N$_2$ and CO$_2$ adsorption on activated carbon fibres prepared from Nomex chars

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Abstract

Activated carbon fibres were obtained by pyrolysis followed by CO$_2$ activation of Nomex [poly (*m*-phenylene isophtalamide)] polymeric fibres in their crystalline form. The materials obtained were characterised by N$_2$ adsorption (77 K), CO$_2$ adsorption (273 K) and XRD. They show BET surface areas up to 1200 m^2 g^{-1}, and they are essentially microporous. The pore size distribution is narrower than using Kevlar as precursor. This feature can be related with the degree of crystallinity obtained with the corresponding chars. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: A. Activated carbon; C. Adsorption, X-ray diffraction; D. Porosity

1. Introduction

Aramid fibres are transformed by pyrolysis into isotropic carbon fibres in a narrow interval of temperatures [1], which makes them suitable precursors for the preparation of activated carbon fibres (ACFs). This paper forms part of a general study about the influence of properties (degree of crystallinity, chemical composition, etc.) of aramid fibres on the features of adsorbents obtained from them. The properties of activated carbon fibres obtained from Kevlar [poly (*p*-phenylene terephthalamide)] and Kevlar pulp have been studied in some detail [2–4]. Its isomer aramid fibre, Nomex [poly (*m*-phenylene isophtalamide)] has been used by Freeman et al. [5] as an alternative precursor. Nomex chars were activated with steam to various burn-offs (BO) and with CO$_2$ to only 50% BO. The resulting ACFs were characterised by nitrogen and water adsorption. The same authors [6] activated Nomex chars with CO$_2$ to other BOs but the resulting ACFs were not studied as adsorbents, at least to our knowledge. Stoeckli et al. [4] activated Nomex chars with steam. The resulting ACFs were characterised by physical adsorption of CH$_2$Cl$_2$ and N$_2$O and immersion calorimetry.

This paper focuses on CO$_2$ activation of chars obtained by pyrolysis of crystalline Nomex and their characterisation by physical adsorption of N$_2$ and CO$_2$ in order to gain

additional information on the porosity of these adsorbents. The study of the texture developed is important, since previous work [2–5] has shown that ACFs prepared from aramid fibres exhibit a narrow distribution of pore sizes that makes them promising molecular sieves (or precursors for them). The obtained ACFs are also characterised by X-ray diffraction (XRD) to establish their structural characteristics and their variation with the BO degree. Results are compared with previous work from the literature in which Kevlar and Nomex were used as precursor materials [2–5]. Some data concerning the preparation of ACFs from Nomex by continuous pyrolysis-activation have been reported elsewhere [7].

2. Experimental

Crystalline Nomex (*tow*), with a moisture content of 5% (by weight), was used as feedstock for the preparation of a batch of pyrolysed material at 1123 K. Its elemental analysis, reported as weight percentages on a dry basis, gave: 71.2% C, 3.9% H, 9.7% N and 15.6% O (theoretical: 70.6% C, 4.2% H, 11.8% N and 13.4% O). Elemental analysis was carried out in a LECO CHNS-932 Micro-analysis apparatus (with a LECO VTF-900 accessory for oxygen).

The pyrolysis was carried out in a quartz reactor, with Ar as flowing gas (50 cm^3 min^{-1}) and a heating rate of 4 K min^{-1}. Portions of 1.5 g of the char were heated up to

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Nomenclature

BO	burn-off degree of carbonized Nomex in CO_2 at 1073 K
d_{002}	pseudographitic (002) interlayer spacing (XRD)
E_0	adsorption energy (DRK equation, CO_2, 273 K)
L	average pore width (DRK equation, CO_2, 273 K)
L_a	crystallite size along the a axis (XRD)
L_c	crystallite size along the c axis (XRD)
S_{BET}	BET surface area (N_2, 77 K)
S_{ext}	external surface area (α_S method, N_2, 77 K)
$S_{\mu p(DRK)}$	equivalent micropore surface area (DRK equation, CO_2, 273 K)
V_p	total pore volume (N_2, 77 K, $p/p^0 = 0.95$)
$V_{\mu p(DRK)}$	micropore volume (DRK equation, CO_2, 273 K)
$V_{n\mu p(\alpha S<1)}$	volume of narrow micropores [α_S method ($\alpha_S<1$), N_2, 77 K]
$V_{\mu p(\alpha S>1)}$	total micropore volume [α_S method ($\alpha_S>1$), N_2, 77 K]

