chosen as pore diameter target to be as close as possible to a ceramic support average pore diameter. In this batch, the target is reached by the supports falling within the distribution's left tail. However, in the case of the right distribution tail (average pore diameter's distribution peak ~500 nm), the filling should be carried out once more to reach the target and ensure high selectivity on the final membrane.

Table 6.4. Results of One-way ANOVA on Δ , Ra, and Rz of asymmetrically filled supports. The relevant factor effect is assumed significant if *p*-value < 0.05, with a confidence interval of 95%.

In-pore morphology (Δ) [μm]					
Factor F-value P-value Significanc					
Support code	0.843	0.702	No		
Avg. profile surface roughness (<i>Ra</i>) [μm]					
Factor	F-value	P-value	Significance		
Support code	15.49	6.39·10 ⁻⁶	***		
Avg. profile height (<i>Rz</i>) [μm]					
Factor	F-value	P-value	Significance		
Support code	10.64	8.7.10-5	***		
Tukey pairwise co	mparison: E14	1-E1, E12-E18	, E12-E3, E12-E14		

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Figure 6.8. Density plot of: (a) Δ , (b) Ra, and (c) Rz for each asymmetrically filled support.



Figure 6.9. Average pore diameter density plot evolution. Comparison between solely polished and etched supports (blue) and asymmetrically filled supports (red).

Filters equipped with interdiffusion barrier

In Table 6.5 the results of the performed One-way ANOVA after interdiffusion barrier deposition are reported. All statistical differences between the supports have been erased by the deposition of the laver, except for the outcome variable Rz. However, the Tukey pairwise comparison detected a difference between two supports, E1 and E12. The differences between supports E1 and E12 in terms of Rz can be explained by the nature of Rz variable, which detects all possible peaks and valleys of the measured profile, retaining more information about the variability of the profile itself. However, the elimination of most statistical differences for all outcome variables highlights how the interdiffusion barrier deposition promotes the uniformity of all morphological characteristics between different supports. This behavior is shown in Figure 6.10, where the density plots for the outcome variables are compared amongst the supports of the batch. Particularly, all the distributions overlap over the same average values of Δ = 6.88 μ m, Ra = 0.814 μ m, and Rz = 5.77 μ m. Even though for some supports (E1, E18, and E14) the Δ distribution is still variable, the average value of Δ is sensibly lower if compared to the previous treatment steps. The same behavior is shown in the density plots for macroscopical roughness parameters Ra and Rz (Figure 6.10b, c), where the distributions sharpened around lower values. This data is well in agreement with Chapter 2 [12], in which the smoothening effect of the boehmite based interdiffusion barrier (dual function of preventing strong Pd-support interaction and reducing the surface roughness of the support) was introduced. It is thus possible to confirm the leveling effect of the barrier thanks to the statistical analysis of the selected support batch, considering the interdiffusion barrier as powerful tool to promote uniformity of the morphological characteristics of different supports. Similarly, in previous composite PSS/interlaver/Pd membrane preparation studies presenting different layers as strategy to prevent interdiffusion and improve superficial morphology of PSS/steel-based alloys, the deposition of an intermediate barrier promoted overall surface morphology improvement, pore mouths diameter reduction and general fullness of the PSS substrates, observed mostly via SEM imaging [31], [15], [17], [50]–[53].

In Figure 6.11, the average pore diameter density plot after the introduction of the interdiffusion barrier is shown. It is quite evident how the additional layer sharpens the density plot towards lower average pore diameter values (<500 nm). Particularly, 4 out of 5 of the supports reach the pore size distribution target (<100 nm) after interdiffusion barrier deposition. This result introduces a further effect of the addition of the interdiffusion barrier: even if the asymmetrical filler design leads to pores larger than 100 nm (~500 nm), the introduction of the additional layer will sharpen the average pore diameter below 300 nm for at least half of the examined supports. Therefore, in view of reproducibility, even if the asymmetric filling design is defective, part of the support batch can be recovered by means of addition of the interdiffusion barrier.

Table 6.5. Results of One-way ANOVA on Δ , Ra, and Rz of supports equipped with interdiffusion barrier. The relevant factor effect is assumed significant if p-value < 0.05, with a confidence interval of 95%.

	lı	In-pore morphology (Δ) [μm]			
	Factor	F-value	P-value	Significance	
	Support code	2.41	0.09	No	
	Avg. pr	ofile surfa [µ	ce roughne m]	ess (Ra)	
	Factor	F-value	P-value	Significance	
	Support code	2.15	0.11	No	
	Factor	F-value	P-value	Significance	
	Support code	3.88	0.017	*	
	Tukey	pairwise co	mparison: E	8-E12	
	1.2 (a) 0.9 (b) 0.6 0.3 0.0 0	5	ο 10 Δ [μm]	Support EL E12 E14 E18 E3	
6- <u>A</u> <u>4</u> - <u>2</u> - <u>0</u> .25 0.50	0.75 1.00 Ra [µm]	Support E1 E12 E14 E18 E3	2- <u>2:</u> <u>2:</u> <u>1:</u> <u>0</u> <u>2:</u>	4 6 Rz [µm	Support E1 E12 E14 E18 E3 8 10

Figure 6.10. Density plot of (a) Δ , (b) Ra, and (c) Rz for each support of the sample batch of supports completed with the γ -Al₂O₃ interdiffusion barrier.


Figure 6.11. Average pore diameter density plot evolution. Comparison between asymmetrically filled supports (red) and supports equipped with interdiffusion barrier (blue).

Reproducibility considerations

The results of the ANOVA highlighted:

- i. Negligible statistical difference between morphological variables of untreated filters.
- ii. Increased statistical difference between polished and etched filters, while promoting surface uniformity.
- iii. Statistically significant increase in superficial pore leveling operated by 5 μm fillers.
- iv. Statistically significant reduction in average pore diameter operated by 18 μm fillers.
- v. Statistically significant increase in pore leveling operated by asymmetric filling, with negligible statistical differences between in-pore behavior of supports filled in the same way.
- vi. Statistically significant smoothening effect of Y-Al₂O₃ interdiffusion barrier.
- vii. Statistically significant reduction in average pore diameter with the introduction of the interdiffusion barrier.

The results confirm the effectiveness of support pre-treatments in smoothening the surface, leveling the pores, and reducing the support's pore diameter; however, they denote variability between the supports and within their profile roughness parameters, highlighting the importance of filter monitoring during the manufacturing process. Suitable targets for support reproducibility are drawn from the analysis of the peaks of density distributions (avg. values) compared with the supports used for best performing membranes as:

- i. *Ra* <0.8 μm.
- ii. *Rz* <7 μm.
- iii. Average pore diameter after asymmetric filling \sim 100-500 nm (with the most effective particle size for pore diameter reduction \sim 18 µm).
- iv. Average pore diameter after interdiffusion barrier deposition ~100 nm.
- v. $\Delta < 6 \,\mu$ m (with the most effective particle size for in-pore leveling <=5 μ m).

