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Ceramic-supported Polymer and Carbon Membranes for Hydrogen Separation

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1 Introduction

The expansion of hydrogen as energy carrier has generated a growing effort to develop processes that can produce high-purity hydrogen suitable for low-temperature fuel cells (mainly PEMFC). This is the case in steam reforming, where membranes can be used to purify hydrogen but also to increase the yield of the reaction using reformers based on membrane reactors. The latter is a powerful concept but demands high-performance membranes, constructed of materials that may withstand the harsh reaction conditions required for steam reforming (i.e., high temperature and a high partial pressure of superheated steam). Processing the reformer product gas to purify hydrogen at low temperature in membrane units coupled to conventional reformers, is an option that may be implemented more easily because the membranes are operated at less demanding conditions.

In this work we focused on the development of polymeric- and carbon-based membranes supported on ceramic carriers for hydrogen purification. Polyimides are versatile materials that have been used in membranes for the separation of gas mixtures, mainly as hollow fiber membranes and other unsupported arrangements with large specific surface area [1]. They may be supported in other polymers to obtain membranes suitable for pervaporation [2], but the manufacture of supported tubular polyimide membranes has difficulties related to poor reproducibility and crack formation [3]. Additionally, hollow fibres fail in mechanical stability at high temperature under high-pressure drops [2]. Therefore, the use of ceramic carriers for developing supported polyimide membranes offers potential for obtaining efficient and mechanically stable membranes [4]. Additionally, controlled thermal treatment of ceramic-supported polyimide membranes yields supported carbon membranes that have promising characteristics for the separation of gas mixtures [5].

2 Experimental

2.1 Preparation of the supported membranes

The preparation of the polymeric membranes supported on tubular ceramic elements was based on a spinning solution technique. The macroporous ceramic support was a 1 kD ceramic membrane of 7.2 cm length and 10 mm of outer radius (Tami). It was mounted horizontally and rotated at constant speed to distribute a uniform layer of around 3 g of a viscous Matrimid solution. The solution was previously prepared by dissolving 10 to 16% w/w of polymer in N-Methyl-2-pyrrolidone (NMP) for 4 hours with mechanical stirring under controlled vacuum. After gelification at room temperature, the polymeric membranes were developed by imidization at 110°C for 24 h (Series 1) + 350°C for 2 h (Series 2). Supported carbon membranes were prepared by pyrolysis of the polymeric membranes. They were heated at 1°C/min to 550°C and maintained at this temperature for 5 h, using a flow rate of 30 NmL/min of nitrogen (Series 3).

2.2 Permeation measurement

Single gas permeation was determined for pure gases (H_2, N_2, CH_4, CO_2 and CO) at trans-membrane pressures from 1 to 3 bars and 25°C. The fluxes of single gases were measured by a soap film flowmeter. The ideal selectivity of the membrane was defined as the ratio of hydrogen permeance to the permeance of the other gases, measured at the same transmembrane pressure and temperature. The real selectivity of the membrane was determined in binary mixtures with hydrogen of 50% vol. The composition of the permeate gas was measured with a mass spectrometer. The influence of temperature on the selectivity of the carbon membranes was determined in experiments performed between 25 and 150 °C.

3 Results and Discussion

3.1 Influence of the polymer concentration on the thickness of the polymeric membranes

The viscosity of the Matrimid in NMP solution had a strong influence on the development of the polymer layer on the ceramic carriers by spinning solution. Figure 1 shows surface and transversal ESEM views of the polymeric membranes obtained with 10%, 13% and 16% w/w polymer solutions. At 10% the viscosity of the solution is too low and the polymer penetrates the macroporous structure of the ceramic carrier (Images A and B), while at 16% the viscosity is too high and it favours the formation of an irregular polymer layer with superficial wrinkles and defects (Images E and F). The best results were obtained using a 13% w/w solution. Images C and D in Figure 1 show that a regular layer of polymer was obtained, and that it only presented minor superficial defects in the form of gas bubbles.

