NANOSTRUCTURED PVDF-HFP CATALYST-LOADED MEMBRANES OBTAINED BY SUPERCRITICAL CO$_2$ PROCESSING

[1]S. Cardea, [1]M. Scognamiglio, [1,2]E. Reverchon*

[1]Department of Industrial Engineering, University of Salerno, Via Ponte Don Melillo, 1 – 84084, Fisciano, Italy.

[2]NANO_MATES, Research Centre for Nanomaterials and Nanotechnology at the University of Salerno, Via Ponte Don Melillo, 1 - 84084, Fisciano, Italy.

ereverchon@unisa.it, Ph. +39-089964232, Fax. +39-089964057

ABSTRACT

The most-used method to generate polymer-based catalytic membranes is the phase inversion (i.e., liquid phase inversion or temperature induced phase inversion) that, however, presents some limitations such as the difficulty in generating an uniform distribution of the loaded materials.

In this work, we use a new process for the formation of catalyst-loaded membranes for potential applications in catalysis: supercritical assisted gel drying, applied to formation of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membranes loaded with palladium (Pd) nanoparticles. We analyzed the effect of process parameters (polymer concentration, catalyst concentration, pressure, temperature, time) on the membranes morphology. Supercritical gel drying allowed homogeneous nanoporous membranes formation at all the tested process conditions: they were characterized by very high porosity (higher than 90%) and an uniform catalyst distribution.

INTRODUCTION

The topic of membrane-based reactive separation has attracted a large scientific interest, since membranes can be efficient chemical reactors, where reaction and separation are combined in a single unit operation; therefore, it has been the object of study for several researchers [1-6]. The major areas of applications for catalytic membrane reactors (CMR) are: (1) Yield-enhancement of equilibrium-limited reactions, (2) Selectivity enhancement. The role of the membrane in a MR could also be to improve the contact between different reactive phases. Recently, polymeric catalytic membrane reactors have been studied in deeper, because they offer further flexibility over their conventional reactor counterparts. The research on polymeric catalytic materials has been focused mainly in liquid phase reactions under mild conditions [4-6].

The main advantage of polymer-based catalytic membranes in the field of fine chemical synthesis concerns the case of their preparation: the control of the thickness, the large scale preparation and the crack-free membrane synthesis are much less problematic than in the case of inorganic membranes. Furthermore, a dense polymer phase can actively take part in the reaction influencing sorption and diffusion of reagents and products. The main method used to generate polymer-based catalytic membranes is the liquid phase inversion [7-9]. It presents some limitations; in particular, the difficulty in generating uniform distribution of the loaded materials, with consequent agglomeration and leaching phenomena.

To overcome these limitations, supercritical fluids assisted methods for the formation of several polymeric membranes have been recently proposed [10-14]; the most interesting are: Phase inversion assisted by supercritical carbon dioxide (SC-CO$_2$) [10-13] and Gel drying

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assisted by SC-CO$_2$ [14]. Until now, these two processes have been only tested for the formation of membranes and in limited cases of drug-loaded membranes [15-16].

In this work, we propose the feasibility of Gel drying assisted by SC-CO$_2$ for the formation of catalytic membranes, and the analysis of the influence of their process parameters. In particular, the formation of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) membranes loaded with palladium (Pd) nanoparticles has been tested. This is one of the most common systems in the field of catalytic reaction and can find application for selective hydrogenation (hydrogenation of methylenecyclohexane).

MATERIALS AND METHODS

Materials

PVDF-HFP (Number Average 199•103, Weight Average 353•103, Polydispersity 1.8, Density 1.78 g cm-3) was kindly supplied by Solvay S.A. (Ixelles, Belgium); palladium nanoparticles (d< 25 nm, purity 99.9%), acetone (purity 99.8%) and ethanol (purity 99.7%) were bought from Sigma-Aldrich; CO2 (purity 99%) was purchased from S.O.N. (Società Ossigeno Napoli, Italy). All materials were processed as received.

