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Effect of the porous stainless steel substrate shape on the ZrO_2 deposition by vacuum assisted dip-coating

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ABSTRACT

The effect of the support shape on the deposition of ZrO_2 by the vacuum-assisted dip-coating method was studied. Disc-shaped and tubular porous stainless steel substrates were used to obtain ZrO_2 coated supports for the synthesis of PdAu alloy composite membranes. The microstructure of the ZrO_2 modified supports was evaluated by scanning electron microscopy and confocal laser microscopy. Besides, a qualitative assessment of the porosity and roughness of the porous substrates was performed by confocal laser microscopy. Dense and continuous palladium-alloy films were deposited on top of the modified tubes after thirteen ZrO_2 deposition-calcination cycles. Cross-section EDS mapping and XRD diffraction analysis showed that a complete PdAu alloy formation was obtained even after annealing at 723 K in hydrogen stream during 5 days.

Introduction

Inorganic membranes have become the focus of attention during the last decades due to the possibility of their use in several industrial applications. Taking into account their almost infinite selectivity to hydrogen, palladium-based membranes are presented as an efficient material to be coupled in membrane reactors for high purity hydrogen production [1]. Furthermore, these membranes could be integrated into several industrial processes for hydrogen recovery from mixed gas streams. Despite the great advances in the development of palladium membranes, the challenge in this area is to improve mechanical stability maintaining high perm-selectivities properties.

One way to reduce cost and increase permeation flux is to use composite membranes where a thin selective layer of a palladium alloy is grown on top of a porous support. Several kinds of materials can be used as substrate for inorganic membranes, among them, the porous stainless steel is attractive due to their superior mechanical strength, and simple connection to the permeation module. Despite this, the surface pore size and roughness of the substrates difficult the deposition of a continuous, thin defect-free palladium layer on top of them. Over the last decade, several groups have considered the implementation of a modifier layer between the stainless steel supports and the palladium alloy with the attempt to avoid inter metallic-diffusion and decrease the surface pore size and roughness [2–5]. Due to

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their thermal and chemical stabilities, zirconia and yttria-stabilized zirconia (YSZ) has been present as good materials to modify porous stainless steel supports [4,6]. PdAg and PdAu layers of a thickness between 1 and 7 μm has been deposited on top of commercially available YSZ porous stainless steel substrates by electroless plating [6,7]. Sanz et al. [8] deposited a 50 μm thick yttria-stabilized zirconia layer on porous stainless steel tubes, and used them for the synthesis of Pd composite membranes. A thickness of 27.7 μm of Pd layer was necessary to achieve a dense and defect-free membrane [8]. In a previous publication, we successfully obtained thin PdAu composite membranes on top of ZrO_2-modified porous stainless steel discs [9]. The modification of the support was performed by means of the vacuum-assisted dip-coating method using a commercial colloidal suspension as a source of ZrO_2. In addition of allowing the decrease of the Pd layer thickness, the ZrO_2 coating between the stainless steel and the Pd-based alloy, effectively avoids the inter-metallic diffusion within their components. In our samples, no composition gradient was detected on thickness after permeation experiments as determined by cross-sectional EDS line scan [9]. Lin and coworkers [10] reported a significant improve in the thermal stability using YSZ as intermediate layer between palladium and porous stainless steel discs substrates at temperatures above 873 K [10]. On the other hand, Okazaki et al. [11] have shown constant hydrogen permeation and selectivities for palladium membranes supported on YSZ-porous supports instead of alumina, at temperature as higher as 923 K [11]. From SEM and XPS experiments, migration of yttria or zirconium was not observed onto the palladium layer [11].

Palladium alloy membranes could be growth on top of porous substrates by mean of several deposition techniques as well as chemical vapor deposition, physical vapor deposition, electroplating and electroless plating [12]. Among them, the electroless deposition techniques have received much attention considering their advantages, namely applicability on substrates of different shapes, low cost and simplicity [12,13]. Although the electroless deposition of composite palladium membranes could be performed on top of planar and tubular substrates, tubular membranes are the more suitable option to be applied at industrial scale. Even though planar membranes are simple to prepare and well-suited with a range of seal designs, they have a low surface area and a large sealing/membrane area ratio. On the other hand, tubular membranes exhibit a higher surface area to volume ratio and they present the advantage of an easier assembly to the permeation module [14].

The main objective of the present study was to optimize the deposition of a ZrO_2 layer on the outer surface of porous stainless steel tubes and analyze the influence of the substrate shape (disc or tube) on the ZrO_2-modification by the vacuum-assisted dip-coating method. The microstructure of the samples after several deposition-calcination cycles was analyzed by scanning electron microscopy (SEM) and confocal laser microscopy (FCOM). PdAu layers were synthesized by the electroless deposition technique on top of the ZrO_2 modified porous stainless steel tubes. The permeation properties of the membranes were studied as a function of temperature and pressure.

Experimental

Membrane preparation

ZrO_2 modification of tubular supports

For the synthesis of the composite membranes, porous stainless steel tubes 0.2 μm grade (Mott Metallurgical Corporation) were used as substrates. The tubes were cleaned and oxidized following the procedure previously reported [15]. With the attempt to avoid inter-metallic diffusion and reduce surface pore size, the outer surface of the tubes were modify with zirconium by the dip-coating method using a commercial ZrO_2 suspension (Nyacol Acetate Stabilized 20 wt.%, particle size between 5 and 10 nm) [9]. The supports were subjected to sequential deposition-calcination cycles; each cycle consisted of three ZrO_2 dip-coatings; afterward, the support was dried at room temperature for 1 h and the following dipping was performed. Finally, it was calcined at 673 K for 3 h. The vaccum-assisted deposition method was used in the last deposition cycles. Additional details regarding modifications are presented on our previously publication [9]. The number of ZrO_2 deposition cycles on the tubular supports was optimized in order to improve the pore-filling. Fig. 1 shows a scheme of the setup used for the ZrO_2 deposition on disc shaped and tubular substrates. For a comparison a porous disc was modified with five deposition-calcination cycles under the same conditions than those reported elsewhere [9].

PdAu layers deposition

The sequentially electroless plating method was used to synthesized the PdAu alloy film on the outer surface of the tubular supports. Before to the metallic deposition, the modified supports were activated using the conventionally sensitization-activation stage described elsewhere [9]. After that, the palladium and gold layers were deposited using the bath compositions reported previously [9]. First, palladium was deposited in two steps for 60 min each at 323 K, followed

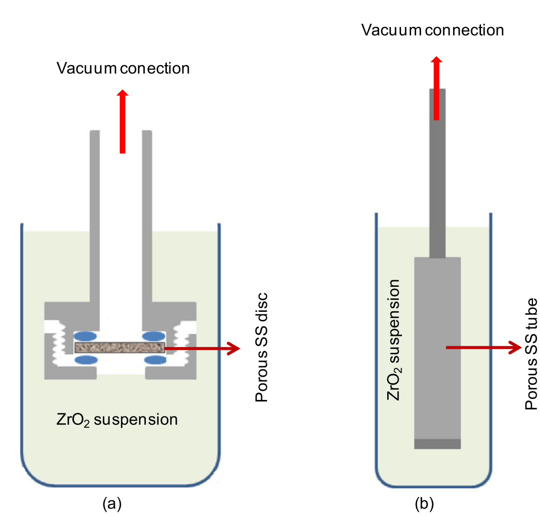

Fig. 1 – Schematic diagram of the vacuum-assisted dip-coating method for disc shaped (a) and tubular (b) supports.

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