Finally, the performance indicators and support characteristics of MR, fabricated on a support with the proposed targets, are shown in Table 6.6.

Table 6.6. MR support characteristic variables (Δ, Ra, Rz, and avg. pore diameter) compared with the proposed support targets and resulting membrane performance after Pd-Ag deposition in terms of: H2 permeance, N2, permeance, ideal H2/N2 selectivity measured at 500 °C and 1 bar trans-membrane pressure.

	SUPPORT		MEMBRA	NE
MR support (Hastelloy X polished, etched/α-Al₂O₃/ γ-Al₂O₃)		MR memb (Hastelloy X polish α-Al₂O₃/γ-Al₂O	rane ned, etched/ ₃/Pd-Ag)	
Ra [µm]	0.782	<0.8	Pd-Ag layer thickness [μm]	6-8
Rz [µm]	5.790	<7.0	H ₂ permeance [mol/s/m ² /Pa]	~6.1.10 ⁻⁷
Δ [µm]	5.115	<6.0	N ₂ permeance [mol/s/m²/Pa]	~2.4.10 ⁻¹¹
d [µm]	0.069	~0.100	H ₂ /N ₂ selectivity [-]	25416

This membrane displays selectivity > 10000 and H₂ permeance of $6.1 \cdot 10^{-7}$ mol/s/m²/Pa at 500 °C and 1 bar, similarly to the membranes summarized in Table 1. The high selectivity is promoted by the filling of the metallic support below the proposed targets. which ensure sufficient pore diameter reduction to promote full pore closure with Pd electroless deposition, at constant Pd-Ag thickness. On the other hand, the filling of the metallic support and the deposition of the interdiffusion barrier result in H₂ permeance values which are lower compared to Pd-based membranes obtained on ceramic supports (i.e. Arratibel et al. [54] could produce α -Al₂O₃/Pd-Aq/y-Al₂O₃ ceramic supported, double skinned membranes which could reach up to 5.10⁻⁶ mol/s/m²/Pa at 500 °C, 1 bar while keeping outstanding H₂ selectivity of 30000). However, for porous metal supports (particularly with media grade $\geq 0.5 \,\mu$ m), the closure of the large superficial pores via introduction of a filler and/or the deposition of an interdiffusion barrier are crucial, unavoidable steps to ensure gas tightness of the metallic supported Pd membrane and prevent Pd-metal interaction. Their presence in the support structure and their design has been shown to significantly impact membrane's H_2 permeation [55]–[57]. By fabricating M3, the proposed support preparation procedure resulted once again in a highly selective membrane (at constant Pd-Ag layer thickness). However, to fully confirm a statistical (and not solely observational) correlation between the Pd layer performance in terms of H₂ permeance and H₂/N₂ selectivity and the support variables Δ , Ra, Rz, and d further DoE studies with an increased number of membrane repetitions must be carried out. To reproduce the supports proposed in this work, the analysis suggests the adoption of the proposed targets for the modification of PSS/steel alloy supports with similar superficial characteristics, rather than a set-in-stone fabrication procedure.

6.5 Conclusions

Twenty Hastelloy X porous supports, drawn from a population of supplied supports, were successfully pre-treated to increase their suitability for Pd deposition via electroless plating. The operated pre-treatments were polishing, etching, symmetric and asymmetric filling with α -Al₂O₃ particles (18 µm, 5 µm, and 1.5 µm) and γ -Al₂O₃ interdiffusion barrier deposition. Each pre-treatment step was thoroughly characterized to elucidate the surface evolution of the supports.

A Design of Experiment coupled with analysis of variance as statistical analysis tool was successfully applied to infer on the morphological effects operated by each pre-treatment on the chosen filter's population. Suitable targets for supports reproducibility were drawn from the analysis as: $Ra < 0.8 \mu$ m, $Rz < 7 \mu$ m, average pore diameter after asymmetric filling ~100-500 nm (most effective particle size for reduction ~18 μ m), average pore diameter after interdiffusion barrier deposition ~100 nm, and in-pore leveling (Δ) <6 μ m (most effective particle size for leveling <=5 μ m).

These considerations offered further insight on employment of statistics as tool of analysis for composite inorganic membrane preparation, as well as targets to reproduce supports with suitable superficial characteristics for Pd deposition via electroless plating.

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Appendix E | Supplementary statistical considerations

Design of Experiment tables for ANOVA

Table E.1. DoE for the study of the morphological variables of untreated supports.

Laser-optical confocal microscopy (Δ)					
Definition	Variable type	Name	Variable levels		
Outcome	Dependent	∆ [µm]	-		
Factor	Independent (A)	Support code [-]	Α,, Ρ		
Average surface roughness (<i>Ra</i>)					
Definition	Variable type	Name	Variable levels		
Outcome	Dependent	<i>Ra</i> [µm]	-		
Factor	Independent (A)	Support code [-]	Α,, Ρ		
Factor	Independent (A) Average p	Support code [-] rofile height (<i>Rz</i>)	Α,, Ρ		
Factor Definition	Independent (A) Average p Variable type	Support code [-] rofile height (<i>Rz</i>) Name	A,, P Variable levels		
Factor Definition Outcome	Independent (A) Average p Variable type Dependent	Support code [-] rofile height (<i>Rz</i>) Name Rz [µm]	A,, P Variable levels –		

Table E.2. DoE for the study of the morphological variables of polished and etched supports.

Laser-optical confocal microscopy (Δ)					
Definition	Variable type	Name	Variable levels		
Outcome	Dependent	∆ [µm]	-		
Factor	Independent (A)	Support code [-]	E1,, E20		
	Average surface roughness (Ra)				
Definition	Variable type	Name	Variable levels		
Outcome	Dependent	<i>Ra</i> [µm]	-		
Factor	Independent (A)	Support code [-]	E1,, E20		
	Average p	rofile height (<i>Rz</i>)			
Definition	Variable type	Name	Variable levels		
Outcome	Dependent	<i>Rz</i> [µm]	-		
		L, _			
Factor	Independent (A)	Support code [-]	E1,, E20		
Factor	Independent (A) Average p	Support code [-]	E1,, E20		
Factor Definition	Independent (A) Average p Variable type	Support code [-] ore diameter (<i>D</i>) Name	E1,, E20 Variable levels		
Factor Definition Outcome	Independent (A) Average p Variable type Dependent	Support code [-] ore diameter (D) Name D [µm]	E1,, E20 Variable levels		

Laser-optical confocal microscopy (
Definition	Variable type	Name	Variable levels			
Outcome	Dependent	Δ variation [µm]	-			
Factor 1	Independent (A)	Filling cycles [-]	20, 30			
Factor 2	Independent (B)	Filler size [µm]	5, 18			
	Average surface roughness (Ra _{reduction})					
Definition	Variable type	Name	Variable levels			
Outcome	Dependent	Ra variation[µm]	-			
Factor 1	Independent (A)	Filling cycles [-]	20, 30			
Factor 2	Independent (B)	Filler size [µm]	5, 18			
	Average profile height (Rzreduction)					
Definition	Variable type	Name	Variable levels			
Outcome	Dependent	Rz variation [µm]	-			
Factor 1	Independent (A)	Filling cycles [-]	20, 30			
Factor 2	Independent (B)	Filler size [µm]	5, 18			
Average pore diameter (Dreduction)						
Definition	Variable type	Name	Variable levels			
Outcome	Dependent	D variation [µm]	-			
Factor 1	Independent (A)	Filling cycles [-]	20, 30			
Factor 2	Independent (B)	Filler size [µm]	5, 18			

Table E.3. DoE for the study of the influence of Filler size and Filling cycles on the supports' morphology.

