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Enhanced stability of catalytic membranes based on a porous thin Pd film on a ceramic support by forming a Pd–Ag interlayer

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Abstract

Pd and Pd–Ag alloy porous thin film membranes on a ceramic α-Al_2O_3 tubular membrane support have been characterized by SEM, XRD and TPR measurements and reactivity studies in the direct H_2O_2 synthesis from H_2/O_2. The brittleness of the Pd film due to formation of palladium-hydride in the presence of H_2 diffusing through the membrane is a major problem, which causes a fast deactivation of the membrane with formation of pinholes and finally rupture of the thin film. The formation of an alloy with Ag prevents this problem, but decreases the catalytic performances in the synthesis of H_2O_2. By preparing multilayer catalytic membranes with a Pd–Ag interlayer between the ceramic support and the final Pd thin film it is possible to couple high catalytic performances and good stability of the membrane.

Keywords: Pd thin film; Pd–Ag alloy; Catalytic membrane; H_2O_2 synthesis; Stability membrane; Pd–Ag interlayer

1. Introduction

There is an increasing interest on the synthesis, features and application of catalytic membranes based on a thin Pd (or Pd-alloy) film on a ceramic support for a range of applications which include (i) high temperature applications (>300 °C) such as the continuous on-line separation of H_2 from steam reforming gases, the isotopic hydrogen separation and alkane dehydrogenation, (ii) medium temperature applications (200–250 °C) such as the direct synthesis of phenol from benzene + O_2 feeding H_2 through the metallic membrane; (iii) low temperature application (room temperature) such as the direct synthesis of hydrogen peroxide from hydrogen and oxygen and the reduction of nitrates in water [1–12].

With respect to dense Pd-based membranes, those based on thin films on a ceramic support offer better flux, lower cost and lower intradiffusional limitations which for reactions such as H_2O_2 and phenol synthesis, as well as for nitrate reduction are an important factor determining the catalytic performances. In addition, when dense membranes are used in applications such as H_2 separation, thin membranes are necessary to have enough H_2 flux and productivity, but this creates problems of wrinkling and stability, especially in consideration of the high temperatures of application and the formation of carbon deposits on the surface during the reaction. Thin Pd films on a ceramic support may in principle combine the selectivity characteristics of the Pd thin film to the robustness characteristics of the ceramic membrane. But this poses new questions regarding the ceramic–metallic adherence and interface.

The issue of stability of metallic thin films of palladium on a ceramic support has been studied in detail for high temperature applications, especially in relation to the separation and purification of hydrogen from gas mixtures and in particular for their application in membrane reactors for steam reforming of hydrocarbons and water gas shift reaction (WGS) [13–16]. Chemical stability and the solutions for its improvement is another area of considerable research interest [2]. In general, making an alloy of Pd with other metals such as Cu, Ni, Fe, Pt and Ag able to maintain high hydrogen permeability, but minimizing α → β PdH phase transition, reduces chemisorption of poison agents such as CO, sulphur and H_2O and minimizing coking in WGS and hydrocarbon steam reforming

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is the most commonly used method to improve the stability. Other possibilities include the preparation of nanophases or amorphous metal membranes, e.g. to control membrane microstructure, and the surface coating of the membrane with another metal [2].

However, for medium and low temperature applications there are very limited results about stability of the Pd thin film membranes and the procedures to improve it. Besides to the different reaction conditions (temperature, feed composition) from the high temperature cases, the main difference is related to the different working principles. In the high temperature applications, the Pd or Pd-alloy thin films operate as hydrogen permeoselective membranes, while in the medium and low temperature applications Pd is the catalyst for the reaction. The formation of a Pd-alloy and/or Pd thin film microstructure may not only modify the catalyst activity, but also change the rate of parallel or consecutive reactions changing the selectivity. Therefore, data for the high temperature applications cannot be simply translated to the medium and low temperatures cases.

The aim of the work reported here is to investigate the stability of Pd and Pd–Ag thin films on a ceramic support used for the reaction of direct synthesis of H_2O_2 from H_2 and O_2. Although these catalytic membranes show several characteristics close to those of the membranes for H_2 separation, the thin Pd or Pd-alloy film is porous and not dense as requested to obtain a good separation factor in the latter membranes where H_2 should dissociate and not diffuse in the molecular form through the membrane as necessary in the case of the synthesis of H_2O_2.

The direct synthesis of hydrogen peroxide from hydrogen and oxygen is known from long time and is in principle the most economic and environmentally acceptable alternative to the commercial antraquinone route. However, problems of activity/selectivity and especially of safety reasons using H_2/O_2 feed mixtures have blocked for long time the industrial application of this process. The increasing need of H_2O_2 to realize new processes with a low environmental impact and the necessity of new solutions for small scale H_2O_2 production has renewed the industrial interest on this synthesis [16–18]. The use of catalytic membranes instead of powder-type catalysts offers some relevant advantages: (i) intrinsically safe operations, because the formation of explosive H_2/O_2 mixtures is avoided due to physical separation between the contact of H_2 and O_2 feeds with the solution (ii) the possibility of a better control of the H_2 and O_2 gradients near to the catalytic sites, a relevant factor determining both the productivity and selectivity [19].

Although different preparation methods may be used to prepare these Pd-based catalytic membranes for H_2O_2 direct synthesis, the method investigated here regards only the preparation by electroless plating deposition (EPD), because this is one of the most commonly used preparation methods for palladium and Pd-alloy composite membranes for high temperature hydrogen separation [20]. Therefore, this method may provide a direct link between the characteristics of the catalytic membranes necessary to obtain stable operations in H_2O_2 synthesis and those for H_2 separation.

