

MOLECULAR SIEVE EFFECTS IN THE ADSORPTION OF ORGANIC VAPORS ON POLYARAMIDE-DERIVED ACTIVATED CARBON FIBERS

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Introduction

Activated carbon fibers (ACFs) constitute a particular type of activated carbon with certain specific advantages in comparison with powdered or granular activated carbons. Thus, they exhibit rapid adsorption/desorption rates, narrow pore size distributions, are easy to handle, can be molded, have no packing or channeling problems and can be used in form of cloths or felts [1]. The use of high-crystallinity fibrous polymers such as Kevlar and Nomex [poly (*m*-phenylene isophthalamide)] as precursors for ACFs was initially proposed by Freeman et al [2-4]. Recently ACFs have been prepared from these precursors by physical activation with CO₂ [5-7], H₂O_(v) [8], and also by chemical activation [9-10]. A particular feature of these precursors is that they yield ACFs with very small and uniform pore size distribution in the range of micropores. In this work, a series of activated carbon fibers was prepared from Nomex, either alone or pre-impregnated with different amounts of phosphoric acid and subsequently activated in CO₂ to various burn-off degrees. Nomex-derived ACFs were studied by N₂ (77 K) and CO₂ (273 K) adsorption. To obtain a more refined microporosity characterization, these materials were used as adsorbents for a series of organic vapors with similar chemical compositions but different molecular structures (benzene, n-hexane, cyclohexane and 2,2-dimethyl butane).

Experimental

The starting material was crystalline Nomex tow, 2.2 decitex per filament (dtf). Carbon adsorbents were prepared from either fresh Nomex (N), or Nomex pre-impregnated with different amounts of H_3PO_4 (NP). Impregnation with H_3PO_4 was carried out in a rotary evaporator using 10 g Nomex and 200 ml of solutions of H_3PO_4 of different concentration to get different impregnation ratios in the product [9]. Pyrolysis/activation of fresh or impregnated Nomex was carried out in a vertical quartz reactor, using 4–5 g of Nomex and an argon (99.999% pure) flow of $50 \text{ cm}^3 \text{ min}^{-1}$. The pyrolysis was programmed at a heating rate of 10 K min^{-1} to a maximum temperature of 1123 K; once this temperature was attained, the sample was cooled down at 10 K min^{-1} to 1073 K and kept at this temperature for 10 min. Then, the gas flow was changed to $50 \text{ cm}^3 \text{ min}^{-1}$ CO_2 (99.98% pure), and it was kept for different time intervals to attain different burn-off (BO) degrees. Then, the samples were cooled down to room temperature under an Ar flow of $50 \text{ cm}^3 \text{ min}^{-1}$. After that, the residues were washed with water in a Soxhlet extractor to eliminate the excess of phosphoric acid [9,10]. Sample reference codes indicate whether Nomex was impregnated (NP) or not (N) with H_3PO_4 , followed by the impregnation ratio and the BO degree in the subsequent physical activation. Thus, NP7-8 was prepared from Nomex impregnated with 7 wt.% H_3PO_4 and CO_2 -activated to 8% BO.

The porous texture of samples was analyzed from physical adsorption isotherms of N_2 at 77 K (measured in an automatic volumetric adsorption apparatus, ASAP 2010, Micromeritics) and CO_2 at 273 K (measured in a semiautomatic volumetric adsorption apparatus, NOVA 1200, Quantachrome). Adsorption isotherms of organic vapors at 298 K were obtained by a static technique, using a high vacuum gravimetric sorption apparatus with quartz springs. Benzene, *n*-hexane, cyclohexane and 2,2-dimethyl butane (2,2-DMB) were used as molecular probes. For the present investigations, it was assumed that the compounds adsorbed were in liquid state.

Results and discussion

Table 1. Porous texture parameters from N₂ (77 K) and CO₂ (273 K) adsorption results.