1073 K at a rate of 10 K min^{-1} under Ar (50 cm^3 min^{-1}); once that temperature was reached, the flowing gas was changed to CO_2 (40 cm^3 min^{-1}), and this flow was kept for several time intervals in order to achieve different burn-off degrees. Once the gasification period was terminated, the atmosphere was changed again to Ar and left to cool until room temperature was attained.

Gases had minimum purities of 99.999% (N_2), 99.98% (CO_2) and 99.999% (Ar). Adsorption isotherms of N_2 (77 K) and of CO_2 (273 K) were obtained in a semiautomatic adsorption apparatus (NOVA-1200, Quantachrome). Samples were outgassed at 523 K overnight before every adsorption experiment. A carbon black (Spheron 6) was used as standard for the α_S method.

X-ray powder diffractograms were recorded with a Siemens D5000 diffractometer using Cu K$_\alpha$ radiation ($\lambda = 0.15406$ nm) at a step size of 0.01° (2θ).

3. Results

Fig. 1 shows the BO degrees achieved at different times of CO_2 activation. Up to 50% BO data could be fitted to a
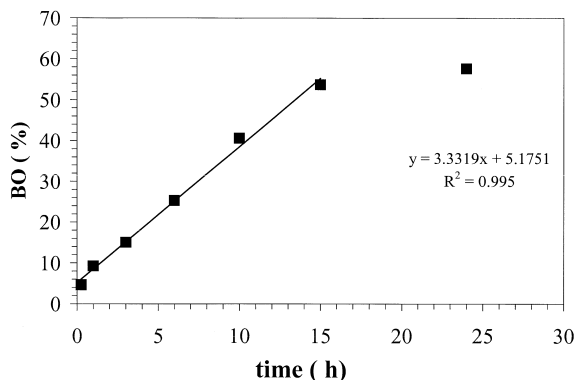

Fig. 1. Burn-off (BO) of carbonized Nomex in CO_2 as a function of time.

straight line, the slope of which provides a measure of the reactivity (6×10^{-4} min^{-1}).

Fig. 2 shows adsorption isotherms of N_2 at 77 K on materials activated to various BO degrees. All isotherms are type I, except that for the pyrolysed and not activated material, which was type II in the BDDT classification. As is well known, appearance of a plateau at relative pressures >0.1 indicates the presence of microporosity in all samples; in what follows, the term 'micropores' will always correspond to the generic IUPAC definition (i.e. pore sizes <2.0 nm).

Table 1 shows textural parameters deduced from N_2 adsorption at 77 K. The volume adsorbed at high relative pressures (0.95) can be considered as the total pore volume (V_p). It can be observed that the total pore volumes and BET surface areas increase with the degree of activation up to BO ~50%. Higher BOs result only in a slightly higher external surface (S_{ext}, Table 1) but not in further development of porosity (V_p, Table 1).

When the α_S-method was applied to the N_2 isotherms two linear parts could be observed in all curves (Fig. 3). In this work we shall adopt a terminology proposed by some authors [8,9] who classify micropores into narrow micropores (filled at $p/p^0 \sim 0.01$) and wider micropores (filled at $p/p^0 \sim 0.2$–0.3) on the basis of these curves. One can notice that the volume of narrow micropores, determined by extrapolation of the linear branch corresponding to $\alpha_S<1$ ($V_{n\mu p(\alpha S<1)}$ in Table 1) increases with the BO up to 54% BO and does not increase further at a higher BO. Values of $V_{n\mu p(\alpha S<1)}$ are only slightly lower than the total micropore volume ($V_{\mu p(\alpha S>1)}$, Table 1) calculated from the linear branch at $\alpha_S>1$.