Table E.4. Scheme of repetitions for each outcome variable for the study of the effect of Filler size and Filling cycles.

Laser-optical confocal microscopy (Δ)					
filling cycles filler size Amount of filters Im		Imaged pores per filter			
[-]	[µm]	[-]	[-]		
20	18	5	5		
20	5	5	5		
30	18	5	5		
30	5	5	5		
	Averag	e surface roughnes	s (Ra)		
filling cycles filler size Amount of filters Imag		Imaged pores per filter			
[-]	[µm]	[-]	[-]		
20	18	5	5		
20	5	5	5		
30	18	5	5		
30	5	5	5		
	Ave	rage profile height (Rz)		
filling cycles	filler size	Amount of filters	Imaged pores per filter		
[-]	[µm]	[-]	[-]		
20	18	5	5		
20	5	5	5		
30	18	5	5		
30	5	5	5		

Capillary flow porometry (D)					
filling cycles filler size Amount of filters Imaged pores per fil [-] [µm] [-] [-] [-]					
20	18	5	-		
20	5	5	-		
30	18	5	-		
30	5	5	-		

Table E.5. DoE for the study of the morphological variables of asymmetrically filled supports and
supports equipped with an interdiffusion barrier.

Laser-optical confocal microscopy				
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	Δ [µm]	-	
Factor	Independent (A)	Support code [-]	E1, E3, E12, E14, E18	
Average surface roughness (<i>Ra</i>)				
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	Ra [µm]	-	
Factor	Independent (A)	Support code [-]	E1, E3, E12, E14, E18	
	Average	e profile height (<i>Rz</i>)	
Definition	efinition Variable type Name Variable levels		Variable levels	
Outcome	Dependent	<i>Rz</i> [µm]	-	
Factor	Independent (A)	Support code [-]	E1, E3, E12, E14, E18	
Average pore diameter (D)				
Definition	Variable type	Name	Variable levels	
Outcome	Dependent	D [µm]	-	
L a star		0 1 5 7		

Filler optimization via Response Surface Methodology (RSM)

Considering the datasets examined in Chapter 3 and Chapter 6, § "Symmetrically filled supports", a statistical analysis via Two-way ANOVA was performed, based on a full factorial two-factors design. The extension of the analysis performed in Chapter 3 via the examination of separate supports for the assessment of the *filler size* and *filling cycles* effect on $\Delta_{reduction}$, *Rareduction*, *Rareduction*, and *dreduction* was proposed to improve statistical inference. Considerations on each factor's contribution to the outcome variable's variance were used to elucidate the effects of the filling parameters on the selected supports and used as a starting point for an asymmetric filling design. However, the ANOVA could not provide precise information on the optimal values for size and cycles, but rather an examination of their effects on the chosen outcome variables which could be coupled with observational considerations.

To build a statistical model which would allow the experimenter to predict an optimum value for both *filling cycles* and *filler size*, a surface response analysis can be carried out. The surface response methodology relies on a central composite design for the experimental campaign, meaning that a portion of an experimental zone is chosen between a maximum and minimum factor level value, requiring observations at the extremes and in a central zone. By combining the information in the datasets of Chapter 3 and Chapter 6, it is possible to retrieve such a design. However, it is important to remark that the data retrieved in Chapter 3 was solely on 3 supports, while in Chapter 6 the sampling was expanded to a larger amount of different supports, thus improving the guality of the repetitions. Therefore, this analysis is to be considered exploratory, and the dataset is to be integrated with an additional amount of supports for data concerning 1.5 µm filler size and 10x filling cycles, in order to improve the predictivity of the proposed model. Moreover, the dataset is to be completed with at least 3 more central observations, meaning that a filler with 9.5 µm size should be acquired. Considering the limitations of the dataset, the application of the surface response model on $\Delta_{reduction}$, Rareduction and Rzreduction (considering their normalization on unfilled support data) via R statistical language is proposed.

The outcome of the model for $\Delta_{reduction}$ (Table E.6) reflects what was previously found with the ANOVA. (RSM presents an ANOVA table within its structure). The quadratic and linear terms of the model are not significant, while the interaction is the only significant term. The lack of fit is insignificant, however, the R-sq is quite low, indicating that the model cannot explain a large percentage of the variation on the means of the outcome variable. This can be explained by the high variability within the dataset, which is typical for samples so different from each other. The low R-sq of the model indicates that the statistical analysis cannot be taken as sole source of optimization, but rather it must be always coupled with a critical observational approach for this particular application, which is why all the statistical assessments presented in this Thesis are always coupled with characterization data. The contour plot and response surface are reported in Figure E.1. The stationary point in both plots corresponds to a local minimum maximizing the reduction in Δ : SP (20x, 12µm).

The outcome of the RSM model for Rareduction and Rzreduction is summarized in Table E.7. For Rareduction, a strong factorial significance is attributed to the variable filling cycles, in contrast with the analysis carried out in Chapter 6, where no significant factorial contributions were attributed to the changes in variance of Ra. The addition of the extra points from Chapter 3 to the dataset could have affected the information contained in the data; however, the high variability of the roughness measurements and the low Rsg of the model suggest that an improvement in the dataset is required, as well as that no linear or quadratic trends in the macroscopical surface roughness parameters is present. Nevertheless, the optimal predicted filler size-filling cycles combination for Ra minimization can be retrieved via stationary point analysis. The contour plot and surface plot for Rareduction are summarized in Figure E.2. The stationary point for Rareduction has mixed signs (negative and positive), meaning it corresponds to a saddle point in the surface. In this case, the optimal point shall be found in in the path of steepest descent for Ra starting from the stationary point as PDD(15x, 10.4 µm). The same considerations can be applied to Rz_{reduction}, where an interaction term is significant. Similarly to Ra_{reduction}, the addition of central data may have added information to the analysis compared to Chapter 6, where no significant terms contributing to Rz_{reduction} were found. However, like above, given the low R-sq of the model, it could mean that no relevant fitting trends are present and therefore the data must be critically observed. In this case, as the stationary point is a saddle point and an interaction term is relevant, the optimum point can be found in the canonical descent path as: CDP(10x, 11 µm).