Sample	S _{BET} (m ² g ⁻¹)	V _t (cm ³ g ⁻¹)	V _{μp} (DR, N ₂) (cm ³ g ⁻¹)	S _{μp} (DR, N ₂) (m ² g ⁻¹)	V _{μp} (DR, CO ₂) (cm ³ g ⁻¹)	S _{μp} (DR, CO ₂) (m ² g ⁻¹)
N-0	1	0.0015	-	-	0.18	499
N-4	556	0.22	0.22	608	0.22	617
NP7-8	584	0.23	0.23	635	0.22	616
NP3-25	898	0.36	0.35	987	0.32	882

Table 1 shows different parameters: BET surface areas (S_{BET}) and total pore volumes (Gurvitsch rule, p/p⁰=0.975) [V_p (N₂)] derived from N₂ adsorption as well as textural parameters deduced by fitting the DR equation to N₂ or CO₂ adsorption data such as micropore volumes [V_{μp} (DR, N₂) and V_{μp} (DR, CO₂), respectively] and micropore surface areas [S_{μp} (DR, N₂) and S_{μp} (DR, CO₂)].

The coincidence between V_p (N₂) and V_{μp} (DR, N₂), except for the non-activated sample, indicates that porosity develops mainly through the creation of new micropores.

Parameters S_{BET}, V_p (N₂), V_{μp} (DR, N₂) and V_{μp} (DR, CO₂) increase with increasing BO degree over the range covered by these samples (independently of whether the Nomex precursor was impregnated or not with H₃PO₄). However, for the non-activated sample (0% BO), V_{μp} (DR, CO₂) is much larger than V_{μp} (DR, N₂), indicating the occurrence of narrow micropores not accessible to N₂ under these conditions. This situation arises from the different relative importance of the dissimilar porosity ranges covered by the two adsorbates [9], which are thought to be 0.3 nm to about 1.4 nm for CO₂ adsorption (273 K) and 0.4 nm to about 50 nm for N₂ (77 K). Thus, the pyrolyzed and non-activated sample would have a porosity restricted to the 0.3-0.4 nm pore width interval. Pore size distributions (PSDs) derived from N₂ adsorption isotherms through non-linear density functional theory (NLDFT) calculations are shown in Fig. 1. All samples present a

bimodal PSD in the micropore region with two maxima at 0.6 and 1.2 nm, separated by a minimum at 1 nm. This minimum is known to be merely an artifact introduced by modelling assumptions [11].

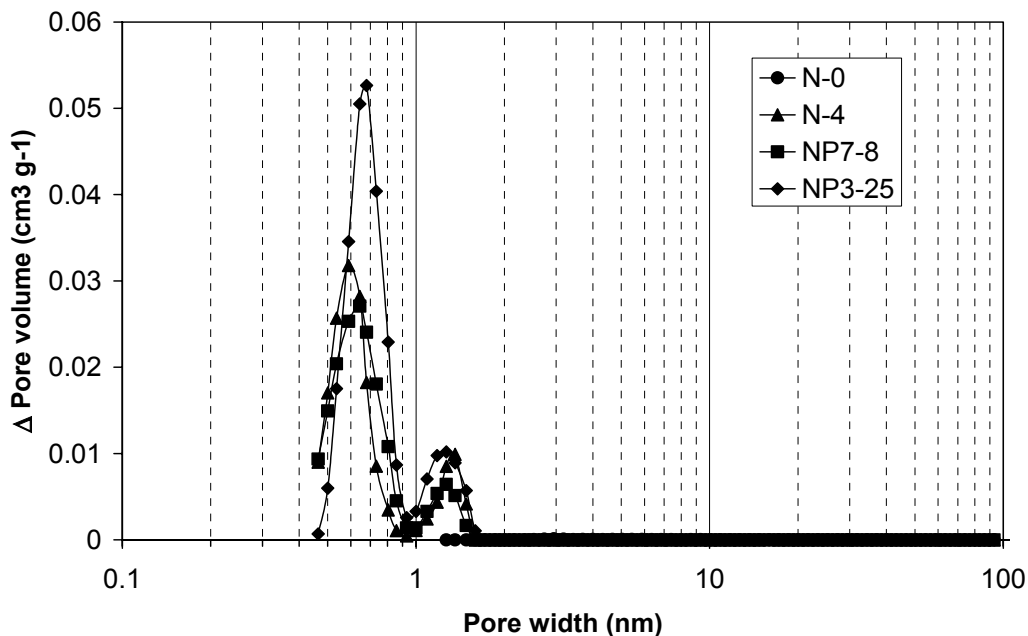


Figure 1. PSDs obtained by the NLDFT method.