CO_2 adsorption isotherms at 273 K are shown in Fig. 4. Textural parameters calculated by application of the Dubinin–Radushkevich–Kaganer (DRK) equation (Fig. 5) are given in Table 2. The thus obtained micropore volume, $V_{\mu p(DRK)}$, is close to either $V_{\mu p(\alpha S>1)}$ and $V_{n\mu p(\alpha S<1)}$ obtained by application of the α_S method to N_2 adsorption at 77 K.

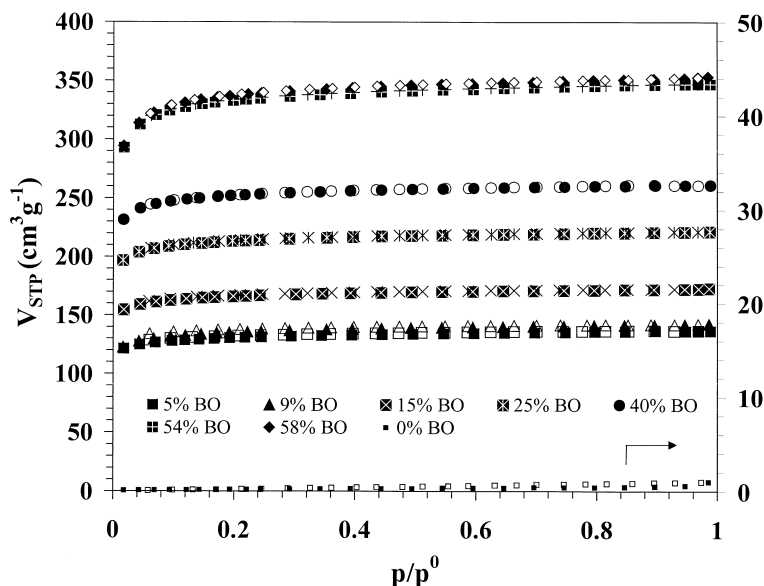Table 3 shows the crystallographic parameters deduced

Fig. 2. Adsorption–desorption isotherms of N_2 at 77 K on ACFs prepared by CO_2 activation at 1073 K of carbonized Nomex. Full symbols, adsorption; open symbols, desorption.

from X-ray diffraction. d_{002} decreases from 0.37 to 0.34 as BO increases from 0 to 58%, whereas L_c increases with the BO. No single trend can be observed for L_a.

4. Discussion

The reactivity of Nomex chars for CO_2 gasification at 1073 K measured in this work (6×10^{-4} min^{-1}) is one half of that found for Kevlar pulp under equivalent conditions (1.2×10^{-3} min^{-1}) [3]. Tomlinson et al. [6] reported three times slower activation rates for Nomex chars than for Kevlar chars under equivalent conditions, and explained the higher reactivity of Kevlar chars as a consequence of the catalytic activity of metallic residues found at the Kevlar surface [6]. A recent surface study has revealed differences at a microscopic level between

Nomex and Kevlar chars [10]. The former's surfaces showed striations parallel to the fibre axis, whereas the latter's exhibited 'fibril and particle-like' areas on a sub-micron scale. These differences could also account for the different reactivity found.

The measured reactivity of 6×10^{-4} min^{-1} is slightly higher than that obtained in the preparation of ACFs from the same precursor by a pyrolysis-activation continuous procedure (5×10^{-4} min^{-1}) [7]. This difference may be due to the fact that weight loss was still observed during the second temperature ramp used to attain the activation temperature in the latter method. In that work [7], activation in CO_2 was carried out at two temperatures, yielding different BO rates (5×10^{-4} min^{-1} at 1073 K and 3×10^{-4} min^{-1} at 1023 K); however, the pore texture depended on the BO degree but not on the activation temperature. Therefore one can conclude that the pore structure de-