RSM outcome table on <i>∆</i> _{reduction} [%]					
Variable	p-value	Significance			
Filling cycles [-]	0.450	No			
Filler size [µm]	0.046	*			
Interaction [-, µm]	0.004	**			
RSM ANOVA table					
Contribution	p-value	Significance			
Factorial (F0)	0.287	No			
Two-way interaction (TWI)	0.010	*			
Quadratic term (PQ)	0.266	No			
Good	Goodness of fit				
Parameter	Indicator	Significance			
Lack-of fit	p-value ~ 0.15	No			
R-sq	. 11%	-			

Table E.6. Surface response methodology results for outcome variable $\Delta_{reduction}$. The contribution to the fit is considered significant if p-value < 0.05.



Figure E.1. Perspective plot and contour plot of outcome variable ∆_{reduction} for factors *filling cycles* and *filler size*. The dots indicate the means of the examined factor levels combinations repetitions.

RSM outcome table on Rareduction [%]			
Variable	p-value	Significance	
Filling cycles [-]	2.95.10-5	***	
Filler size [µm]	0.220	No	
Interaction [-, µm]	0.146	No	
RSM AN	NOVA table		
Contribution	p-value	Significance	
Factorial (F0)	2.65.10-5	***	
Two-way interaction (TWI)	0.253	No	
Quadratic term (PQ)	0.591	No	
Goodi	ness of fit		
Parameter	Indicator	Significance	
Lack-of fit	p-value ~0.95	No	
R-sq	17%	[-]	
RSM outcome ta	able on Rz _{reduction} [%]	
Variable	p-value	Significance	
Filling cycles [-]	0.0014	**	
Filler size [µm]	0.090	No	
Interaction [-, µm]	0.030	*	
RSM AN	NOVA table		
Contribution	p-value	Significance	
Factorial (F0)	0.006	**	
Two-way interaction (TWI)	0.06	No	
Quadratic term (PQ)	0.48	No	
Good	ness of fit		
Parameter	Indicator	Significance	
Lack-of fit	0.19	No	
R-sa	12%	-	

Table E.7. Surface response methodology results for outcome variable Rareduction, Rzreduction. The
contribution to the fit is considered significant if p-value < 0.05.</th>



Figure E.2. perspective plot and contour plot of outcome variable (a) Ra decrease and (b) Rz decrease for factors filling cycles and filler size. The dots indicate the means of the examined factor levels combinations repetitions.

When analyzing the average pore diameter decrease via RSM method (Table E.8), the R-sq of the model significantly increases, well-representing the variation of each outcome variable. This is to be attributed to the lower amount of repetitions per sample, as only one measure can be carried out on each support for average pore diameter. The lower amount of repetitions implies a lower data variability and overall an improved fit (and in turn model prediction). Moreover, the variability of the average pore diameter between different supports on which the same pre-treatment was operated was found to be quite low from the analysis in Chapter 6. In this case, the interaction between *filler size* and *filling cycles* is relevant, and not solely the *filler size* as in Chapter 6. The contour plot and response surface for $d_{reduction}$ are reported in Figure E.3. Considering the canonical path

from the stationary point, a larger reduction in diameter is given by the combination of a large amount of *filling cycles* and larger *filler sizes*, confirming the results of previous observations: CP(44x, 22µm).

RSM outcome table on <i>d</i> reduction [%]					
Variable	p-value	Significance			
Filling cycles [-]	0.0008	***			
Filler size [µm]	0.013	*			
Interaction [-, µm]	0.0007	***			
RSM ANOVA table					
Contribution	p-value	Significance			
Factorial (F0)	3e-5	***			
Two-way interaction (TWI)	0.0004	**			
Quadratic term (PQ)	0.700	No			
Goodn	Goodness of fit				
Parameter	Indicator	Significance			
Lack-of fit	0.5	No			
R-sq	94%	-			

Table E.8. Surface response methodology results for outcome variable $d_{reduction}$. The contribution to the fit is considered significant if p-value < 0.05.



Figure E.3. Perspective plot and contour plot of outcome variable *d_{reduction}* for factors *filling cycles* and *filler size*. The dots indicate the means of the examined factor levels combinations repetitions.

By gathering all the optimal points per outcome variable:

- *Ra_{reduction}* (15x, 10.4 μm),
- *Rz_{reduction}* (10x, 11 μm),
- $\Delta_{reduction}$ (20x, 12µm),
- dreduction (44x, 22 $\mu m),$

it is possible to confirm that a filling size that best matches the pore diameter is the optimal choice for filler design. In particular, fillers of larger diameter operate a significant reduction on the pore diameter, while a large amount of cycles is best for in-pore morphology improvement but might cause Ra and Rz to increase overall. Finally, the results on Ra, Rz and Δ are always to be coupled with routine characterizations due to the intrinsical variability between repetitions, while the dataset is to be improved with relevant central observations and supports repetitions.

Chapter 7 | Conclusions and outlook

This work focused on the development of Pd-based membranes supported onto rough, large media grade, porous sintered metal filters. The selected Hastelloy X porous filters represented a cheaper option with respect to other commercially available metallic supports, at the expense of surface quality. Therefore, tailored pre-treatments had to be developed to allow the deposition of a H₂ selective Pd-based layer. In this Thesis, the process of membrane fabrication on the selected supports has been resolved with a with a vertical step-by-step approach, with emphasis on procedure characterization, standardization, and reproducibility.

Firstly, the problem of Pd deposition via ELectroless Plating (ELP) onto the selected filters has been tackled in **Chapter 2**. As the main deterrent to uniform Pd layers deposition was identified as the large surface roughness of the filters, several methods have been analyzed to render their *Ra* and *Rz* comparable to the one of ceramic supports. Following this strategy, it was proven that deposition via electroless plating of a continuous Pd-Ag layer onto the selected filters can be achieved via wet-polishing of the rough Hastelloy X filters, coupled with the addition of a γ -Al₂O₃ smoothening interdiffusion barrier. Scanning Electron Microscopy (SEM) imaging of the surface of supports residing in the polishing environment for different times showed that the action of media sliding onto and around the filters promotes both material removal and plastic deformation of the surface. The polishing time was set as 6 h, selected as a tradeoff between *Ra* reduction, *Rz* reduction, and gas permeation preservation of the filters.

The introduction of a continuous, delamination-free $\gamma\text{-}Al_2O_3$ interdiffusion layer was proposed to:

- i. Prevent strong Pd-support interaction.
- ii. Further reduce the filter's average surface roughness by means of surface coverage and uniformity.