2. Experimental

2.1. Preparation of the catalytic membranes

The membranes in a tubular form were prepared using an asymmetric ceramic support supplied from HITK (Germany) on which the Pd or Pd–Ag thin film were deposited by electroless plating deposition (EPD). In this technique palladium metallic particles are produced by reduction from the plating bath consisting of amine-complexes of palladium in the presence of a reducing agent. Metallic particles grow on palladium nuclei which have been pre-seeded on the substrate surface through a successive activation and sensitisation procedure and which also act as a catalyst for the reduction of the palladium complexes. The α-alumina asymmetric membrane consists of an α-alumina macroporous support (3 μm pore size) with a α-alumina external mesoporous layer (pore size 50–100 nm).

The ceramic support, in a tubular shape (1 cm diameter, 10 cm long) is first cleaned from grease and other contaminations with a washing procedure using isopropylic alcohol followed by drying at 100 °C (3 h). Pd was then deposited on these membranes as a thin layer (3–30 μm thick) by EPD method. This technique consists in two main consecutive steps: (i) first Pd–Sn seeds are created on the membrane surface (ii) then Pd or Pd–Ag deposition occurs by reducing the Pd and Ag complexes in solution using the electrons generated in the reduction of hydrazine occurring over the Pd–Sn seeds. A homogeneous Pd or Pd–Ag thin film forms with this method on the ceramic support and for this reason the step of deposition of the Pd or Pd–Ag is often called plating.

2.1.1. Creation of Pd–Sn seeds

For the creation of the Pd–Sn seeds, two solutions are prepared (100 ml): (i) solution A: $SnCl_2$ is solubilized in a HCl aqueous solution (0.1N) in the amount as to have a concentration of 0.1 wt.%; (ii) solution B: $PdCl_2$ is solubilized in a HCl aqueous solution (0.2N) in the amount as to have a concentration of 1.0 wt.%. The ceramic tubular membrane (closed at the end in order to have deposition only on the external surface) is first immersed in solution A (under stirring) for 15 min at r.t., washed with distilled water, and then immersed in solution B (under stirring) for 15 min at r.t. and washed with distilled water. This cycle is repeated five times. Then the tubular membrane is reduced at 400 °C (3 h) in a H_2 flow.

2.1.2. Formation of the thin porous Pd film

For the plating of Pd the following solution is prepared: 0.2 g $PdCl_2$ is added together with 3.0 g EDTA to 150 ml NH_4OH (25%) (solution C). The solution is then heated to 65 °C under stirring and then the ceramic membrane pre-seeded with Pd–Sn is immersed in this solution, starting at the same time to add N_2H_4 (1 M) drop by drop. Ten milliliters of N_2H_4 are added in total. The following reaction occurs:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-$$

The reaction occurs on the Pd nuclei of the Pd–Sn seeds and the electrons generated in this reaction reduce the Pd–amine complexes causing their deposition on the ceramic support. After 5 h under stirring, the membrane is washed with distilled water and dried in an oven at 100 °C (3 h). The procedure could be repeated various times to increase the thickness of the deposited porous Pd thin film.

The catalytic membrane is then treated with a H_2O_2 35% solution for 1 h at r.t., because this treatment improves the performances of these materials in the synthesis of H_2O_2.

2.1.3. *Formation of the thin porous Pd–Ag interlayer or film*

The procedure to prepare a Pd–Ag interlayer or film is similar to that described in the Section 2.1.3, apart that the solution C was prepared using 100 ml NH_4OH (25%). A second solution was also prepared as follows: $AgNO_3$ in the amount as to have a Pd:Ag ratio of 10:1 is added together with 0.4 g EDTA to 50 ml NH_4OH (25%) (solution D). The solution D is then added to solution C, and the resulting solution used to deposit the Pd–Ag thin porous film over the ceramic membrane pre-seeded with Pd–Sn. The remaining procedure was similar to that described in Section 2.1.2, but the Pd–Ag alloy was formed by treating the membrane at 500 °C in N_2. This treatment was not necessary for the Pd-only thin film membranes. As for Pd-only catalytic membranes, the procedure could be repeated various times to increase the thickness of the deposited noble metal film.

If a further Pd-only layer should be deposited, e.g. if the Pd–Ag thin film is an interlayer between the membrane and the final Pd-only thin layer, after formation of the Pd–Ag alloy the final Pd-only thin layer could be deposited following the same procedure described in Section 2.1.2.

2.2. *Characterization*

EDX-SEM characterization studies of the membranes were made with a scanning electron microscope Jeol 5600 LV. Elemental analysis was carried out via energy dispersion analysis using an X-ray analytical system EDX OXFORD, coupled to the scanning electron microscope. The tubular membrane was cut for this characterization.

X-ray diffraction (XRD) patterns were recorded with a Ital-Structures XRD diffractometer using Cu Kα radiation (λ = 1.5405 Å). Data were collected in the 10–80° (2θ) with a resolution of 0.1°.

Temperature programmed reduction (TPR) tests were measured using a Micromeritics Autochem II apparatus after room temperature helium pre-treatment. The rate of temperature increase was 10 °C/min in a flow of 5% H_2/Ar. A cryostat was used to reach temperatures below r.t.