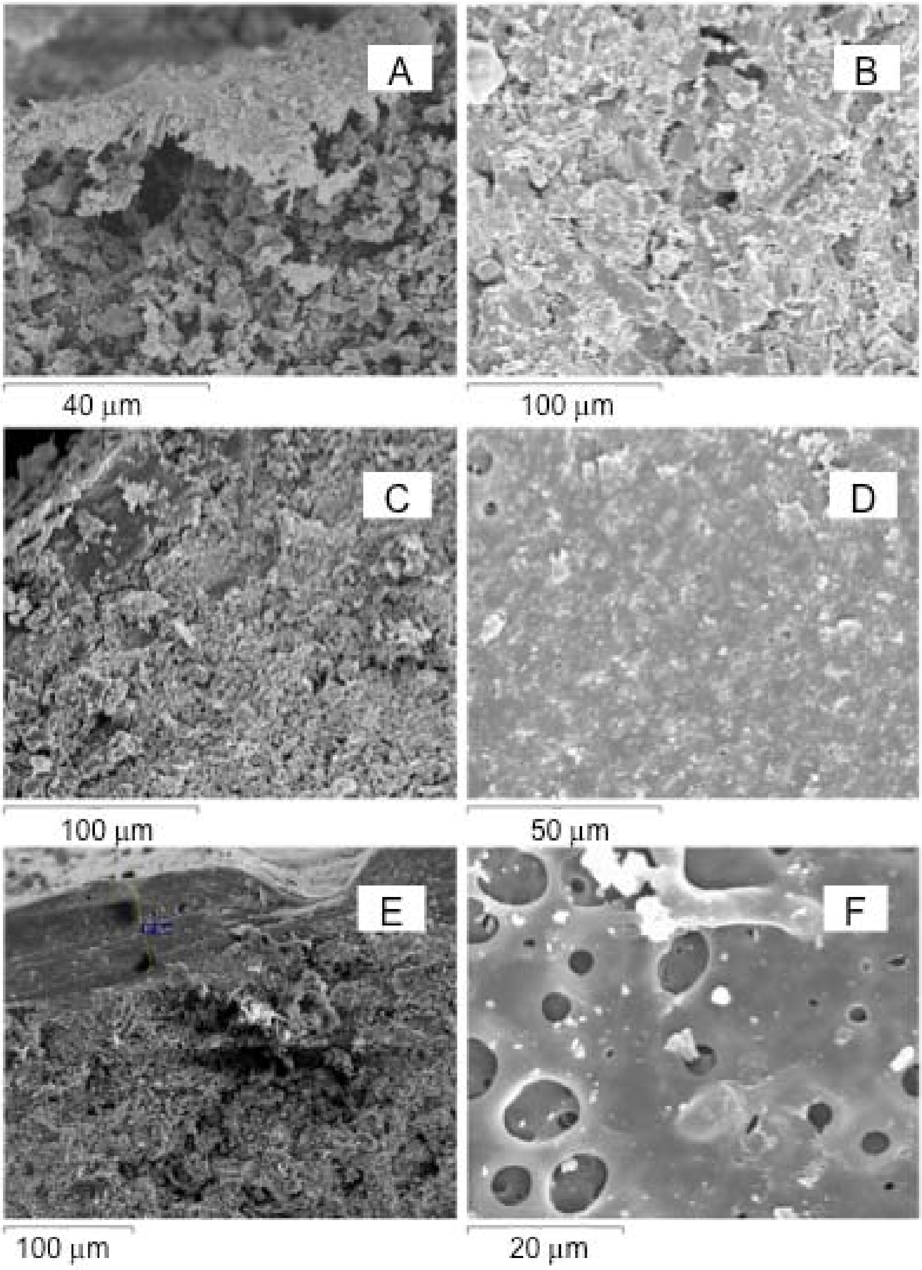

Figure 1: **ESEM images of the polymer layers deposited on the ceramic carrier at 10% (A, B), 13% (C, D) and 16% (E, F) w/w of Matrimid in NMP (A, C and E, section view; B, D and F, surface view).**

3.2 Influence of the Imidization temperature on the permeation of pure gases.

Imidization temperature plays a determinant role on the permeation properties of pure gases, because it affects the development of the structure of the polymeric membrane. With membranes prepared with the 13% w/w Matrimid solution the small surface defects disappeared completely when the imidization temperature was above 250°C, as shown in Figure 2 where a transversal view of the ceramic support and the deposited and imidized polymer layer are shown.

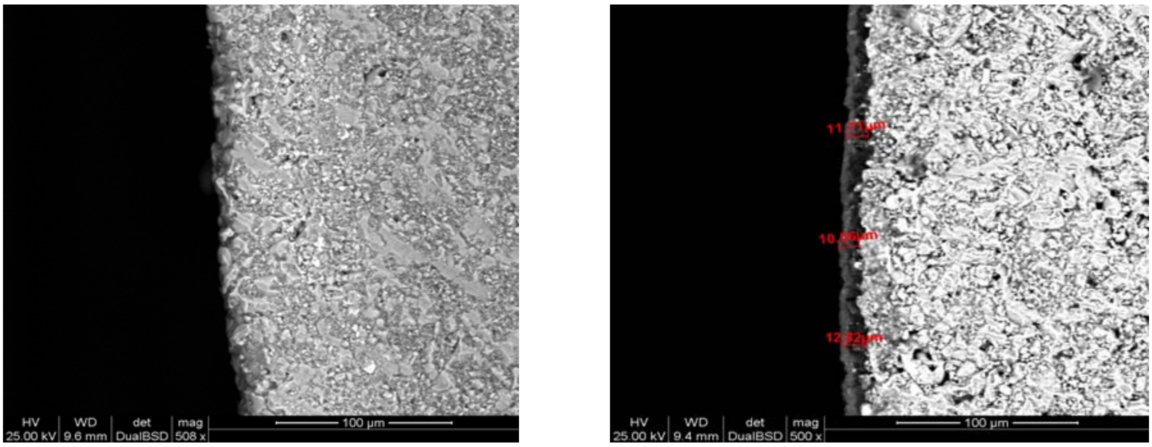

Figure 2: Supported polymer membrane (series 2): ceramic support (left) and supported membrane (right)