The adsorption isotherms of the four studied probe molecules on ACF samples are shown on Fig 2. There are remarkable differences in adsorption capacity depending on the sample and on the adsorptive used. The adsorption capacity increases with increasing BO degree for all the probes. The non-activated Nomex char only adsorbed small amounts of benzene and *n*-hexane and is completely inaccessible to 2,2-DMB molecules. This suggests a very narrow predominant pore size for this sample, in agreement with N₂ adsorption data. The samples activated to 4 and 8 % BO adsorb almost the same amounts of benzene and *n*-hexane. In contrast, in the sample activated to 25% BO, benzene is adsorbed to a lesser extent than *n*-hexane. Also in this sample, cyclohexane and 2,2-DMB molecules are adsorbed to a lesser degree than the other probes.

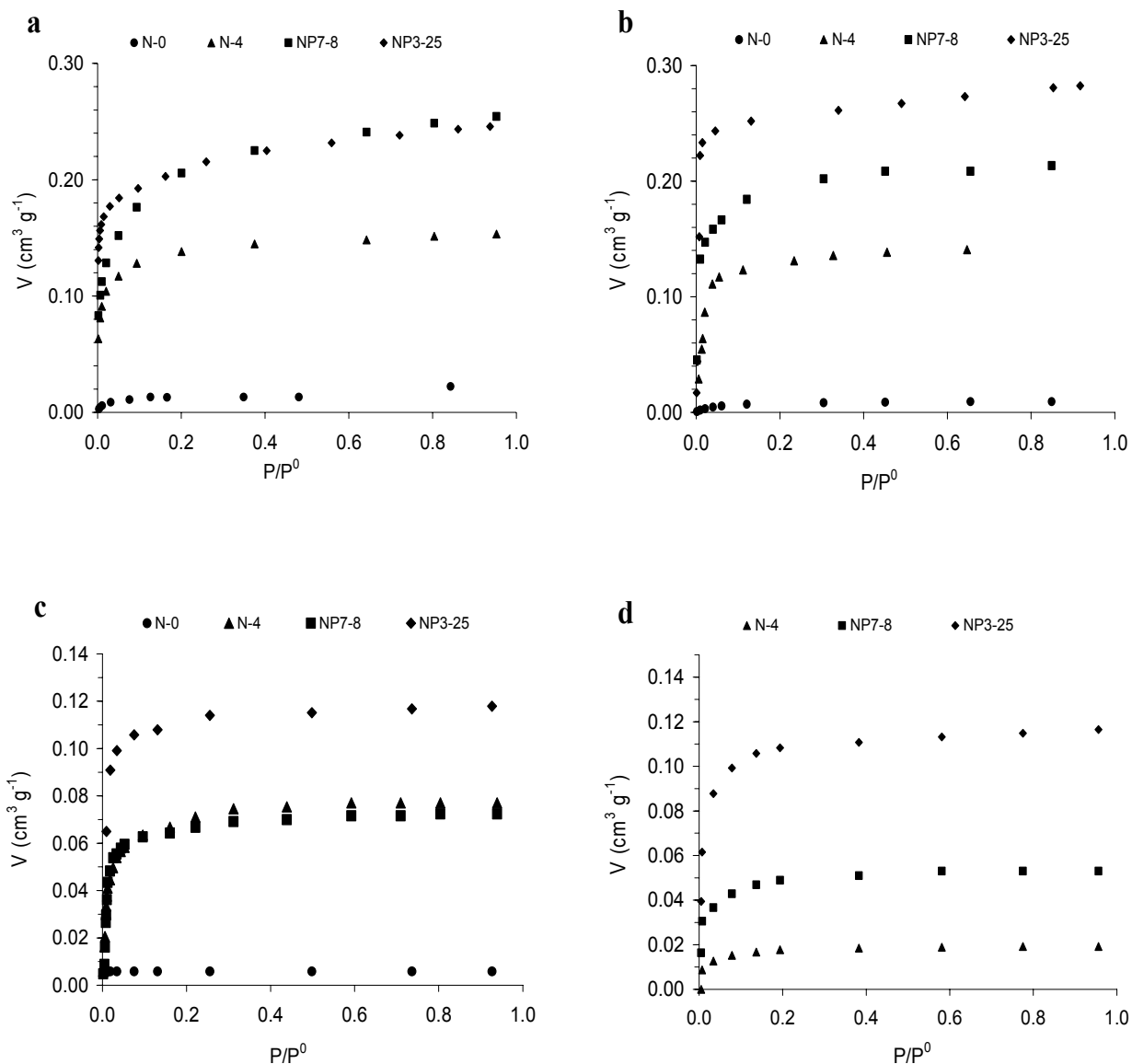


Figure 2. Adsorption isotherms of vapors: benzene (a), *n*-hexane (b), cyclohexane (c) and 2,2-DMB (d).

To evaluate the extent of the accessible porosity in the investigated samples, the micropore volumes according to the DR equation (W_0) were calculated. The results are presented in Table 2. The fact that W_0 is practically coincident with the saturation volume (V_s) for all samples and all probes indicates the microporous character of all samples. The molecular sieve effects were very significant for the benzene/cyclohexane and *n*-hexane/ cyclohexane couples irrespective of the preparation conditions,

indicating that the pore width (obviously intermediate between the molecular sizes of these two adsorbates) is remarkably constant. The mean molecular dimensions of *n*-hexane, benzene and cyclohexane are 0.45, 0.52 and 0.57 nm, respectively [12]. This means that, in agreement with the PSDs obtained by NLDFIT, most of the microporosity of the samples has a pore width near 0.6 nm. Moreover, this microporosity is very narrow in such a way that allows the adsorption in greater extent of the smaller molecules: *n*-hexane and benzene.