2.3. *Reactivity tests in H_2O_2 synthesis*

Reactivity tests in H_2O_2 synthesis were carried out in a semi-batch recirculation reactor [19], where the membrane was sealed in a tubular holder. From the inner side H_2 was fed at constant pressure (2–5 bar), while an oxygen-saturated acidic solution was continuously circulated on the outer side of the membrane (where Pd was deposited) by means of a peristaltic pump (25 ml/min) equipped with special Tygon® MH tubing. The circulating solution was 100 ml of water containing 0.03 M H_2SO_4 and 6 ppm of NaBr. H_2O_2 concentration was determined by permanganometric titration.

3. Results and discussion

3.1. *Pd-only membrane (Pd/Al_2O_3)*

The composite membrane prepared by electroless plating deposition (EPD) of palladium on the α-Al_2O_3 asymmetric ceramic support leads to the formation of an uniform and smooth Pd thin film without the presence of cracks and pinholes, as evidenced from experiments monitoring the formation of bubbles at the membrane–water interface (external side of the tubular membrane) on increasing the differential pressure between the inner part (where N_2 is fed) and the external part immersed in water at atmospheric pressure.

The SEM image of the surface of the Pd film (Fig. 1a) reveals the presence of a dense assembling of nearly-round shaped grains with dimensions of few microns and which are formed by closely connected Pd-crystals with mean dimension of few hundred of nanometers. Note that no high temperature annealing has been made in this Pd-only film, but instead a r.t. oxidation treatment with H_2O_2, being this treatment useful to improve the catalytic performances in the synthesis of H_2O_2 [19]. The high temperature annealing is not necessary in these membranes, which should be porous (see below) and not dense as, for example, the membranes for H_2 separation.

The surface after formation of the Pd thin film shows a significantly higher roughness with respect to the surface of the ceramic membrane after the deposition of the Pd–Sn seeds which dimensions were of the order of few nanometers (Fig. 1c). Note, however, that for the use as catalytic membranes in H_2O_2 synthesis it is not necessary to obtain a dense thin film, but a porous layer. In this thin film cracks and pinholes should be absent (they will lead to a preferential bypass of H_2), but the pore diameter should be enough to allow H_2 to diffuse in the molecular form and not only as spillover H species as requested to have high permeoselectivity in similar membranes for H_2 separation. In fact, the flux of H_2 through the membrane determines the productivity in H_2O_2 synthesis, but it is also necessary that the O_2 present in the solution diffuse inside the thin film, because the selective synthesis of H_2O_2 requires to optimize both the H_2 and O_2 gradients inside the catalytic membrane [19]. Therefore, the Pd-based thin film membranes for H_2O_2 synthesis should have a controlled microporous.

The thickness of the Pd thin film is about 3 μm (Fig. 1b), but depending on the time and temperature of the plating stage, as well as on the number of cycles during the stage of formation of the Pd seeds, the thickness of the film may be changed in the 1–10 μm range. The inset of Fig. 1b shows also a lower resolution