The layer was developed starting from a boehmite/PVA/PEG dispersion. The composition of the dispersion (both in terms of additive concentration and solid load) was shown to influence its rheological properties, which eventually affected the dispersion's storage and reusability, as well as the resulting interdiffusion layer thickness, continuity, and coverage effect. The rheological properties of the boehmite based dispersions were studied via viscosimetry for different boehmite loadings. Storage and reuse were proven difficult due to the anti-thixotropic nature and gelation of the coating (as early as 5 min from preparation for the highest solid concentration). However, it was shown that increasing the solution's boehmite loading leads to increased layer thickness and support's *Ra* reduction. Therefore, 1.2 wt.% solid loading was selected as tradeoff between dispersion stability and sufficient support coverage. By coating supports polished for various amounts of time (3 h, 6 h, and 9 h), it was shown that a longer polishing time leads to less coating retention, thinner layers, and less average surface roughness reduction. The analysis of the selected pre-treatments parameters (polishing time, coating solid load, and amount of layered coatings) and their effect on relevant

measurable or qualitative outcomes (*Ra*, *Rz*, N₂ permeance, coating viscosity, layer thickness, observed layer continuity, and observed surface uniformity) led to the selection of a preliminary support pre-treatment procedure prior to electroless deposition of Pd-Ag onto the selected filters: 6 h polishing, 1.2 wt.% boehmite load coating sintered once at 550 °C. The selected pre-treatments proved themselves crucial for surface roughness improvement, promoting *Ra* reduction from ~6 µm to ~0.7 µm after interdiffusion barrier deposition and allowing the formation of delamination-free Pd-Ag layers. However, while allowing for Pd-Ag ELP deposition, Pd-Ag membranes prepared on the pre-treated supports showed the presence of partially covered pore mouths, which resulted in open defects on the Pd-Ag layer, hindering H₂ selectivity (H₂/N₂ = 540 at 400 °C, 1 bar). Moreover, the membranes exhibited low hydrogen permeance (H₂ permeance = $2 \cdot 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ at 400 °C, 1 bar), which was attributed to the closure effect promoted by polishing and the additional resistance to gas permeance given by the γ -Al₂O₃ layer.

To mend the gas permeance hinderance given by the polishing treatment, in Chapter 3 an etching treatment is introduced right after wet-polishing. A 30 s etch in Agua Regia was proven to promote full recovery of the gas permeance lost by polishing while increasing Ra solely by 20%. Laser-optical microscopy images of the filter's surface showed the opening of interconnected valley veins between polished superficial islands, to which the increase of N₂ permeance is to be attributed. To promote full closure of the filter's superficial pore mouths by electroless Pd deposition, the reduction of the filter's average pore size was treated as a sizing issue and therefore extra filler particles were introduced into the filter's pores to reduce their average diameter. Both filler particle size and amount of undergone filling cycles were evaluated as significant treatment parameters, considering Δ , Ra, and Rz as a measurable outcome variables. The outcome variables were measured and analyzed via suitable Design of Experiment (DoE) coupled with Two-Way ANalysis Of VAriance (ANOVA) as statistical analysis tool, in order to infer on the population of pores of three supports. It was found that 1.5 μ m and 5 μ m α -Al₂O₃ filler particles coupled with 20 undergone cycles promoted a statistically significant increase in pore filling. By coupling the statistical analysis of in-pore and superficial morphology with Capillary Flow Porometry (CFP) measures of the supports before and after filling, it was shown that 18 μ m α -Al₂O₃ particles contribute to the most significant reduction in the average pore diameter of the supports. These observations were completed by imaging of support pores filled with α -Al₂O₃ particles of each size, which allowed to conclude that 18 µm particles mainly allocate themselves well-within the pore necks of the support reducing its average pore diameter, while 5 µm and 1.5 µm particles lay on the pore mouth's entrance, contributing to in-pore leveling and morphology improvement. Based on the filler particles analysis, an asymmetric filling design consisting of consequentially layering 18 µm, 5 µm, and 1.5 µm particles within the supports pores was proposed. The asymmetrically filled support showed an average pore diameter of ~100 nm, which decreased to ~60 nm after the y-Al₂O₃ interdiffusion barrier deposition discussed in Chapter 2. The deposition of a Pd-Ag layer onto the asymmetrically filled support led to a membrane with H₂/N₂ selectivity of 43200 at 400 °C, 1 bar and H₂ permeance of 7.10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 400 °C, 1 bar, significantly improving the support's pore size and consequential membrane performance. Therefore, the filters pre-treatment procedure was developed on the basis of the considerations of Chapter 2 and Chapter 3

In **Chapter 4**, two main applications for the employment of metallic supported Pd-based membranes are explored in short-term operation regime: ammonia decomposition and

methane steam reforming in membrane reactors. In particular, the previously elucidated filter's pre-treatment procedure proved suitable to achieve a support with superficial pore size ~60-90 nm, resulting in a Pd-Ag membrane with H_2/N_2 ideal selectivity at 500 °C and 1 bar of ~38000 (M1) after Pd electroless deposition and annealing, H₂-N₂ mixture permeation tests on the prepared M1 membrane showed an effect of concentration polarization on the H₂ permeation, resulting in lower H₂ fluxes when N₂ concentration in the feed is increased. Tests for M1-assisted ammonia decomposition showed the overcoming of the conventional thermodynamic conversion of NH₃, reaching NH₃ conversions >99% for temperatures including and above 475 °C. The hydrogen recovered from the feed was > 60% for the same temperature range. Another highly selective Pd-Aq membrane (M2) (H₂/N₂ selectivity ~20200 at 500 °C and 1 bar) could be replicated. H₂-CO mixture permeation tests on the prepared M2 membrane showed inhibition effect due to the presence of CO. A reduction in H₂ permeance with respect to pure H₂ gas was observed and decoupled into 59% of H₂ flow reduction due to CO inhibition and 48% of the same due to mass transfer limitation. The presence of CH₄ was detected in the permeate stream, confirming the membrane's support catalytic activity towards methanation reaction and thus the support's ability to remove CO traces from the permeate stream. This property proves convenient in case of downstream PEM fuel cell units, avoiding possible CO poisoning. The tests for M2-assisted Steam Methane Reforming (M2-assisted SMR) showed the ability to overcome the conventional thermodynamic conversion of CH₄ for all the explored operating conditions, promoting an increase of methane conversion with respect to a conventional process up to 58% at 500 °C and 4 bar, while guaranteeing at least 99.3% of hydrogen purity.

In **Chapter 5**, the concept of membrane reactors was further investigated by adopting an alternative configuration: a Catalytic Membrane Reactor (CMR) where the membrane serves both as catalyst and separator. For this purpose, the concept of a catalytic layer to be deposited onto the H₂ selective Pd-Ag layer was proposed. In particular, the development of a mesoporous γ -Al₂O₃ substrate to be deposited onto prepared Pd-Ag membranes was investigated with a dual aim:

- i. In the presence of defects, enhance the Pd-Ag membrane's selectivity by narrowing the membrane's defect distribution.
- ii. Suitably allocate Ru nanoparticles, obtaining a Ru/γ-Al₂O₃ catalytic layer for ammonia decomposition in a catalytic membrane reactor.

