

Carbon molecular sieves for air separation from Nomex aramid fibers

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Abstract

Activated carbon fibers prepared from aramid fibers have proved to possess an outstanding homogeneity in pore size, most of all when using Nomex aramid fiber as precursor. Taking advantage of this feature, microporous carbon molecular sieves for air separation have been prepared through carbon vapour deposition of benzene on Nomex derived carbon fibers activated to two different burn-off degrees. Carbon molecular sieves with good selectivity for this separation and showing acceptable adsorption capacities were obtained from ACFs activated to the two burn-off degrees chosen.

Keywords: Activated carbon fibers; Adsorption; Microporous materials; Molecular sieves.

Carbon molecular sieves (CMSs) are nanoporous materials which can provide molecular separations of gases from their mixtures on the basis of the different adsorption kinetics of the species involved. Unlike other molecular sieve materials, such as zeolites, they possess good thermal and chemical stability and high hydrophobicity. Besides, a certain versatility can be introduced in the preparation process, enabling the optimization of the pore entrance size (1) and surface modification (2) to enhance the selectivity for specific target molecules. As a result of these attractive features, they have been considered as catalyst supports (3), porous membranes (4) and adsorbents for pressure-swing

adsorption processes (5). A number of procedures and precursors for preparing CMSs have been proposed since Emmett (6) first discovered the molecular sieving property of Saran char. Among the preparation processes, great attention has been paid to the chemical vapor deposition (CVD) of amorphous carbon on porous activated carbons (7-11). It has been predicted that CMSs with fibrous shape can be the best adsorbent for pressure-swing adsorption application (9) because of their rapid adsorption/desorption rate and large adsorption capacity. Nevertheless, earlier efforts on modifying the pore structure of activated carbon fibers (ACFs) to make them suitable for air separation have been only partially successful (9,10).

In this paper, we describe the preparation of CMS useful for air separation from Nomex-based ACFs through CVD of benzene. Nomex, or poly (*m*-phenylene isophthalamide), is the polycondensation product of 1,3-diaminobenzene and terephthalic acid. Besides showing high carbonization yields (12), this polymeric material has proved to yield ACFs with very small and uniform pore sizes irrespective of the activation conditions (13-18). For these features, Nomex-based ACFs have recently been suggested as promising precursors for CMSs (17,18). However, an evaluation of the separation ability of these materials is still lacking.

To the authors' knowledge, this is one of the first successful preparations of fibrous shape CMS materials for air separation (10) and the first one through CVD of benzene on any kind of ACFs (Nomex-based and others). The strategy followed consisted of choosing two ACFs activated to two different burn-off degrees, selected on the basis of homogeneity in pore size (17,18), and carrying out CVD treatments on them during different periods of time. Detailed information about the preparation and characterization of the ACF precursor materials is given elsewhere (17,18). Several batches of each of them were prepared to have the necessary amount for further treatments made in this work. CVD

treatments were carried out in a tubular quartz reactor. The samples (~1 g) were heated at 10 K min^{-1} up to 1023 K under a N_2 flow of 50 ml min^{-1} . At that temperature, a gas flow of 163 ml min^{-1} with a 2.3 % C_6H_6 concentration by volume in N_2 is introduced in the reactor during different periods of time to deposit different amounts of carbon. After this, the samples are cooled down to room temperature in an N_2 flow of 50 ml min^{-1} . Samples prepared in this way will be referred to as BO- t , where BO will indicate the percent burn-off of the precursor material (either 21 or 42 %) and t will specify the period of time (in minutes) of the CVD treatment. Whereas the evolution of adsorption capacity was investigated by the parameters deduced from physical adsorption isotherms of N_2 (77 K) and CO_2 (273 K), the progress of selectivity was followed by adsorption kinetic experiments.