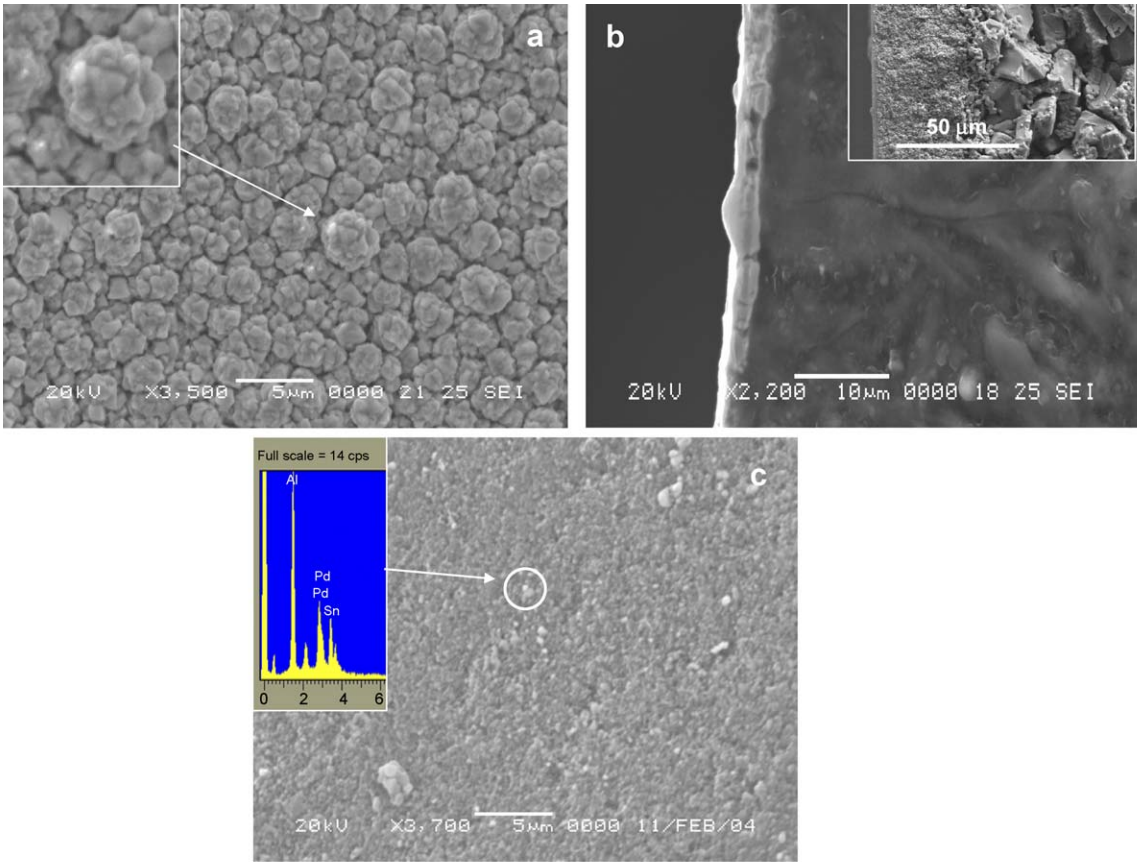

Fig. 1. SEM images of Pd thin films prepared by EPD on the α-Al_2O_3 asymmetric membrane (Pd/Al_2O_3): (a) surface and (b) cross-section. In the inset of (a) an expansion of one of the Pd grains is reported, while in the inset of (b) a lower resolution image of the cross section of the whole image is reported to show the asymmetric structure of the ceramic membrane. For reference, the SEM image of the surface of the ceramic membrane after creation of the Pd–Sn seeds is reported in (c). In the inset of this figure, the EDX of one of the bright nanoparticles is shown to evidence that these are the Pd–Sn seeds.

image of the membrane where the asymmetric structure of the ceramic membrane is well evidenced.

Reported in Fig. 2 are the catalytic performances of this Pd/Al_2O_3 thin film membrane in the direct synthesis of H_2O_2 from H_2 and O_2 at room temperature and ambient pressure. Considering that the amount of Pd deposited on the whole membrane is about 40 mg, the productivity in H_2O_2 synthesis which can be estimated from the results of Fig. 2 is about $19\,\mathrm{mmol}_{H_2O_2}/g_{\mathrm{pd}}1$ which is in good agreement with the productivity reported for supported Pd catalysts in analogous reaction conditions [19].

During the reaction of direct oxidation of hydrogen to H_2O_2 a structural instability of the thin Pd film was observed. SEM images of the surface of the Pd/Al_2O_3 thin film catalytic membrane after 5 h of reaction in H_2O_2 synthesis (Fig. 3a) reveals a complete restructuring of the surface with the disappearance of the dense assembling of Pd grains and the formation of a smooth-faced surface characterized by the presence of several nanoholes (with dimensions in the 100–400 nm range) and some residual grains on the top, but having lost completely the original shape (see inset in Fig. 1a). The weaker interaction with the alumina surface with respect to the starting sample leads also to problems of detachment of the Pd thin film from the supporting ceramic membrane, as evidenced in Fig. 3b.

It should be noted that even if O_2 is present in the solution in contact with the membrane and an oxidation pre-treatment was made before the catalytic tests (see Section 2), a fast reduction of Pd occurs when H_2 starts to flow through the membrane [19]. It is known that at room temperature a flux of H_2 through a thin palladium film causes the formation of palladium hydride

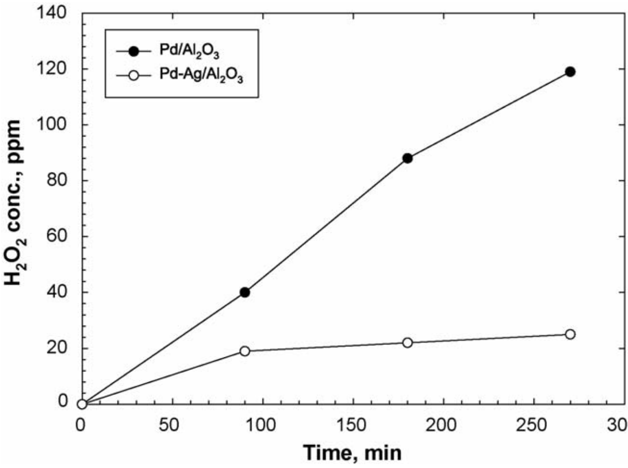

Fig. 2. Comparison of the catalytic performances of Pd/Al_2O_3 and Pd–Ag/Al_2O_3 thin films in the synthesis of H_2O_2 at r.t. and ambient pressure. See Section 2 for the reaction conditions.

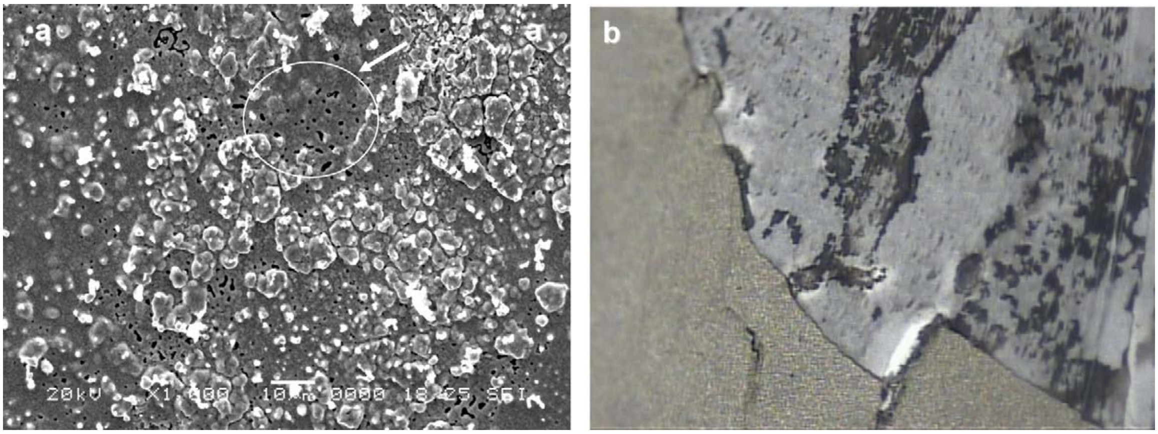

Fig. 3. SEM images of the surface of the Pd/Al_2O_3 thin film after 5 h of catalytic tests in H_2O_2 synthesis: (a) top view and (b) lower resolution image to evidence the characteristics of the thin film.