SC-CO$_2$ assisted gel drying

Loaded gels of PVDF-HFP were prepared by dissolving the polymer in acetone under vigorous stirring. Then, different amounts of catalyst were added to the homogeneous solution warmed at 50°C, obtaining a catalyst suspension. Then, ethanol was added as the non-solvent to induce the phase separation. The suspensions were placed in a formation cell (steel caps with a diameter of 2 cm and height of 200-300 µm) and put in a freezer at -20 °C until a gel was formed (~1 h). The gel was rapidly (ca. 30 s) put inside the preparation vessel to avoid the evaporation of the solvents. Then, the vessel was closed and filled from the bottom with SC-CO$_2$, up to the desired pressure using a high- pressure pump (Milton Roy–Milroyal B, France). We operated in continuous mode for about 1h at a constant CO$_2$ flow rate of 1.5 kg/h, then, the vessel was slowly depressurized for 10 min and the aerogel was removed from the support.

Scanning electron microscopy (SEM)

The porous structures were examined by cryofracturing them with a microtome (Bio-optica S.p.A, Italy, Mod. Microm HM 550 OMVP), then the samples were sputter coated with Gold and viewed by scanning electron microscope (SEM) (mod. LEO 420, Assing, Italy).

Energy Dispersive X-Ray analyzer (EDX)

Palladium dispersion in the membranes was measured using an Energy Dispersive X-Ray analyzer (EDX mod. INCA Energy 350, Oxford Instruments, Witney, UK), using the signal of Palladium atoms to detect the catalyst nanoparticles.

Structure porosity

Porosity (ε) represents the "void space" inside the structure and is calculated from the density of the sample (ρ_m) and the density of untreated PVDF-HFP (ρ_p=1.78 g cm-3):

$$\varepsilon = 1 - \rho m/\rho p$$

The structure density is determined by measuring its volume and weight. The samples volume has been calculated using the Archimede's principle. They have been waterproofed by a varnish and placed inside a liquid of known density and the volume of the displaced liquid has been measured. This operation has been performed on 5 samples for each experiment.

RESULTS
We verified the possibility of generating PVDF-HFP catalyst-loaded aerogel based membranes by supercritical gel drying processing. This process allows to obtain polymeric aerogels that show all the morphological characteristics necessary to work as membranes. We prepared PVDF-HFP gels starting from PVDF-HFP, acetone and ethanol solutions and processed them at different pressures and temperatures. Polymer concentration ranged between 5 and 12% w/w (acetone content has been maintained constant at 60% w/w, whereas ethanol content has been varied with polymer content). Temperature and pressure were fixed at 200 bar and 35°C, because we verified in a previous work [14] that this process parameters do not influence the supercritical drying process and, as a consequence, do not interfere with the membranes morphology formation. In this process, the Pd concentration was also varied from 1 to 10% w/w with respect to PVDF-HFP content.

Effect of supercritical processing
The operation at supercritical conditions plays a crucial role in the production of stable aerogels in the gel drying process; indeed, it is known that, only when near zero surface tension is obtained, the collapse of the solid structure is avoided since no cohesive forces are present between the fluid and the solid phase. The use of CO_2 at supercritical conditions (P > 73.8 bar, T > 31°C) could be not sufficient to correctly process the gel; indeed, when CO_2 diffuses in the gel, it forms a solution with acetone and ethanol. Only if the formed solution is also at supercritical conditions, the near zero surface tension conditions are obtained. A solution is at supercritical conditions when the operation is performed above its Mixture Critical Point (MCP), that is (at a given temperature) the pressure at which the mixture becomes supercritical. In presence of acetone and ethanol the MCP of the two systems acetone-CO_2 and ethanol-CO_2 has to be considered. However, operating at 35°C the MCP for both systems is located at about 80 bar [17]. Since the pressure used is 200 bar, we always operated well above the MCP of the formed fluid phase. Operating above the MCP of the mixture, the gel structure does not collapse and, the aerogel formed by the SC-CO_2-assisted process, preserves both dimensions and shape of the gel before the drying treatment. The result is a well-dried aerogel having the structural stability necessary to work as a membrane reactor.

