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Effect of carbonization process on the structure and the gas permeation properties of polyimide hollow fiber membranes.

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1. Introduction

Membrane processes are considered as very effective technologies for the separation of gaseous mixtures at the industrial scale due to their high efficiency, simple operation and low (capital and operating) costs. In most cases, gas separation membranes are based on amorphous glassy polymers (polysulfones, polycarbonates, polyimides) and formed as asymmetric hollow fibers by using a phase inversion method in spinning machines [1]. Carbon membranes are usually prepared by suitably heating polymeric precursors, such as various types of polyimides or polyacrolynitriles, at a temperature region between 500 and 1000 ºC using an inert or a reactive environment [2].

2. Experimental, Results and Discussion

Membrane preparation: Matrimid® 5218 hollow fibers were prepared by the dry/wet phase inversion process in a spinning set up described in detail previously [3]. The respective carbon fibers were produced by using three different pyrolysis protocols, at a final temperature of 900 ºC. By selecting different gas atmosphere during pyrolysis, three different types of carbon fibers have been produced. Membrane 1 (M1) was prepared by using N_2 (99.95%), membrane 2 (M2) by using N_2 saturated with water and membrane 3 (M3) by using CO_2 (99.995%) as pyrolysis media. In all cases, the flow-rate was kept constant and equal to 150 cm^3/min.

Gas permeation measurements: The permeance range is between 52.2 GPU (H_2/M2/100ºC) and about 0.046 GPU (Ar/M1/40 ºC). Usually, for gas molecules with kinetic diameters lower than 4 Å the permeance are in accordance with the order of their kinetic diameters. These results indicate that the main separation mechanism is determined by molecular sieving. In terms of pyrolizing conditions, membranes prepared in CO_2 environment (M3) are more permeable than those carbonized in H_2O (M2) and N_2 (M1). This leads to the conclusion that the M3 membranes are more porous when compared with the two others, which is in accordance with the porosimetry results shown in detail in Table 1. In all cases the increase of temperature leads to higher permeance values, while this effect is more pronounced in the more porous M3 membranes. The M3 membrane is the most permeable and exhibits high selectivity coefficients. For instance, the highest selectivity value for the H_2/CH_4 pair (132.87) is obtained for the M3 membrane at 60 ºC. High selectivity values (37, 54) are also obtained for H_2/CO_2-M1-40 ºC and H_2/CO-M3-60ºC, respectively.

N_2 porosimetry: Table 1 summarizes the results of N_2 porosimetry at 77 K as expressed in terms of microporous volumes, total porosity and specific surfaces for the three different carbon hollow fiber membranes. From the pore size distribution of the microporous membranes (Fig. 1) it is depicted that the average radius of the separating layer is of the order of 7 Å. It is should be noted that this value is the average radii

measured throughout the whole sample placed in the porosimeter and not for a specific region of the fiber. M1 sample shows the smallest number and volume of micropores when compared with the M2 and M3 samples. This is due to the fact that the latter samples were prepared in reactive atmospheres (H_2O saturated and CO_2 respectively) forming a more porous network. The effect of the specific internal membrane structure on the gas permeation properties will be shown in the following section.

		Membrane		
		M1	**M2**	**M3**
Micropores Volume (cm^3/g)	**Langmuir**	0.039	0.481	0.662
	DR	0.042	0.515	0.704
Specific Area (m^2/g)	**BET**	128.6	1403	1888
	Langmuir	108.4	1354	1449
	DR	122.3	1449	1978
Calculated Microporosity	**Langmuir**	0.081	0.525	0.604
	DR	0.091	0.542	0.618

Table 1. Results of N_2 Porosimetry

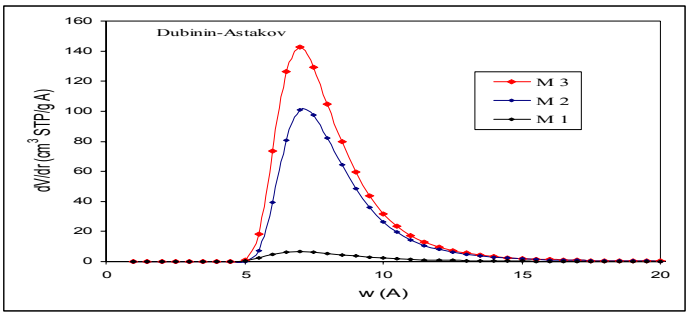

Fig.1 Pore Size Distribution

All membranes were studied with a Philips 505 Scanning Electron Microscope (SEM).

3. Conclusions

The activation process results in carbon structures with higher microporosity, total volume of pores and BET specific surface. The carbon membrane retains the asymmetric structure of the starting material, but with a smaller number of macrovoids in the fiber wall. On the contrary, the separating layer on the top of the inner fiber diameter is significantly denser and without macropores or cracks. The developed carbon fibers exhibit a H_2 permeance varying from 20 to 52 GPU with a very high H_2/CH_4 selectivity coefficient (137). In most cases, permeation properties are slightly affected by the feed pressure indicating the absence of compaction or plasticization phenomena. These results verify previous studies indicating that it is not necessary to start with a dense non-porous hollow fiber precursor in order to prepare selective carbon membranes.

References

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