Adsorption isotherms of N_2 (77 K) and CO_2 (273 K) were assessed in a Micromeritics ASAP 2010 and a Quantachrome NOVA 1200 volumetric adsorption analyser, respectively. Samples were outgassed overnight under vacuum at 523 K prior to every adsorption experiment. Separation ability properties of the samples for the gas mixtures O_2/N_2 and CO_2/CH_4 were tested by the adsorption kinetics of these gases at $298 \pm 0.1 \text{ K}$. They were determined gravimetrically in a CI vacuum microbalance. Prior to every adsorption experiment, the samples (~ 0.05 g) were degassed overnight at 523 K at a vacuum better than 1×10^{-6} bars. After cooling under vacuum, the gas was admitted in the system to a pressure of $1 \pm 0.01 \text{ bar}$. The experimental results have been corrected for buoyancy effects (19).

Table 1 shows porous texture parameters deduced from physical adsorption data: BET surface areas calculated through the standard BET method, S_{BET} , and total micropore volumes obtained through application of the Dubinin-Radushkevich theory to N_2 adsorption data, $V_{\mu\text{p}}(\text{DR}, \text{N}_2)$ and the analogous $V_{\mu\text{p}}(\text{DR}, \text{CO}_2)$, from CO_2 adsorption data. CO_2

at 273 K and at subatmospheric pressures is known to cover only a limited microporosity range, from around 0.3 nm to about 1.4 nm (20), whereas N₂ adsorption at 77 K covers the whole micropore size range from around 0.4 nm (21). Thus, while $V_{\mu p (DR, CO_2)}$ only accounts for narrow microporosity, $V_{\mu p (DR, N_2)}$ refers to the total microporosity excluding the narrowest micropores, where N₂ adsorption is diffusion-limited.

Table 1. Textural properties derived from physical adsorption data of N₂ (77 K) and CO₂ (273 K).

Samples	S_{BET} (m ² g ⁻¹)	$V_{\mu p (DR, N_2)}$ (cm ³ g ⁻¹)	$V_{\mu p (DR, CO_2)}$ (cm ³ g ⁻¹)
21	936	0.38	0.26
21-120	680	0.27	0.25
21-150	650	0.18	0.24
21-180	128	0.05	0.23
21-210	73	0.03	0.23
42	1329	0.56	0.29
42-30	839	0.36	0.29
42-150	221	0.09	0.24
42-240	0	0.00	0.24
42-270	45	0.02	0.24

From the data in Table 1, it can be seen how increasing CVD treatment times bring about a continuous decrease in the parameters derived from N₂ adsorption (S_{BET} and $V_{\mu p (DR, N_2)}$) until they nearly fall to zero, as the porosity range covered by this adsorbate is gradually blocked by the deposited carbon. On the other hand, the micropore volume for the narrowest micropores, given by $V_{\mu p (DR, CO_2)}$, decreases in the first stages of the treatment while, from a certain CVD treatment time, it reaches a constant value (0.23 cm³ g⁻¹, for the series derived from sample 21 and 0.24 cm³ g⁻¹, for the other) indicating that the narrowest microporosity is retained throughout the CVD process. Thus, the samples

experience two different situations when comparing $V_{\mu p (DR, N_2)}$ and $V_{\mu p (DR, CO_2)}$ (20). $V_{\mu p (DR, N_2)}$ is greater than $V_{\mu p (DR, CO_2)}$ for the starting ACFs and those treated for the shortest periods of time (21-120 and 42-30), as usually found for activated carbons with medium-to-high BO. On the contrary, for CVD treatments longer than 150 minutes, $V_{\mu p (DR, N_2)}$ becomes lower than $V_{\mu p (DR, CO_2)}$, the typical situation with chars, carbons activated to low BOs or CMSs. For similar CVD treatment times, the relative decreases for S_{BET} and $V_{\mu p (DR, N_2)}$ are different for the two series of samples (compare 21-150 and 42-150). This could be explained by the possibility of dissimilar mechanisms of deposition occurring for ACFs activated to different BOs, as the kinetic regime of the CVD process depends on the texture of the precursor used (11).