Table1 shows that the membranes produced at an imidization temperature of 110°C (Series 1) had lower permeance than those obtained at 350°C (series 2) for all the gases we studied. At the latter temperature permeance diminished in the order H_2>CH_4>CO>CO_2. Estimation of the ideal selectivity (i.e., the ratio of permeance of pure gases) in Table1 shows that it decreased from 2.9 to only 1.9 for H_2/CH_4 and from 4.5 to 2.8 for H_2/CO when imidization temperature was raised from 110 to 350°C, while it remained nearly constant for H_2/CO_2. Real selectivity was determined in experiments using binary gas mixtures with hydrogen containing equimolar proportions, and it was always below the ideal values. In fact, ideal and real selectivities were below those that may be expected if transport through the membrane was governed by pure Knudsen diffusion, which points out to the existence of a fraction of pores with large diameters in the membrane.

Table 1: Average permeance and selectivity of pure gases and binary mixtures with hydrogen in polymer membranes at room temperature and trans-membrane pressure below 2.5 bar.

	H_2	CH_4	CO	CO_2	H_2/CH_4	H_2/CO	H_2/CO_2
Molar mass (g/mol)	2	16	28	44	-	-	-
Kinetic diameter (nm)	0.29	0.38	0.43	0.33	-	-	-
Series 1 membranes							
Permeance (GPU)*	40.0	14.0	8.82	9.62	-	-	-
Ideal selectivity	-	-	-	-	2.9	4.5	4.2
Real selectivity	-	-	-	-	1.8	2.1	1.7
Series 2 membranes							
Permeance (GPU)*	875.	455.	314.	204.	-	-	-
Ideal selectivity	-	-	-	-	1.9	2.8	4.3
Real selectivity	-	-	-	-	1.8	1.8	2.2
Knudsen selectivity	-	-	-	-	2.83	3.74	4.69

*GPU= 10^{-6} cm^3 (STP)/(cm^2·s·cm_{Hg})

3.3 Supported carbon membranes.

Supported carbon membranes (series 3) were obtained by controlled pyrolysis of a Matrimid layer coated on the ceramic carrier. Figure 3 shows that their permeance varied with the inverse of the square root of the molar mass of the gas, which suggests the existence of Knudsen diffusion as the main transport mechanism. However, Figure 4 also shows that permeance was dependent on the trans-membrane pressure, which indicates the existence of viscous flow. The ideal selectivities calculated from the permenaces of pure gases were below those corresponding to a situation in which pure Knudsen diffusivity was the sole transport mechanism (Figure 5), in agreement with the coexistence of viscous flow.

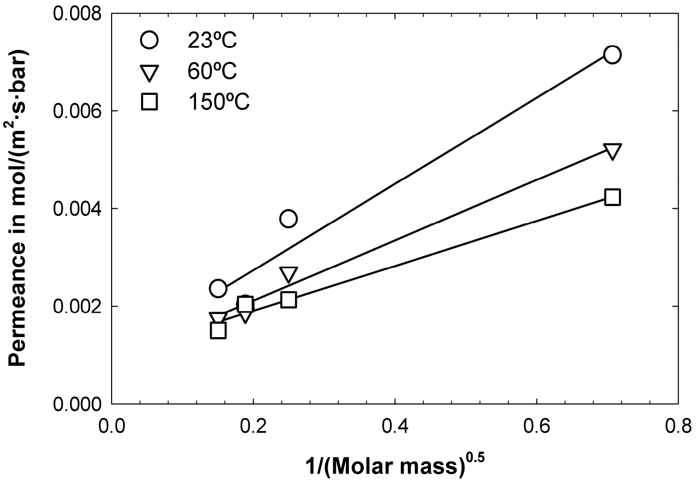

Figure 3: Dependence of pure gas permeances in a carbon membrane (series 3) with the molar mass of the gas at different temperatures and a trans-membrane pressure of 2.0 bar.