Table 1
Textural parameters deduced from N_2 (77 K) adsorption

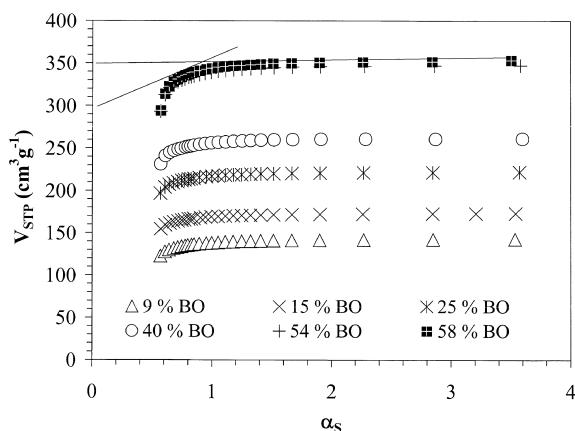| BO (%)	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	α_S-method		
			S_{ext} (m^2 g^{-1})	$V_{\mu p(\alpha S>1)}$ (cm^3 g^{-1})	$V_{n\mu p(\alpha S<1)}$ (cm^3 g^{-1})
0	0.7	0.001	0.7	0.001	0.001
5	434	0.21	0.8	0.21	0.18
9	450	0.21	0.8	0.21	0.18
15	551	0.26	1.9	0.26	0.23
25	805	0.34	1.9	0.34	0.29
40	929	0.40	1.5	0.40	0.35
54	1228	0.53	1.8	0.53	0.45
58	1247	0.54	4.4	0.53	0.45

Fig. 3. α_S-plots drawn from N_2 adsorption isotherms on ACFs prepared by CO_2 activation at 1073 K of carbonized Nomex.

veloped is a characteristic of carbons derived from Nomex and not a function of the rate of activation.

The N_2 adsorption isotherms (Fig. 2) are highly rectangular. The 'knee' opens slightly only at the highest BO degree studied (58%), indicating a slight widening of pores. The slope of the horizontal part does not increase appreciably with increasing BO, suggesting that the external surface (S_{ext}) remains nearly constant. Accordingly, S_{ext} values obtained by applying the α_S-method to N_2 adsorption (Table 1) are very low and increase slightly only for the sample activated to the highest BO degree. The slope of isotherms obtained with Kevlar chars was higher, in agreement with the larger values found for the

external surface (29–41 m^2 g^{-1}) by application of the α_S-method [7].

The total pore volume (V_p) and the total micropore volume ($V_{\mu p(\alpha S > 1)}$) determined by N_2 adsorption (Table 1) increase in parallel with the degree of activation and are totally coincident with each other, indicating that only micropores are formed during CO_2 activation of Nomex chars. The pore size interval is narrower than using Kevlar pulp as feedstock under identical conditions [3].

For the pyrolysed and not activated material (BO=0%) the micropore volume obtained by applying the DRK equation to CO_2 adsorption ($V_{\mu p(DRK)} = 0.19$ cm^3 g^{-1}) is considerably higher than the total micropore volume obtained by N_2 adsorption ($V_{\mu p(\alpha S > 1)} = 0.001$ cm^3 g^{-1}). As usual with many chars, this difference is attributable to restricted diffusion of N_2 at 77 K in pores of molecular dimensions. Upon activation, micropore volumes determined with N_2 and CO_2 ($V_{\mu p(\alpha S > 1)}$ and $V_{\mu p(DRK)}$, respectively, Tables 1 and 2) remain similar over the 5 to 25% BO range. On further activation the value obtained from N_2 adsorption becomes larger (compare Tables 1 and 2). The pore width obtained by application of the DRK equation to CO_2 adsorption (L, Table 2) increases slightly with the BO, being ~1 nm. This is in agreement with a slight decrease in adsorption energy (E_0) as the BO increases (Table 2).

In summary, Nomex chars have been found to be less reactive than Kevlar chars, in terms of rate of pore formation, but more reactive in terms of pore volume development. Another difference lies in that the N_2 uptake by Nomex-derived ACFs is very similar at 54 and 58% BO, whereas a decrease was observed in this BO range
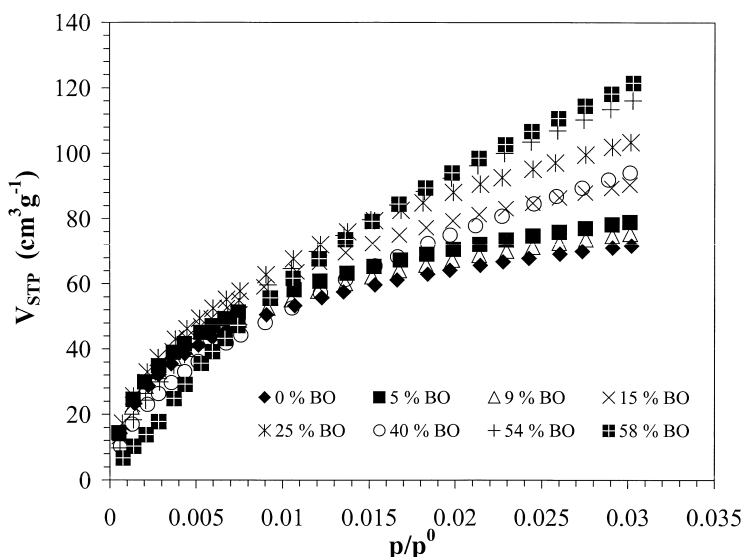

