**Effect of some precursor characteristics on the porous texture of activated carbon
fibres prepared from Nomex aramid fibres**

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Abstract

The influence of some characteristics of Nomex [poly (*m*-phenylene isophthalamide)] fibres on the porous texture of activated carbon fibres (ACFs) prepared from them by pyrolysis and CO₂ activation has been comparatively analysed. The features studied were the degree of crystallinity and the presence of dying additives on the precursor. The obtained ACFs were characterised by N₂ (77 K) and CO₂ (273 K) adsorption, and X-ray diffraction. Results show that the texture developed is mainly related to the degree of burn-off (BO) achieved. Crystallinity differences or presence of carbon black dye in the precursor originated little differences in porous texture, the main ones appearing at low and high BOs.

Keywords: Activated carbon fibres; Carbon dioxide adsorption; Microporosity; Nitrogen adsorption; Nomex.

The porous texture of activated carbon fibres (ACFs) is closely related with the properties of their precursors and the treatments undergone by them. Thus, highly crystalline aramid fibres originate microporous ACFs with narrow porosity distributions [1-5], whereas low crystallinity precursors, such as rayon, lead to ACFs with a wider pore

size distribution [6]. As for the effects of textile and other treatments, cotton mercerisation favours the creation of mesoporosity in ACFs derived from it [7], while addition of carbon particles produces the same effect on ACFs from polyacrylonitrile [8] (thus, dyeing textile fibres with carbon black could have a similar effect).

The aim of this work was to compare the porous texture of ACFs prepared from Nomex [poly (*m*-phenylene isophthalamide)] with different degrees of crystallisation and with and without dyeing additives. The starting materials were non-crystalline Nomex (NCN) and carbon black-dyed Nomex (BN); ACFs were prepared by pyrolysis in Ar followed by CO₂ activation at 1073 K under identical conditions as when crystalline Nomex (CN) was used as precursor in previous work [9]. N₂ (77 K) and CO₂ (273 K) adsorption-desorption isotherms were measured in a volumetric adsorption apparatus NOVA 1200 (Quantachrome). A carbon black (Spheron 6) was used as standard for the α_s method. The CO₂ adsorption isotherms were measured at low relative pressures ($p/p^0 < 0.035$). X-ray diffraction (XRD) patterns were obtained in a Siemens D5000 powder diffractometer, using Cu K α radiation ($\lambda = 0.15406$ nm) and a step size of 0.02°.

N₂ adsorption isotherms on NCN-derived materials (not shown) belonged to type I of the BDDT classification, except those for 0 and 5% BO, which were type II. The slope of the isotherms at $p/p^0 > 0.1$ was very low and almost constant for all the BO degrees except at 64% BO, where there was a significant increase in the slope; this was indeed the only sample exhibiting a (small) adsorption hysteresis loop at high partial pressures of N₂, suggesting slight widening of pores at that high BO degree. BN-derived materials yielded N₂ isotherms having many features in common with those from NCN; those corresponding to low BO degrees exhibited hysteresis at low relative pressures.

Table 1. XRD structural parameters.

Series	BO(%)	d ₀₀₂ (nm)	L _c (nm)	L _a (nm)
<i>NCN</i>	0	0.37	1.0	5.1
	5	0.37	1.1	5.5
	13	0.37	1.0	5.3
	36	0.37	1.1	5.9
	64	0.36	1.2	7.2
<i>BN</i>	0	0.37	1.0	4.0
	7	0.37	1.1	4.7
	20	0.37	1.1	6.1
	37	0.36	1.1	6.4

The BET surface area and total pore volume (V_p , calculated from the volume of nitrogen adsorbed at $p/p^0 \sim 0.95$; Figure 1) increased with the BO for the three series of ACFs. At a given BO, no clear difference could be found among the BET surface areas of ACFs prepared from different precursors. The total micropore volume obtained by applying the α_s method to N_2 adsorption isotherms ($V_{\mu p \alpha > 1}$) was almost identical to V_p in the entire BO range, for all the precursors used, with the exception of the sample prepared from NCN at 64% BO, confirming the widening of porosity in this material. The similarity between $V_{\mu p \alpha > 1}$ and $V_{\mu p \alpha < 1}$ (volume of micropores filled at $\alpha_s < 1$, i.e., at $p/p^0 < 0.4$), especially at intermediate and high BO degrees, indicates that most of the porosity created in the studied materials is very narrow.

At low BOs ($\leq 7\%$), the adsorbents prepared from NCN exhibited lower values for the textural parameters calculated from N_2 adsorption (BET surface area and pore volumes: see V_p , $V_{\mu p \alpha < 1}$ and $V_{\mu p \alpha > 1}$ in Fig. 1) than for the corresponding CN and BN-derived ACFs.

However, the micropore volume calculated by application of the Dubinin-Radushkevich-Kaganer (DRK) equation to CO₂ adsorption at 273 K ($V_{\mu p \text{ DRK}}$) is similar for ACFs obtained from the three precursors (Fig. 1). This indicates the occurrence in low BO, NCN-derived ACFs, of very narrow micropores where N₂ adsorption at 77 K is diffusion-restricted whereas CO₂ adsorption at 273 K is not [10]. The pore width (L), also calculated by applying the DRK equation to the CO₂ adsorption data, changed little with the degree of BO or with the variety of Nomex used as precursor, although there was a slight increase in pore width with increasing BO for the three series of studied ACFs (it ranged from 0.93 nm to 1.22 nm).

Fig. 1. Evolution of pore volumes as a function of BO for CN, NCN and BN series of ACFs.

As Table 1 shows, the XRD-derived interlayer spacing (d_{002}) and average height of pseudographitic stacking units (L_c) in materials derived from NCN and BN are essentially constant and independent of the BO. This is in some contrast with a slight decrease in both parameters with increasing BO observed in the case of CN [9,11], which was attributed to preferential gasification of the least ordered fractions, expected to be more reactive [12]. However, the average width of the pseudographitic stacking units (L_a) increases with increasing BO (Table 1) for both NCN and BN series, as it did in previous work with CN [9,11]. This would suggest that selective gasification, if any, progresses more quickly along the c-axis than along the a-axis for the NCN and BN-derived materials.

In comparing the measured crystallite size parameters with those in a number of activated carbons from different origins and preparation methods [14,15], Nomex derived ACFs exhibit an intermediate degree of structural order on the basis of d_{002} and L_c , and slightly higher on the basis of L_a . In comparison with chars and ACFs from Kevlar [poly (*p*-phenylene terephthalamide)] [13], lower d_{002} , L_c and L_a values are systematically obtained with all Nomex varieties; the possibility of this being related to the lower crystallinity degree of Nomex regarding Kevlar remains open to discussion.

In summary, one can conclude that the porous texture and crystal structure of Nomex-derived ACFs are little dependent on the crystallinity degree of Nomex or the presence therein of carbon black as a dying additive, porosity being chiefly associated to the BO. The lack of dependence of texture and structure on precursor characteristics suggests that used Nomex and/or its by-products can substitute

virgin Nomex as a precursor for ACFs, thus providing an interesting recycling route for these residues.

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