(PdH_x) with the formation of large dislocation densities to accommodate the abrupt volume change between the two phases [21], due also to the formation of superabundant vacancies in the metal hydride [22]. Therefore, this transformation results in shear stresses in the interface between the metal film and the oxide support [23]. The presence of oxygen in solution does not alters significantly this process of formation of the palladium hydride phase (β-PdH, being the more stable phase at r.t.). This phase transformation leads to the formation of pinholes (probably in correspondence of the pores of the underlying ceramic membrane) and ultimately to the membrane failure with formation of crack and metal peeling.

3.2. Pd–Ag alloy membrane (Pd–Ag/Al_2O_3)

The palladium hydride formation may be limited or suppressed by formation of a palladium alloy with group IB metals. This is well documented for H_2 separation membranes [2], but also for catalytic reactions it has been reported that the formation of bimetallic alloys leads to an inhibition of the formation of the β-PdH phase [24]. This could be demonstrated also in our case by temperature programmed reduction (TPR) experiments (Fig. 4). In these tests the reducibility of Pd supported on alumina and Pd–Ag (10:1) alloy supported on alumina is compared. The positive peak at about 75 °C is due to the reduction of PdO to metallic Pd, while the negative peak at about 120 °C (present in the Pd/Al_2O_3, but absent in Pd–Ag/Al_2O_3) is due to the decomposition of the palladium hydride phase [25,26]. The temperature of this transition indicates a high H content in the PdH_x phase (>0.5) [27], which is in agreement with the low dispersion of Pd which could be obtained by the EPD method.

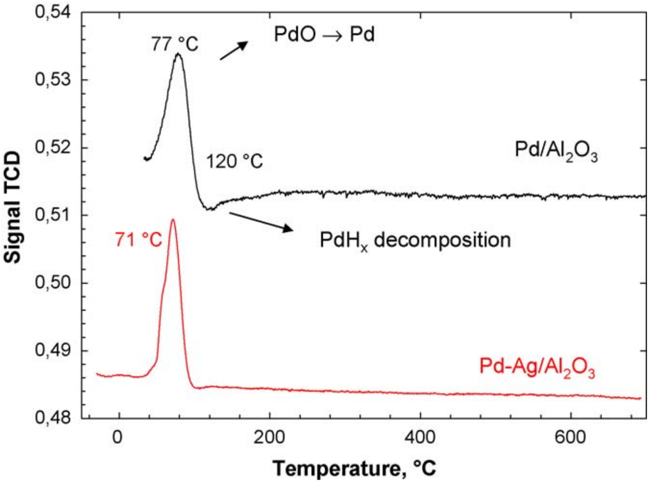

Fig. 4. Comparison of the TPR curves of Pd/Al_2O_3 and Pd–Ag/Al_2O_3 thin films after the synthesis of H_2O_2 at r.t. and ambient pressure.

The SEM images of the composite Pd–Ag/Al_2O_3 thin membrane (Fig. 5) indicate a different surface structure from that obtained for the Pd/Al_2O_3 thin membrane. The membrane consists of sub-micron grains having a rounded-cubic shape, in agreement with the results obtained for poorly crystalline Pd–Ag alloys obtained by crystallization from glass-type films [28], but different from the structure obtained for Pd–Ag/Al_2O_3 composite membranes prepared by EPD, but annealed at 600 °C in H_2 [29]. The presence of Ag induces a change in the crystal structure and therefore is reasonable to observe a morphological change in the structure of the Pd and Pd–Ag thin film supported on the ceramic membrane.

The thickness of the Pd–Ag thin film is about 8–10 μm (Fig. 5b) and shows a well uniform and crack-free structure, but is not characterized by the columnar-type structure observed for Pd–Ag/Al_2O_3 composite membranes prepared by EPD, and annealed at 600 °C in H_2 [29].

The X-ray diffraction (XRD) patterns of the Pd–Ag thin film obtained after EPD (sample 1), and after annealing at 850 °C (sample 2) or 500 °C (sample 3) in N_2 flow are reported in Fig. 6. The film immediately after plating (sample 1) consists of individual Pd and Ag seeds without formation of the Pd–Ag alloys, in agreement with Pap et al. [30]. The annealing in nitrogen at 500 °C gives rises to the formation of the Ag–Pd alloy [31,32], as shown from the shift of the (1 1 1) reflection of Pd from about $2\theta = 40.1–39.7^\circ$ (Pd–Ag) and the simultaneous disappearance of the Ag reflection at about 38.1° [32]. Further annealing at higher temperature (850 °C) does not further change the situation.