Fig. 4. Adsorption isotherms of CO_2 at 273 K on carbonised Nomex and ACFs prepared from it by CO_2 activation at 1073 K of carbonized Nomex.
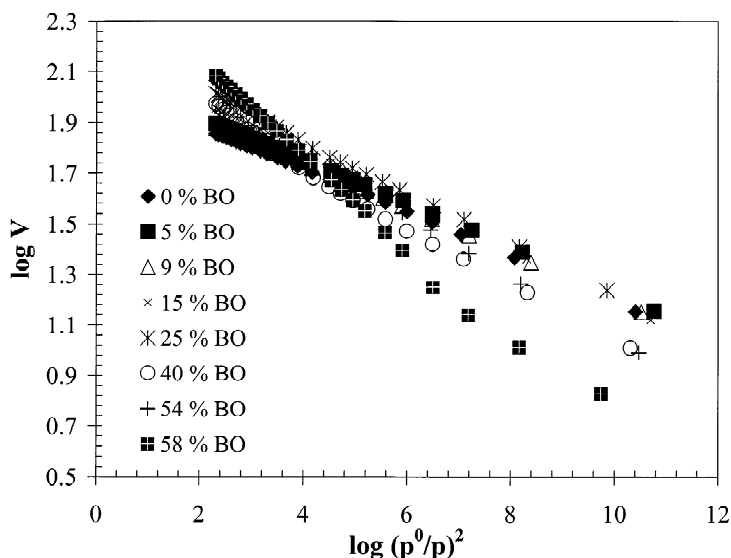
Fig. 5. DRK plots drawn from CO_2 adsorption isotherms on ACFs prepared by CO_2 activation at 1073 K of carbonized Nomex.

Table 2
Textural parameters deduced from CO_2 (273 K) adsorption

BO (%)	$V_{\mu p(DRK)}$ (cm^3 g^{-1})	$S_{\mu p(DRK)}$ (m^2 g^{-1})	L (nm)	E_0 (kJ mol^{-1})
0	0.19	524	0.93	27.8
5	0.21	578	0.94	27.7
9	0.20	555	0.94	27.5
15	0.26	705	1.00	25.9
25	0.29	796	1.02	25.4
40	0.28	767	1.12	23.3
54	0.37	1024	1.17	22.3
58	0.52	1420	1.35	19.2

when Kevlar was used as precursor material [3]. These differences could be associated with less order and lower crystallite size of Nomex chars (Table 3) in comparison with Kevlar chars [11].

There is a clear tendency for d_{002} to decrease, and for L_c to increase with increasing BO (Table 3). This trend was

Table 3
Crystallographic parameters deduced from X-ray diffraction

BO (%)	d_{002} (nm)	L_c (nm)	L_a (nm)
0	0.37	1.2	5.4
9	0.37	1.4	6.8
15	0.37	1.4	6.1
25	0.37	1.4	6.6
40	0.36	2.0	7.5
54	0.36	2.0	6.6
58	0.34	2.0	6.3