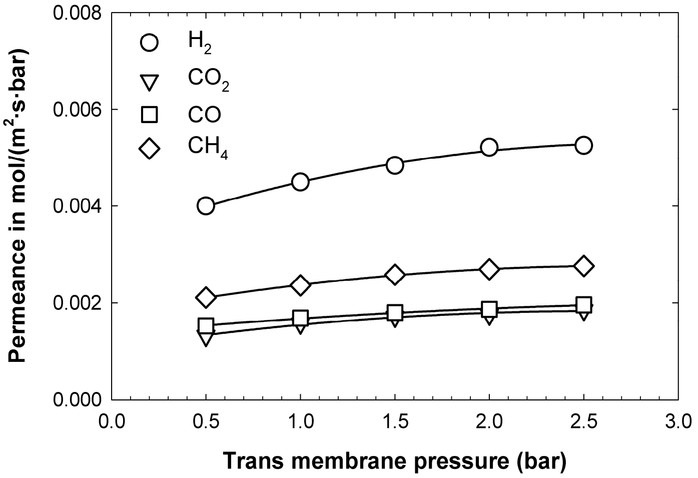

Figure 4: Permeances of pure gases in a carbon membrane (series 3) at a temperature of 60°C.

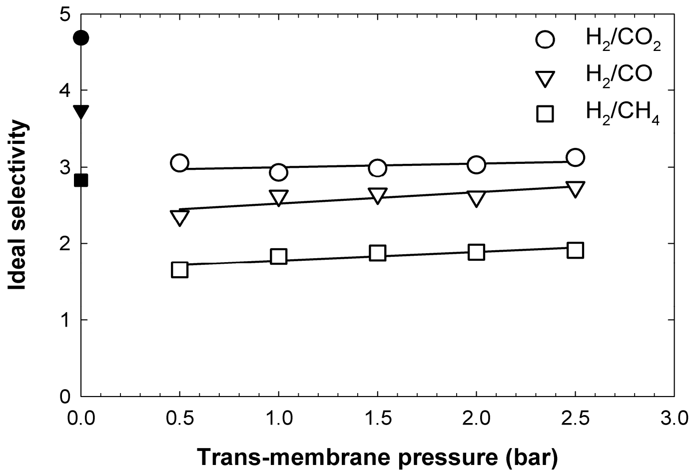

Figure 5: Effect of trans-membrane pressure on the ideal selectivity in a carbon membrane (series 3) at 23°C. Solid symbols correspond to the Knudsen selectivity.

Figure 3 show that temperature decreased the permeance of the carbon membranes, especially for hydrogen. In addition, calculation of the ideal selectivity at several temperatures shows that temperature increased selectivity slightly, except for CO_2/H_2 mixtures that remained independent of temperature (Figure 6). Measurements of the pore size distribution of carbon samples extracted from the membrane by CO_2 adsorption isotherms and the NLDFT model gave an average pore size of 0.50 nm. This value implies that in addition to Knudsen mechanism and viscous flow contribution, the pore size obtained a 550°C is so close to the kinetic diameter of the molecules considered for hydrogen separation that would imply existence of additional transport mechanisms.

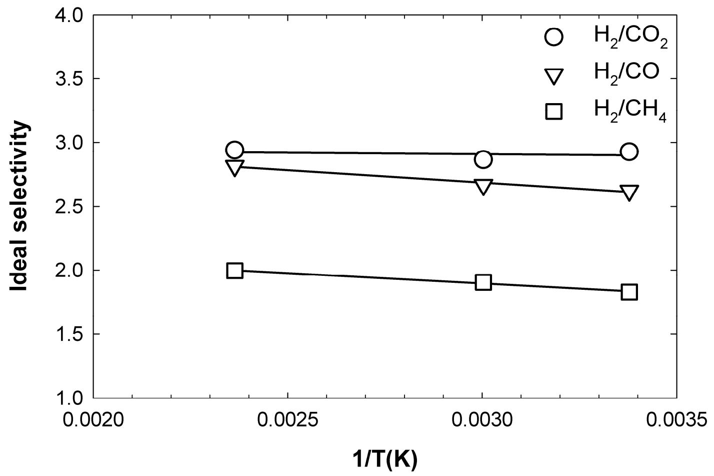

Figure 6: Effect of temperature on the ideal selectivity in a carbon membrane (series 3) at 1 bar.

Gas transport in carbon membranes is a complex interaction of several mechanisms, as already reported by Haraya et al [6], and for pore sizes below 1 nm activated diffusion is also present [7].

4 Conclusions

Supported polymer and carbon membranes were formed in the outer surface of tubular ceramic carriers by a spinning coating method. Imidization temperature plays an important role in the change of permeation values for polymeric membranes, but not in their ideal selectivity. By controlled pyrolysis of the supported polymer membranes, carbon membranes with smooth surfaces and absence of cracks were obtained. Characterization of the membrane at different trans-membrane pressures indicated that a fraction of pores with large diameters is present, which reduced the selectivity of the membranes. The pore diameters in carbon membrane are close to the kinetic diameter of the gas molecules we tested, which may favour activated diffusion.

Acknowledgments

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