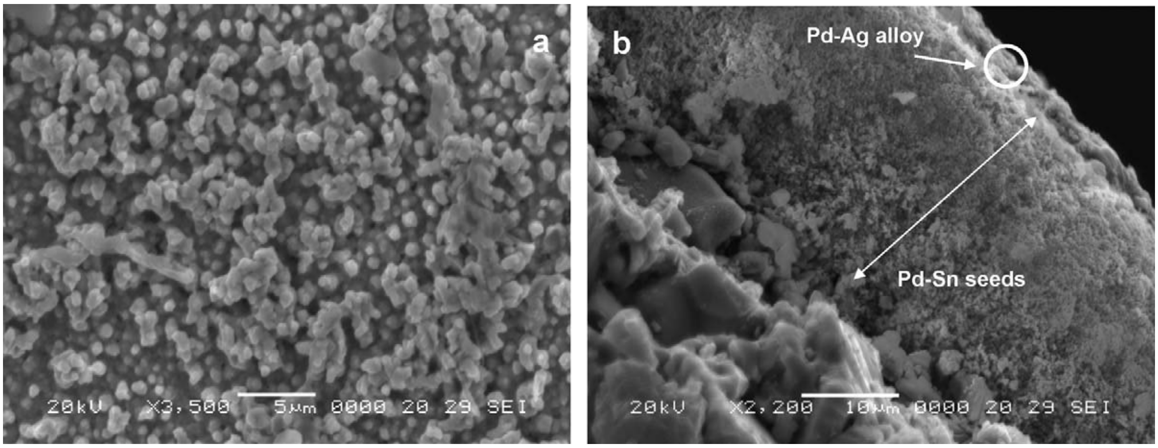

Fig. 5. SEM images of Pd–Ag/A_2O_3 composite membrane: (a) surface and (b) cross-section.

The performance of the Pd–Ag/Al_2O_3 membrane in the direct H_2O_2 synthesis is shown in Fig. 2. A drastic reduction in the catalytic performances is observed and even more relevant in the productivity per gram Pd or Pd–Ag is considered. This could be either attributed to the change of the surface coordination sites of Pd and/or to the change in the preferentially exposed crystalline planes, as shown from the comparison of the SEM images of Pd/Al_2O_3 (Fig. 1) and Pd–Ag/Al_2O_3 (Fig. 5) thin films. On the other hand, no macroscopic morphological change in the microstructure of the Pd–Ag thin film was observed after catalytic reaction, differently from the case of Pd/Al_2O_3 thin films (Fig. 3).

3.3. Pd/Pd–Ag multilayer membrane (Pd/Pd–Ag/Al_2O_3)

In order to overcome the conflict between improvement of stability, but lowering of the catalytic performances, a Pd/Pd–Ag/Al_2O_3 multilayer catalytic membrane was developed. In this case, the Pd–Ag thin film was produced and after annealing at 500 °C to form the alloy a stable interaction with the ceramic substrate was obtained. On this layer a second plating process was made using the Pd-only solution (5 h). The SEM image of the surface and cross section of the produced membrane is reported in Fig. 7 (Fig. 7a and b, respectively).

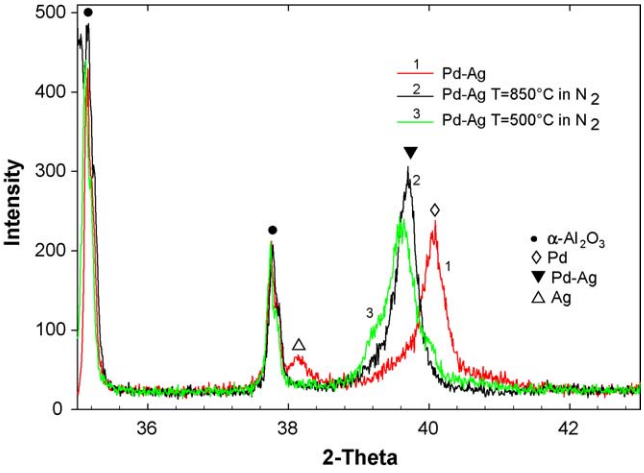

Fig. 6. Comparison of the XRD patterns of Pd–Ag/Al_2O_3 thin films after the plating stage (1) and after the consecutive annealing in N_2 flow at 850 °C (2) or 500 °C (3).

The surface microstructure is analogous to that observed for the Pd/Al_2O_3 membrane, while the cross section reveals that a first layer at the contact with the ceramic membrane (about 1 µm thickness) having the expected Pd:Ag = 10:1 composition (from EDX analyses) is present and on the top of this layer the Pd-only thin film (with thickness about of 7–8 µm) grows.

Notwithstanding still some problems of weak adherence to the ceramic substrate (the noble metal film could be easily detached from the ceramic substrate, as shown in Fig. 7c and d), no surface reconstruction and formation of pinholes were detected. The film after the catalytic reaction (inset in Fig. 7c) remains well compact.

The adherence to the ceramic substrate, however, can be improved by increasing the thickness of the Pd–Ag interlayer by consecutive plating. Three steps of deposition of this interlayer lead to a thickness of about 10 µm on the top of it the final Pd thin layer could be deposited. The resulting catalytic membrane is quite robust, with a good adherence to the ceramic support (Fig. 8a). The membranes do not show relevant microstructural changes after catalytic tests and after 20 h of reaction in the direct H_2O_2 synthesis from H_2/O_2 the morphology of the surface thin Pd film (Fig. 8b) resembles closely the initial one. Therefore, enough thickness of the Pd–Ag interlayer preserves the final Pd layer from major reconstruction in the presence of H_2 and the formation of Pd-hydride.