Boehmite-PVA-PEG coatings were successfully deposited onto two modified metallic supported Pd-Ag membranes and sintered into γ -Al₂O₃ mesoporous substrates in N₂ and air atmosphere, respectively. The presence of continuous 3 µm thick γ -Al₂O₃ layers was confirmed via SEM and laser-optical microscopy, while the effect of the different sintering atmospheres was evaluated via X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and ThermoGravimetric Analysis (TGA) characterizations. The XRD pattern of the air sintered sample presented extra peaks attributable to the presence of PdO below the γ -Al₂O₃ layer. Etching assisted XPS further confirmed the presence of PdO below the γ -Al₂O₃ layer of the air sintered sample. The polymeric degradation of the coating was studied via TGA, showing complete polymeric degradation in air atmosphere and almost full polymeric pyrolysis in N₂ atmosphere, with ~7% char formation. As the presence of PdO is to be considered detrimental for the structural integrity of the H₂ selective Pd-Ag layer and given the almost total carbon loss of the N₂ sintered sample, N₂ atmosphere was preferred as sintering environment. Three defective metallic

supported Pd-Ag membranes were characterized via CFP before and after mesoporous y-Al₂O₃ layer deposition, showing average defect's diameter distribution shift from 150-600 nm to 30-100 nm. The consequential defective membranes selectivity increase was \sim 50% to \sim 120%, studied by single gas permeation testing. A highly selective metallic supported Pd-Ag membrane (H₂/N₂ selectivity ~20000 at 1 bar, 500 °C) was prepared and equipped with the y-Al₂O₃ mesoporous substrate, increasing its selectivity to \sim 65000 at 500 °C and 1 bar. The analysis of the permeation properties of the membrane allowed to prove the positive effect of mesoporous v-Al₂O₃ deposition on membrane's H₂ selectivity. The y-Al₂O₃/Pd-Ag layer was further functionalized with Ru nanoparticles via deposition-precipitation method. The resulting metallic supported Ru/v-Al₂O₃/Pd-Ag membrane, integrated in an ammonia cracking reactor without any catalyst bed, showed activity for ammonia cracking under a 100 mL_N min⁻¹ pure NH₃ flow, promoting 65.8% NH₃ conversion at 500 °C. The presence of Ru on the mesoporous y-Al₂O₃ substrate was gualified via post-mortem XPS surface scan of the layer. The encouraging results showed the conceptual possibility for metallic supported active-metal/y-Al₂O₃/Pd-Aq membranes to be employed as self-standing catalytic membrane reactors.

Finally, this work was concluded by diving into support (and thus membrane) reproducibility considerations in Chapter 6. Given the random nature of each support's pore network and superficial characteristics, the application of a fixed procedure for each filter proved unrealistic. To achieve highly selective membranes such as the ones tested in Chapter 4, each filter had to undergo a tailored amount of filling cycles to reach a suitable pore size for full pore closure via Pd electroless deposition. In order to provide more precise reproducibility targets for each of the relevant quality parameters, in Chapter 6 a design of experiments (DoE) coupled with analysis of variance (ANOVA) as statistical analysis tool was successfully applied to infer on the morphological effects operated by each pre-treatment on the population of the chosen filters. Twenty Hastellov X porous filters, drawn from a population of supplied filters, were successfully pre-treated to increase their suitability for Pd deposition via electroless plating, with the full procedure discussed in Chapter 3. The statistical analysis results confirmed the effectiveness of support pre-treatments in smoothening the surface, leveling the pores, and reducing the support's pore diameter; however, they denoted morphological variability between the filters themselves and within their profile roughness parameters, highlighting the importance of filter monitoring during the manufacturing process. Suitable targets for the reproducibility of the filters were drawn from the analysis of the peaks of density distributions (avg. values) as: Ra <0.8 µm, Rz <7 µm, average pore diameter after asymmetric filling 100-500 nm (most effective particle size for reduction ~18 µm), average pore diameter after interdiffusion barrier deposition ~100 nm, and in-pore leveling Δ <6 µm (most effective particle size for leveling <=5 µm).

7.1 Further research

In this Thesis, the proposed Pd-based membranes (both conventional and layered) preparation procedure and support reproduction targets were proven suitable for further optimization and utilization in both ammonia decomposition and methane steam reforming membrane reactors. However, several optimization studies can still be performed on the basis of this work. Firstly, as introductory tool, a Strengths, Weaknesses, Opportunities, Threats (SWOT) analysis of this research is proposed in Figure 7.1. Thereafter, possible future research is listed with a "layer by layer" approach, starting from the innermost membrane component.



Figure 7.1. Strengths, Weaknesses, Opportunities, Threats (SWOT) summary of the research presented in this Thesis.

Porous sintered metallic supports

Through this thesis, Hastelloy X porous sintered tubes with 0.5 μ m media grade were the preferred choice for membrane fabrication due to their price and availability. However, several options exist for further exploration. Particularly interesting are porous AISI316L tube of equally large or larger media grade, which can represent an even cheaper alternative [1]–[6]. Regardless from the chosen steel alloy, it would be necessary to explore the long-term stability of the supports in prolonged high-temperature and/or reactive conditions, with particular care in optimizing the welding cords fabricated [7]. Moreover, different metal alloys can react differently to the explored pre-treatments, as well as interact differently with the chosen filler/interdiffusion materials. However, varying the porous sintered metal material is not expected to hinder the main findings of this work in terms of pre-treatment concepts, but rather to tune the existing procedure in terms of materials interaction.

Besides wet polishing, several other techniques for surface finishing may be explored (i.e electropolishing [8], sand-blasting [9], dry polish with different grit particles [10], etc.) in

order to find the best match that allows for surface uniformity. If the average surface roughness of the support material can be pushed to $Ra \sim 0.8 \ \mu\text{m}$, the surface shall welcome the deposition of Pd. The goal would be not so the reduction of the average surface roughness itself, but rather a way to reduce it in the most uniform way possible, controlling leftover streaks or peaks through the whole support surface. A full comparative work summarizing the main surface characteristics, resulting from the different polishing techniques applied to different support alloys (AISI316, Hastelloy, AISI 441, etc.), comprehensive of SEM imaging, laser-optical confocal imaging, profilometry and gas permeation behavior of the examined supports would represent an additional source of information for the state of the art.

An exploratory study shall be performed to tune the etching process for the selected porous metal filter's material. For stainless steel materials, FeCl₃ is a widely employed etchant, while etching temperature and etchant concentration are sensible parameters which could influence surface finish. In this Thesis, rey water was used to etch Hastelloy X, which is notoriously resistant to corrosion. However, other etchant options can be explored, such as HNO₃, HCl, HCl-FeCl₃, HF, as well as electrochemical etching.

All of these etching approaches for steel and steel alloys are widely studied in surface finishing literature [11]—[14]. However, the correlation between the chosen etching procedure and relevant parameters for Pd-based membrane final performance is not as straightforward. Therefore, a comparative study similar to the one proposed for the polishing procedure tunability would represent an additional step to the optimization of the membrane preparation procedure.