Fig 1 shows pore size distributions (PSDs) obtained through the application of the non local density functional theory to the CO_2 adsorption data (20) in the micropore size range from 0.4 nm to 1 nm (lower confidence limit and upper limit of sensitivity, respectively, of subatmospheric CO_2 adsorption at 273 K to the pore sizes) for the samples in each series CVD treated for the shortest (21-120 and 42-30) and the longest periods of time (21-210 and 42-270). The CVD process must be capable of promoting the deposition of carbon at the pore mouths to create the constrictions responsible for separation selectivity while preserving a high micropore volume responsible for adsorption capacity. This achievement can be ascertained for both series from the data displayed in Fig. 1: On the one hand, the narrowing of the pore mouths reflects itself in the net diminution of the pore volume in the widest pore size range (0.63-1 nm) as the CVD time increases. On the other hand, the retention of a significant adsorption capacity is indicated by the fact that the pore volume in the narrowest pore size range (0.4-0.63 nm) barely changes throughout the CVD treatment. From the information extracted from the PSDs, the use of a fiber activated to a higher BO (42%) as starting material does not seem to introduce any advantage (one

might have expected to increase the adsorption capacity in this way). Comparing samples 21-210 and 42-270, it can be seen that the pore volume for the narrowest pore sizes (intervals 0.4-0.5 and 0.5-0.63 nm) is lower for 42-270 than for 21-210 while the pore volume for the widest pore sizes (0.63-0.8 and 0.8-1 nm) is still larger for 42-270.

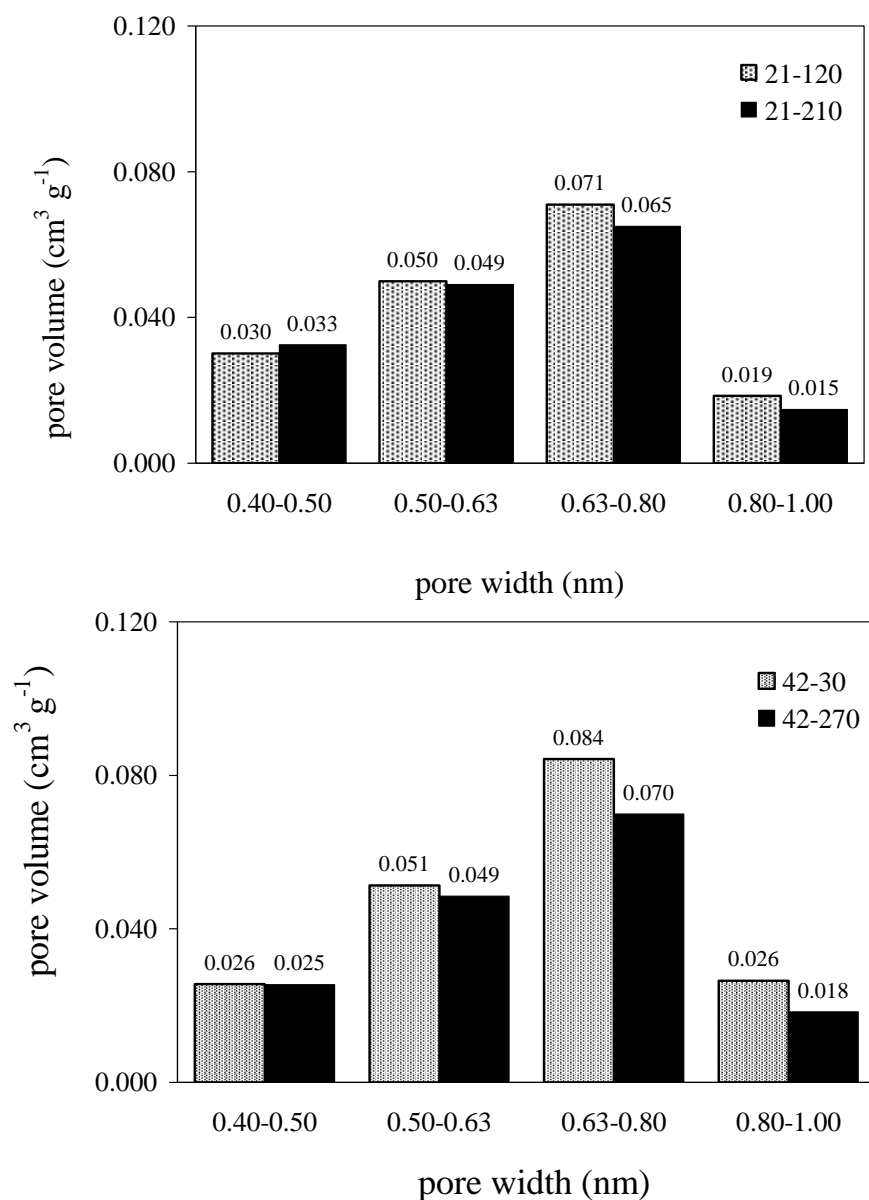


Figure 1. PSDs derived from CO₂ adsorption data for the samples CVD treated for the shortest and the longest period of time in the series coming from sample 21 (a) and sample 42 (b).