Table 2. DR parameters from vapor adsorption isotherms at 303 K.

Sample	Adsorbate	W_0 ($\text{cm}^3 \text{g}^{-1}$)	E_0 (kJ mol^{-1})	L_0 (nm)	V_s ($\text{cm}^3 \text{g}^{-1}$)	p/p^0 range
N-0	benzene	0.016	11.21	2.31	0.022	0.003-0.02
	<i>n</i> -hexane	0.009	7.67	3.39	0.009	0.009-0.06
	cyclohexane	0.006	-	-	-	-
	2,2-DMB	-	-	-	-	-
N-4	benzene	0.145	16.81	1.51	0.153	0.006-0.09
	<i>n</i> -hexane	0.137	14.50	1.77	0.135	0.04-0.7
	cyclohexane	0.077	12.99	1.99	0.077	0.008-0.9
	2,2-DMB	0.019	14.14	1.82	0.019	0.07-0.2
NP7-8	benzene	0.188	16.02	1.59	0.254	0.05-0.8
	<i>n</i> -hexane	0.188	16.20	1.57	0.213	0.009-0.06
	cyclohexane	0.073	14.64	1.75	0.072	0.01-0.9
	2,2-DMB	0.054	15.04	1.70	0.054	0.07-0.2
NP3-25	benzene	0.201	25.40	0.93	0.246	0.003-0.02
	<i>n</i> -hexane	0.261	24.57	0.97	0.282	0.009-0.4
	cyclohexane	0.116	19.88	1.26	0.118	0.02-0.1
	2,2-DMB	0.116	18.50	1.36	0.116	0.07-0.2

Conclusions

N₂ and CO₂ adsorption results indicated that the studied ACFs are essentially microporous and possess a remarkably narrow pore size distribution despite a wide difference in burn-off levels. The different degree of access of the organic vapors to the pores in these adsorbents allowed one to further refine the microporosity characterization. Thus, a Nomex char not submitted to pre-impregnation nor activation only adsorbed small amounts of benzene and n-hexane. For the ACFs, molecular sieve effects were very significant for the benzene/cyclohexane and n-hexane/cyclohexane couples irrespective of the burn-off degree, indicating that the pore width is remarkably constant.

Acknowledgements

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