Support filler

The reduction of the pore size distribution of the porous sintered metal tubes is a critical step for the deposition of durable, defect free layers. Through this Thesis, the focus has been on the development of a preliminary procedure, which would allow to reach target membrane H₂ selectivity performance in short term operation conditions. For this purpose, the pore size distribution narrowing of the filters has been treated merely as a sizing problem, where the material of the filler itself played a marginal role in the procedure optimization. This means that if the particle size of the filler is comparable to the α -Al₂O₃ particles proposed in this Thesis, the closure effect of the procedure would be preserved. However, this Thesis lacks sufficient long-term testing of the prepared membranes to be able to assess the effect of the filler material itself. By considering the nature of the materials in fact, one important factor is their thermal expansion coefficient. Best matches between Hastelloy X (and/or stainless steel) and Pd films shall be considered as ceramic filler materials. In Figure 7.2, taken from the review of Aligue et al. [15] a useful representation of thermal expansion coefficients for the main membrane constituent materials is shown. Particularly interesting are materials which can match with both palladium and Hastellov X (and/or stainless steel), in close proximity with their thermal expansion zone in Figure 7.1 (i.e. Ceria, titania, zirconia, alumina or blends of all). All these materials have been investigated extensively as metallic supported membranes fillers/interlayers and proven to be able to withstand Pd deposition [16]-[21]. By utilizing the same filling procedure proposed in this Thesis and comparing different filler materials in long term stability tests, it would be possible to select the best particles for long-term membrane usage, further favoring membrane scale up. Moreover, further optimization of the filling procedure itself can be carried out by acquiring specific industrial equipment which would allow for a more controlled particle aspiration environment, allowing a more precise optimization of the filling parameters and possibly a more uniform filling through the whole support's pore distribution.



Figure 7.2. Thermal expansion coefficient for Pd-based membranes constituent materials. (Alique et al. [15]).

Interdiffusion barrier

The same considerations can be applied to the choice of the interdiffusion barrier. Several works propose solely a filler ceramic layer as enough to prevent intermetallic diffusion. However, it would be preferable to deposit at least a very thin ceramic layer in order to maximize H₂ permeance but keeping the coverage of the whole integrity of the support surface, minimizing the contact between palladium and porous metal underneath. To have a uniform layer, the method chosen through this Thesis was sol-gel coating of ceramic-polymeric (boehmite-PVA-PEG) sols, which allowed to achieve a very adhesive, robust layers which could adapt to the shape of the chosen substrate. However, colloidal type of sol-gels could also be explored, as well as different ceramic nanoparticles sols (i.e. YSZ sol, CeO, etc.). Similarly to the filler, also in this case the thermal expansion coefficient of the chosen materials and their match is expected to influence the membrane's performance in long-term conditions.

Thus, comparisons between several sol-gel coatings, matched or mixed with a suitable filler to best match the thermal expansion difference would pose an interesting exploratory work which, if coupled with reproducible, factual targets would boost the production of durable metallic supported Pd membranes.

Selective layer

Similarly to thin ceramic supported Pd membranes, also metallic supported membranes can undergo optimization in terms of Pd layer thickness. The membranes proposed in this thesis are 6-8 μ m thick, however, 1-5 μ m membranes could be achieved on tuned ceramic supports with 100 nm and 0.5 μ m surface roughness [22][23]. If further optimization studies of the presented preparation procedure can yield to even more controlled superficial characteristics of the selected filters, particularly the control of the tails of the pore size distribution of filled filters, Pd deposition with the electroless plating parameters retrievable in the works of Tanaka et al. [24] would be sufficient to achieve ultra-thin layers, as electroless deposition of Pd onto suitable supports is quite well-known in Pd membranes literature [25][15][26][27].

Additional layers

Considering additional layers to be added onto the H₂ selective Pd, on the basis of the mesoporous γ -Al₂O₃ substrate proposed in Chapter 5, interesting ramifications can be explored.

- i. The completion of in-depth characterization and performance assessment of Ru/γ -Al₂O₃/Pd-Ag catalytic membranes as possible self-standing catalytic membrane reactors for ammonia decomposition.
- ii. The possibility for functionalization of γ -Al₂O₃ mesoporous layers with different active metals for different applications (i.e. Rhodium, Nickel for catalytic membrane reactors for steam methane reforming applications).
- iii. The possibility to explore and compare different porous/mesoporous substrate materials (i.e. ZrO, CeO, YSZ, etc.).

H₂ production applications

The main applications for the Pd-based membranes proposed in this Thesis are H_2 production via ammonia decomposition and steam methane reforming. As discussed in Chapter 1, membrane assisted ammonia decomposition has gained increasing interest for decentralized H_2 production, while membrane assisted steam methane reforming is being demonstrated at Technology Readyness Level (TRL) 7 within the framework of the MACBETH project, which funded this research. On the basis of the work reported in Chapter 4, substitution between the currently employed ceramic supported membranes and the metallic supported membranes proposed in this Thesis would be possible whether long-term stability testing would confirm the continued performance of the fabricated membranes for >800 h of operation. For this purpose, once the previously reported exploratory works on a comparison between filler materials would be carried out, a long-term testing campaign for both applications would provide a definitive proof of concept which would enable the utilization of the technology.

Statistical approach

Finally, the optimization works proposed in this section would greatly benefit from a DoE approach, similarly to the one adopted in Chapter 6. As a base preparation procedure yielding to metallic supported Pd-based membranes with acceptable H₂ selectivity has been presented in this Thesis, the reproduction of several treatments for a representative membrane sample batch would be less time consuming than when a base preparation procedure was not set. This would enable the possibility for much more expanded statistical work, which ultimately would lead to quantifiable targets for membrane preparation parameters related to final membrane performance, significantly contributing to the state of the art, speeding up membrane scale-up, as well as providing reproducible membranes.

Support, pre-treatments, and membrane costs

In research performed during the Eu-funded MEMBER [28] project, the production cost of a ceramic supported Pd-based membrane was calculated as:

$$Membrane \ cost = A \cdot (support \ cost + Pd \ layer \ cost + production \ costs)$$
(1)

Where A is the membrane area in m^2 and the support cost, Pd layer cost, and production costs are expressed in $\in m^{-2}$.