Further studies are necessary to clarify more in detail this effect (improve stability creating a Pd–Ag interlayer on enough thickness), but an interpretation could be advanced based on some recent literature observations. Studying palladium–ceramic membranes prepared by different methods, Tosti et al. [23] noted that (i) the thickness of the metallic layer plays a key role on the physical and chemical stability (ii) Pd–Ag films show better stability that Pd-only membranes, because the higher atomic interdiffusion increases the strength of the interface. Zuo et al. [33] observed that the formation of an interlayer between a ceramic substrate and a Pd-based electrode

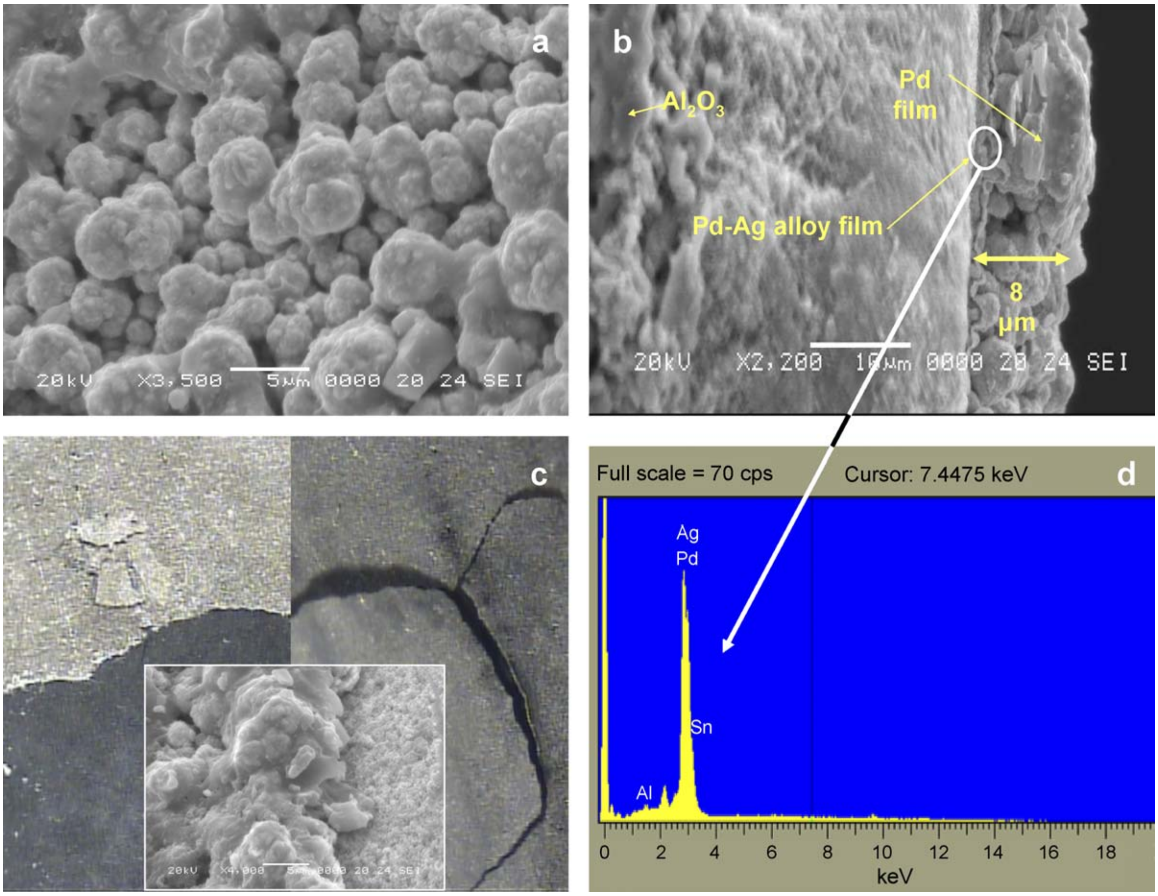

Fig. 7. SEM images of the surface of the Pd/Pd–Ag/Al_2O_3 multilayer membrane (one plating with Pd–Ag): (a) top view, (b) cross section, (c) top view (low resolution) after the catalytic tests in H_2O_2 synthesis (in the inset a higher resolution images evidencing the noble metal membrane); (d) EDX of the Pd–Ag interlayer.

improves the multilayer stress distribution and lower the interfacial stress gradient, resulting thus in an improved stability [34].

In our case the Pd–Ag interlayer has thus the effect of (i) inhibiting the formation of palladium-hydride phase, reducing the stress at the metal–ceramic interface and at the same time of (ii) improving the strength of the interaction due to the higher atomic interdiffusion. Silver generally tends to migrate to the surface at the contact with air to reduce the surface free energy [35,36], but in our case the Pd–Ag alloy is present as an interlayer between the oxide ceramic support and the surface Pd layer. Therefore, reasonably the silver tends to migrate to the oxide (support) side, creating ideally a two layer interface, with a Ag-rich Pd–Ag alloy at the contact

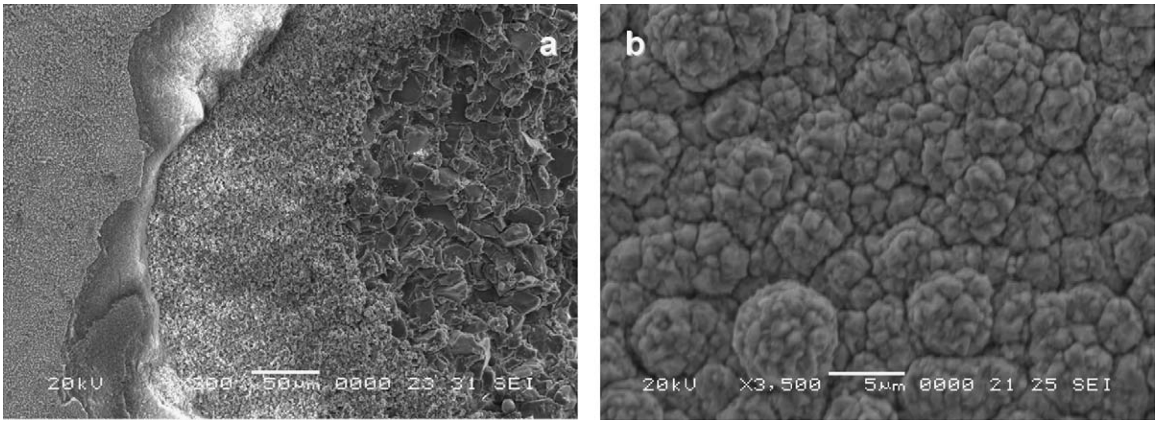

Fig. 8. SEM images of surface of the Pd/Pd–Ag/Al_2O_3 multilayer membrane (one plating with Pd–Ag): (a) low resolution image after manually removing part of the noble metal membrane to better evidence the microstructure and (b) top view of the surface.