Selectivities for the CO_2/CH_4 and O_2/N_2 pairs and the corresponding capacities for CO_2 and O_2 are reflected in Table 2. Commercial Takeda 3A CMS has been included for comparison; this material is designed for separation of air constituents. The selectivities for CO_2/CH_4 and O_2/N_2 separations have been defined here as the ratio of the uptakes for the corresponding gases at 2 min, and the capacities are given by the amounts of CO_2 and O_2 adsorbed in the same period of time, following the same criterion as Kawabuchi et al. (9). The CO_2/CH_4 pair has been included both because of the interest of this separation in itself (23) and as a way of following the process through which selectivity for the O_2/N_2 separation is imparted. The order in molecular sizes being $\text{CO}_2 < \text{O}_2 < \text{N}_2 < \text{CH}_4$, attaining selectivity for the O_2/N_2 separation implies possessing it for CO_2/CH_4 and, therefore, longer CVD treatments are needed for that purpose. In fact, while good selectivity for the CO_2/CH_4 separation is achieved for both series of materials for carbon deposition times greater than 150 min, selectivity for the pair O_2/N_2 is not good enough yet at this stage of the treatment. CO_2 uptakes are comparable (better) to those obtained at similar times for the commercial CMS used in this work or those in other studies (24,25), so these samples (21-150, 42-150) could be in principle used for the CO_2/CH_4 separation. An improvement of the selectivity for the O_2/N_2 couple in both series for treatment times longer than 150 min can be ascertained from data in Table 2. However, comparing both series, even with longer CVD treatment times (1 hour more), the selectivity imparted is worse for samples in the series derived from ACF 42 than that imparted to ACF 21 and, moreover, this is achieved at the expense of a great loss of capacity for O_2 adsorption. Comparing the values obtained for selectivity and capacity for the samples under study with those of the commercial CMS Takeda 3A, the samples 21-180, 21-210 and, to a lesser extent, 42-240 seem adequate for O_2/N_2 separation.

Table 2. CO₂/CH₄ and O₂/N₂ selectivities (s) as well as CO₂ and O₂ adsorption capacities (c) on the samples 2 min after the admission of gas in the system in adsorption kinetics experiments (mmol g⁻¹).

Samples	s(CO ₂ /CH ₄)	c _{CO2}	s(O ₂ /N ₂)	c _{O2}
Takeda 3A ^a	149.2	1.68	5.5	0.32
21	2.5	2.38	~1	0.23
21-120	2.2	2.36	~1	0.36
21-150	∞ ^b	2.34	4.5	0.24
21-180	∞ ^b	2.12	∞ ^b	0.26
21-210	∞ ^b	2.16	∞ ^b	0.37
42	2.2	2.43	1.8	0.26
42-30	2.4	2.83	1.2	0.29
42-150	919.6	2.03	1.4	0.32
42-240	∞ ^b	1.94	6.8	0.40
42-270	∞ ^b	1.77	∞ ^b	0.03

^a Values for selectivity and capacity in agreement with those found with a similar criterion by Gómez-de-Salazar (22).

^b CH₄ or N₂ are not adsorbed at this time.

This is, to the authors' knowledge, the first report on successful modification through CVD of benzene of ACFs to yield fibrous CMSs valid for air separation. CMS prepared from Nomex-derived ACFs are found to be appropriate for CO₂/CH₄ and O₂/N₂ separations from the point of view of both selectivity and capacity. An intermediate BO of 21% is convenient for this purpose, a higher BO not introducing further improvements in the separation ability. Thus, the lower BO precursor would be preferable from a practical point of view as it provides better results and higher yields in the global activation-CVD process.

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