The cost of the selective Pd layer (in $\in m^2$) was estimated by considering the density of pure Pd ($\rho_{Pd} = 12007 \text{ Kg} \cdot m^3$), the current market cost of Pd ($30000 \in \text{Kg}^1$), and the Pd layer thickness ($\sigma_{Pd} = 6 \ \mu m$):

$$Pd layer cost = \rho_{Pd} \cdot price_{Pd} \cdot \sigma_{Pd}$$
(2)

Therefore, if the production costs associated with membrane manufacturing (in ${\rm (in e-m^2)}$ are considered as the fixed costs for the deposition of the Pd layer (labor and ELP), the total price of a membrane unit depends solely on the cost of the support. For metallic supports, this cost would include the untreated substrate cost and the costs of its pre-treatments. In the work of Fernandez et al. [20], outstandingly selective metallic supported membranes were fabricated by using the pre-treated, 0.1 μm media grade Mott corp. supports. On the substrate, an α -Al_2O_3 + YSZ interdiffusion barrier was added, and a sintering treatment was performed at 750 °C 5 times. The cost of sintering (in €) can be calculated as:

Sintering cost = oven power rating
$$(T) \cdot \text{sint. time } \cdot \text{energy cost} \cdot \text{sint. cycles}$$
 (3)

Assuming 10 cm of active membrane length, 1.1 cm membrane diameter, the sintering oven being a Carbolite Gero gradient furnace (employed at TU/e), and the current energy costs in the Netherlands as $0.35 \in KWh^{-1}$, the cost of a highly selective metallic supported membrane produced with 5 sintering cycles of 2 hours each at 750 °C would amount to $169 \in$ per membrane. In this Thesis, the sole sintering cycle required for the interdiffusion barrier deposition is carried out at 550 °C for 2 hours. By decreasing the sintering temperature, the amount of sintering cycles and the untreated support costs, the price of a produced membrane was already reduced to $80.5 \in$, accounting for the price of the alumina filler as $1.5 \in$ per membrane (calculated as *price from quotation · amount of α-Al₂O₃ dispersed in H₂O)*. However, these preliminary considerations would greatly benefit

from a more in-depth techno-economic assessment of the whole membrane preparation process, completed with a life cycle assessment in order to pinpoint the most critical preparation steps for further economical optimization.

Final remarks

To conclude, several research ramifications can be drawn from the general exploratory work proposed in this Thesis. Each ramification dives into a specific research field (i.e. surface finishing of steel-based materials, ceramic materials and coatings, Pd and Pd alloys chemistry, membrane separation technology, process engineering, and statistics) and it involves a more in-depth study of a membrane preparation step which was identified as relevant for optimization by the research performed in this work. Therefore, this Thesis aims to represent a starting point towards a standardized, optimized preparation procedure for easily scalable, reproducible H_2 selective metallic supported Pd-based membranes.

7.2 Bibliography

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Research output

Peer-reviewed publications

- S. Agnolin, J. Melendez, L. Di Felice & F. Gallucci (2022). "Surface roughness improvement of Hastelloy X tubular filters for H₂ selective supported Pd–Ag alloy membranes preparation." *International Journal of Hydrogen Energy*, Volume 47, Issue 66.
- S. Agnolin, F. Apostolo, L. Di Felice, J. Melendez Rey, A. Pacheco Tanaka, M. Llosa Tanco & F. Gallucci (2023). "Development of selective Pd–Ag membranes on porous metal filters," *International Journal of Hydrogen Energy*, Volume 48, Issue 65.
- V. Cechetto, S. Agnolin, L. Di Felice, A. Pacheco Tanaka, M. Llosa Tanco & F. Gallucci (2023). "Metallic Supported Pd-Ag Membranes for Simultaneous Ammonia Decomposition and H₂ Separation in a Membrane Reactor: Experimental Proof of Concept." Catalysts, 13, 920.
- S. Agnolin, L. Di Felice, A. Pacheco Tanaka, M. Llosa Tanco, W. J. R. Ververs & F. Gallucci (2024). "Intensification of Hydrogen Production: Pd–Ag Membrane on Tailored Hastelloy-X Filter for Membrane-Assisted Steam Methane Reforming." *Processes*, 12, 40.
- S. Agnolin & F. Gallucci (2024). "Unravelling the effects of surface modification pre-treatments on porous Hastelloy X supports for H₂ selective Pd-based membranes preparation with a statistical approach," *Journal of Membrane Science*, vol. 700, p. 122690.

Conference presentations

- Agnolin, S., Cechetto, V., Di Felice, L., Pacheco Tanaka, D., Llosa Tanco, M. & Gallucci, F. (2023), "On the development and testing of H₂ selective Pd-Ag membranes supported on porous metal filters for ammonia cracking and steam methane reforming membrane reactors," 16th international conference on Catalysis in membrane reactors (ICCMR16), Donostia-San Sebastian, Spain. Awarded "Best oral presentation".
- Agnolin, S., Di Felice, L., Pacheco Tanaka, D., Llosa Tanco, M. & Gallucci, F. (2023), "Development of selective Pd-Ag membranes on porous metal filters," 14th European Congress of Chemical Engineering and 7th European Congress of Applied Biotechnology (ECCE/ECAB), Berlin, Germany.
- Agnolin, S., Di Felice, L. & Gallucci, F. (2022), "Surface finishing treatments and modification via boehmite sol-gel coating of Hastelloy X tubular filters for H₂ selective supported Pd-Ag alloy membranes preparation," *15th international conference on Catalysis in membrane reactors (ICCMR15)*, Tokyo, Japan.

Contributions

- V. Cechetto, A. Arratibel Plazaola, L. di Felice, S. Agnolin, G. Anello, F. Gallucci. (2023), "A comparison between Pd-Ag and carbon molecular sieve membranes for hydrogen separation during ammonia decomposition in a membrane reactor." 2nd Symposium on Ammonia Energy, Orléans, France.
- D. Maccarrone, G. Giorgianni, *S. Agnolin*, S. Perathoner, G. Centi, F. Gallucci, S. Abate. (2024), "Boosted Ammonia Decomposition over Ruthenium Catalysts: A Comparative Study in a Traditional Fixed Bed, Membrane-Assisted, and in a Catalytic Membrane Reactor." *Unconventional Catalysis, Reactors and Applications*, Warsaw, Poland.

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Serena

Curriculum Vitae



Serena was born on April 11, 1995, in Colleferro, Rome, Italy. She completed her high school education in 2014 at Liceo Scientifico Tecnologico "Leonardo Da Vinci" in Arzignano, Vicenza, Italy. She received her bachelor's degree in Chemical and Materials Engineering at Università Degli Studi di Padova, Padua, Italy with a thesis on heat integration in the beamhouse processes of the tanning industry. She then continued with her master's education in Chemical and Process Engineering at Università degli Studi di Padova, Italy. She worked on her master's thesis at Eindhoven University of Technology, in

the Sustainable Process Engineering group, by winning the Erasmus+ mobility program scholarship. In 2019, she received her master's degree in Padua, presenting a thesis titled "Development and testing of carbon molecular sieve membranes (CMSMs) for gas separation", under the supervision of Dr. A. Rahimalimamaghani, Prof. Dr. Eng. F. Gallucci and Dr. Eng. M. Roso.

On the 13th of January 2020, Serena started a PhD project at Eindhoven University of Technology in the Sustainable Process Engineering group, as part of the European project MACBETH. During her PhD, under the supervision of Prof. Dr. Eng. F. Gallucci, she studied functional membrane materials, developing metallic supported Pd-based membranes and assessing their suitability for application in membrane reactors for H₂ production. This dissertation is a summary of the main results obtained during her 4 years as PhD researcher.

Since January 2024 Serena has been employed in the Sustainable Process Engineering, Inorganic Membranes and Membrane Reactors group of Prof. Dr. Eng. F. Gallucci as postdoctoral researcher, working on inorganic membrane materials and membrane assisted gas separation processes.