with the ceramic and a Pd-rich Pd–Ag alloy at the contact with the Pd surface layer. This would improve the strength of interaction between the layers at both side, but reasonably it is necessary to have an enough thickness of this interlayer to realize this situation. In agreement, Bukaluk [39] reported that the interdiffusion region extends to over 1–2 μm in Ag/Pd bilayers. This explain why the increase of the thickness of the Pd–Ag interlayer above a threshold improves the stability of our membranes.

The presence of Ag would also promote the oxidation of Pd [37] creating nanosized metal-oxide particles, which reduce the formation of Pd-hydride phase and inhibit the α → β PdH transition [21]. The formation of an alloy also significantly slow down the dissociative chemisorption of H_2 which is the rate limiting step of the formation for α or β phase PdH formation [38]. Therefore, the formation of the Ag-rich Pd–Ag alloy at the contact with the ceramic interface inhibits the formation of Pd-hydride phase reducing the stress in the interface layer, which causes detachment if the force is larger than the strength of the interface.

This model of the nature of interlayer could also explain the positive effect on the reactivity and not only on the stability of our catalytic membranes. In Fig. 9 the behavior of a Pd/Pd–Ag/Al_2O_3 multilayer membrane is compared with that of a Pd/Al_2O_3 thin membrane. The presence of the interlayer promotes the catalytic behavior in H_2O_2 synthesis. Note that the performances are significantly better than those of Pd–Ag/Al_2O_3 membrane (Fig. 2), suggesting that using this multilayer approach the surface enrichment of Ag probably present in the Pd–Ag/Al_2O_3 membrane is not present. On the other hand, the inhibition on the formation of palladium-hydride due to interlayer positively promotes the performances, bacause the dissociative chemisorption of O_2, which negatively influences both the productivity and the selectivity in H_2O_2 synthesis [19], is probably enhanced by the formation of palladium hydride.

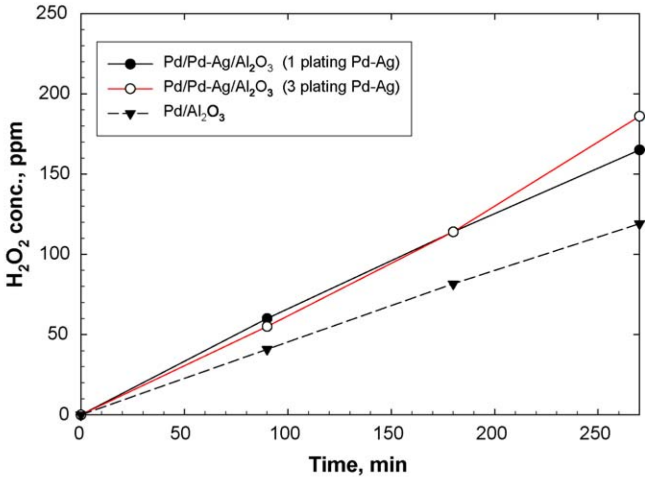

Fig. 9. Comparison of the catalytic performances of Pd/Al_2O_3 and Pd/Pd–Ag/Al_2O_3 multilayer membrane (one and three plating for the formation of the Pd–Ag interlayer) in the synthesis of H_2O_2 at r.t. and ambient pressure. Reaction conditions as in Fig. 2.

4. Conclusions

The results of the microstructure characterization of Pd and Pd–Ag alloy porous thin film membranes on a ceramic α-Al_2O_3 tubular membrane support and the analysis of their r.t. reactivity in the direct H_2O_2 synthesis from H_2/O_2 indicates that also in this low temperature application the problem of brittleness of the Pd film due to formation of palladium-hydride in the presence of H_2 diffusing through the membrane is present and that the formation of an alloy with a second metal (Ag in this specific case) could prevent or limit this problem. However, differently from the high temperature applications for H_2 separation the microstructural change determines also a lowering of the catalytic performances.

To overcome this problem it is necessary to prepare multilayer catalytic membranes with a Pd–Ag interlayer, which improves both the catalytic performances and the stability of the materials, although the thickness of this interlayer film should be above about 10–15 μm to have stable performances for longer time.

A model of this effect has been proposed based on the formation of an Pd–Ag alloy interlayer rich in Ag on the oxide (support) side and rich in Pd at the interface with the final Pd layer. This reduces the interface stress, increases the strength of the interaction with the support, and limit the formation of hydride phase, but preserving the surface structure necessary to improve the catalytic performances in H_2O_2 direct synthesis. Further studies, however, are necessary to better understand this effect which characterization is made difficult from the necessity of in situ characterizations during the H_2O_2 synthesis, because even the exposure to air at room temperature gives rise to a fast reoxidation of the surface and probably also a surface restructuring [19].

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