Effect of polymer and catalyst concentration in the gel
The aerogel/membrane were characterized by an uniform nanofibrous network (with fibers size of about 300 nm) and top and bottom porous skins, for all polymer concentrations tested. An example of loaded PVDF-HFP membranes obtained starting from 10% w/w of polymer and 5% w/w of suspended Pd nanoparticles is reported in figure 1.
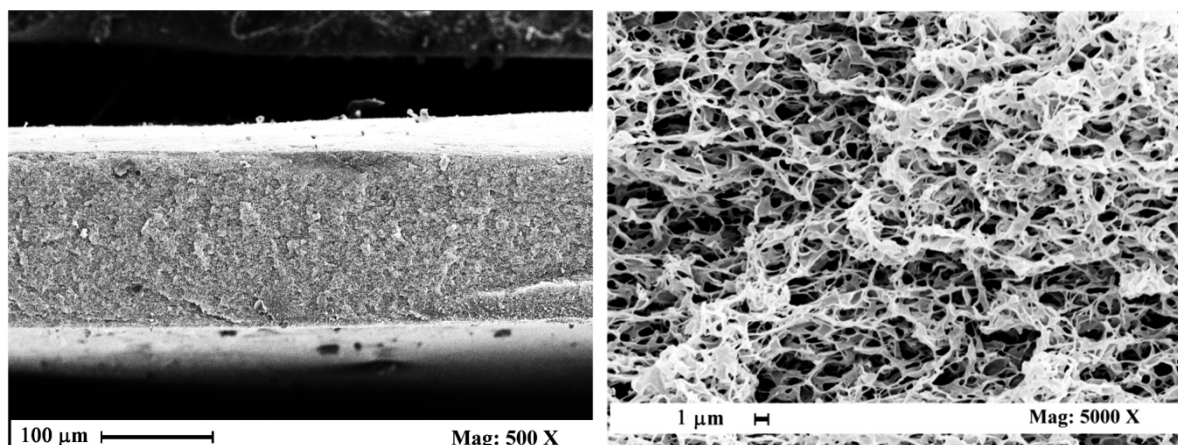
Figure 1: PVDF-HFP aerogel/membrane obtained by supercritical gel drying at 200 bar and 35°C, starting from 10% w/w polymeric solution with 5% w/w of suspended Pd nanoparticles; left) the whole membrane section, right) enlargement of the section showing the nanostructured network.

Increasing the polymer concentration, we verified that the membranes porosity decreases. In particular, staring from 5% w/w PVDF-HFP gel, a 97.2% of porosity was obtained; whereas, starting from 12% w/w PVDF-HFP gel, a porosity of 91.1% was measured. This result can be explained considering a fixed volume of solution: increasing the polymer concentration, the void space inside the liquid phase (i.e., the porosity) decreases.

The Pd nanoparticles are not visible in SEM images; but, increasing the Pd concentration up to 10% w/w, a modification of membranes morphology was observed. Indeed, from 1 to 5% w/w of Pd, the membrane presents the classical nanofibrous network observed in figure 1. On the contrary, when we performed experiments with a loading of 10% w/w of Pd, a leafy morphology was obtained, as reported in figure 2.
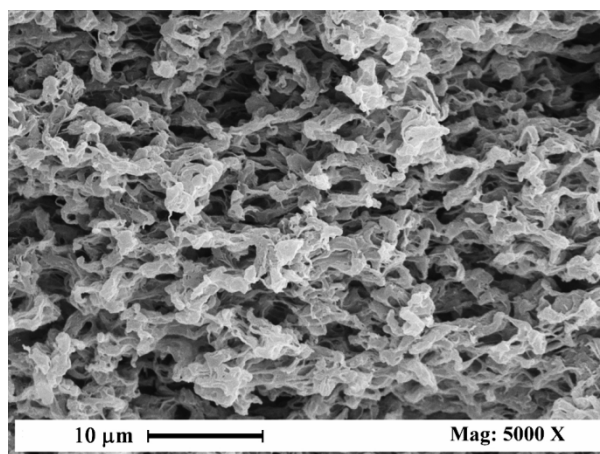

Figure 2: PVDF-HFP aerogel based membrane section, obtained at 200 bar and 35°C, starting from 10% w/w polymeric solution with 10% w/w of suspended Pd nanoparticles.