observed too with Nomex-derived ACFs obtained by a different activation procedure [7], and implies that the increase in pore volume with increasing BO is accompanied at a microscopic level by a shortening of the distance between graphenes and by an increase in the thickness of the stack of pseudographitic layers. It has been proposed [12,13] that active sites for CO_2 gasification of activated carbons and their precursor chars are to be found inside the micropores, although keeping in mind that slit-shaped narrow micropores formed between two basal planes will have a much lower active site concentration than wider micropores [14]. With this basis, it has been reported [12] that after an initial step in which microporosity is created at the surface by reaction in active sites, pores in ACFs would become deeper as activation progresses by gasification of carbon atoms at the outer or inner edges of basal planes forming the pore walls. Results from the present work indicate that no significant widening of the pores takes place with increasing BO (Tables 1 and 2) and point to creation of new narrow micropores, probably by pore deepening through CO_2 gasification of the cavity floor of the pore. CO_2 is known to have a high configurational diffusion coefficient [12,15], and thus it is plausible that it enters narrow micropores and reacts at their bottom end.

Kumar et al. [16], in comparing measurements of adsorption on activated carbon cloth with XRD results, found a decrease in L_c upon gasification and attributed it to pore widening with increasing activation. High temperature treatment in an inert atmosphere provoked the opposite effect (increase in the degree of structural order), which is not unexpected [16,17]. In the present work the pore width changes very little upon activation and there is

no difference in the maximum temperature to which the samples were heated. Therefore, the only plausible explanation for increase in structural order upon activation lies in selective gasification of the least ordered carbon fractions in the ACF precursor char. Pyrolysis chars are known to be somewhat heterogeneous and their gasification can be expected to take place sequentially beginning with the most disordered moieties [18]. This would lead to the observed increase in the height of stacking unit and decrease in the interlayer spacing between pseudographitic planes as activation progresses.

5. Conclusions

Using crystalline Nomex as feedstock material it is possible to obtain activated carbon fibres whose surface area and pore volume increase with the burn off degree up to ca. 54% BO. These adsorbents exhibit a narrow pore size distribution, which is related to the structural characteristics of the chars.

Acknowledgements

References

[1] Mosquera MEG, Jamond M, Martínez-Alonso A, Tascón JMD. Chem Mater 1994;6:1918–24.

[2] Freeman JJ, Tomlinson JB, Sing KSW, Theocharis CR. Carbon 1995;33(6):795–9.

[3] Martínez-Alonso A, Jamond M, Montes-Morán M, Tascón JMD. Microporous Mater 1997;11:303–11.

[4] Stoeckli F, Centeno TA, Fuertes AB, Muñiz J. Carbon 1996;34(10):1201–6.

[5] Freeman JJ, Tomlinson JB, Sing KSW, Theocharis CR. Carbon 1993;31(6):865–9.

[6] Tomlinson JB, Freeman JJ, Sing KSW, Theocharis CR. Carbon 1995;33(6):789–93.

[7] Blanco López MC, Martínez-Alonso A, Tascón JMD. Microporous Mesoporous Mater, in press.

[8] Rodríguez-Reinoso F, Garrido J, Martín-Martínez JM, Molina-Sabio M, Torregrosa R. Carbon 1989;27(1):23–32.

[9] Carrott PJM, Roberts RA, Sing KSW. Carbon 1987;25(1):59–68.

[10] Bradley RH, Daley R, Cuesta A. In: Eurocarbon '98 Extended Abstracts and Programme, Strasbourg (France), vol. I, 1998, pp. 357–8.

[11] Cuesta A, Martínez-Alonso A, Tascón JMD, Bradley RH. Carbon 1997;35(7):967–76.

[12] Alcañiz-Monge J, Cazorla-Amorós D, Linares-Solano A. Carbon 1994;32(7):1277–83.

[13] De Koranyi A. Carbon 1989;37(1):55–61.

[14] Wigmans T. Carbon 1989;27(1):13–22.

[15] Walker PL, Austin LG, Nandi NP. In: Walker PL, editor, Chemistry and Physics of Carbon, vol. 2, New York: Marcel Dekker, 1966, pp. 257–371.

[16] Kumar K, Saxena RK, Kothari R, Suri DK, Kaushik NK, Bohra JN. Carbon 1997;35(12):1842–4.

[17] Kaneko K, Ishii C, Ruike M, Kubawara H. Carbon 1992;30(7):1065–73.

[18] Rodríguez-Reinoso F, Molina-Sabio M, Torregrosa R. Carbon 1992;30(7):1111–8.