Probably, the presence of a large amount of Pd nanoparticles interfere with the gelation process, causing a modification of the gelation step. In a previous work [14], it has been verified that PVDF-HFP aerogels are characterized by leafy morphologies when a higher gelation temperature is used (-4°C), i.e., a slower gelation step is obtained. As a consequence,

the increase of Pd concentration in the starting suspension can be compared to an increase of gelation temperature that corresponds to a decrease of the gelation rate.

Catalyst distribution

In figure 3, we reported the EDX analysis of a PVDF-HFP aerogel based membrane loaded with 5% w/w of suspended Pd; the green color represents the element (i.e. palladium) present only in the catalyst: its uniform distribution along the membrane section shows an uniform distribution of the catalyst. However, a quantitative analysis is required to have information about the catalyst distribution. Therefore, in table 1 we reported the % w/w of Pd detected by EDX along the section of the membrane. The distribution of catalyst along the whole membrane thickness is homogeneous and is practically equal to the loading of Pd in the starting polymeric gel; this also means that all the catalyst initially loaded in the polymer is entrapped in the solid structure. Subsequently, we have also verified that uniform distribution of Pd was obtained at all polymer and Pd concentrations tested. This result was absolutely not obvious; indeed, as previously discussed, other membranes formation techniques (for example, traditional phase inversion) can generate structures characterized by a non-uniform catalyst distribution since part of the drug migrates towards the membrane top (or bottom) surface. Moreover, when nanoparticles are used, a problem of agglomeration due to the electrostatic forces acting among the nanoparticles could occur. This interesting result depends on one of the advantages of the gel drying process with respect to the other membranes formation processes: a semi-solid structure (i.e. the gel) is formed avoiding the movement of the suspended matter during the drying step.
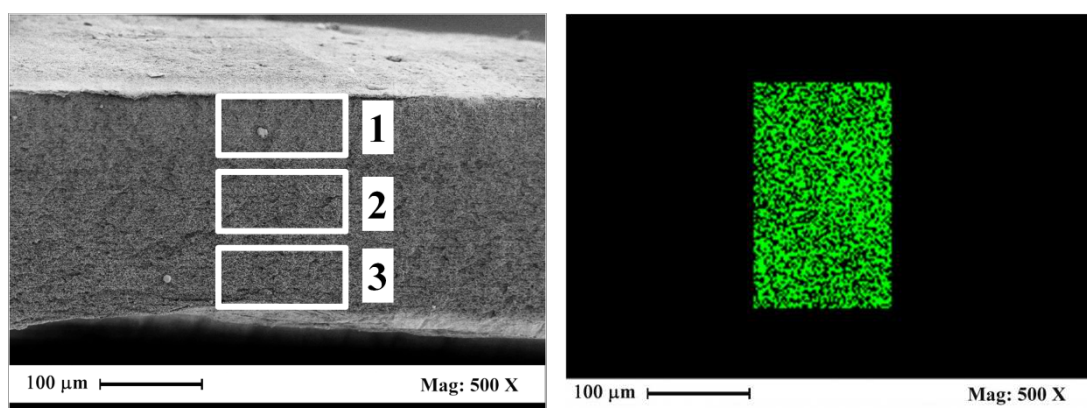

Figure 3: EDX analysis of a PVDF-HFP membrane loaded with 5% w/w of suspended Pd: left) quantitative analysis is reported in table 4, right) qualitative analysis; the green color represents palladium along the whole membrane section.

Spectrum	Pd,%
Spectrum 1	5.42
Spectrum 2	4.91
Spectrum 3	5.81
Mean	*5.38*

Table 4: Quantitative EDX analysis performed on PVDF-HFP aerogel based membrane loaded with 5% w/w of suspended Pd. Spectrums are referred to figure 3.

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CONCLUSIONS

Supercritical gel drying allows homogeneous catalytic membranes formation at all conditions tested: however, at the highest catalyst concentration tested (> 10% w/w), a change of morphology was observed. In the next future, tests on the catalytic activity of the generate membranes will be performed.

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