Porous texture evolution in Nomex-derived activated carbon fibers

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Abstract

In the present work, the textural evolution of a series of activated carbon fibers with increasing burn-off degree, prepared by the pyrolysis and steam activation of Nomex aramid fibers, is followed by measurements of physical adsorption of N\textsubscript{2} (77 K) and CO\textsubscript{2} (273 K) and immersion calorimetry into different liquids (dichloromethane, benzene, cyclohexane). The immersion calorimetry results are discussed in depth, paying special attention to the choice of the reference material. The activated carbon fibers studied possess an essentially homogeneous microporous texture, which suggests that these materials may be applied in gas separation, either directly or with additional CVD treatment.

Keywords: Activated carbon; Adsorption, Microcalorimetry; Immersion enthalpy, Microporosity.

1. Introduction

Due to their excellent adsorption properties, activated carbons play an outstanding role in many areas of modern science and technology, such as separation, purification and
catalysis (1, 2). In recent years, novel fibrous adsorbents known as activated carbon fibers (ACFs) have been developed by the pyrolysis and activation of organic fibers. ACFs have a number of advantages over the conventional activated granular/powdered carbons: high adsorption rates and capacity, a more homogeneous porous system which gives them greater adsorption selectivity, the possibility of their being molded into different shapes, etc.

In recent years, attempts have been made to obtain ACFs with novel porous texture characteristics. Thus, Freeman et al (3, 4) first reported on the outstanding homogeneity in pore size of ACFs prepared from highly ordered polymers, such as aramid fibers. Indeed, ACFs prepared from aramid show a narrower pore size distribution than those reported in the literature (5) for ACFs derived from more disordered precursors.

The high price of some aramid fibers prevents them from being used as feedstocks for obtaining carbonaceous adsorbents. However, previous works from one of the authors’ laboratories (6, 7) have shown that low value by-products from the manufacture of aramid fibers can be an alternative option for the production of low cost ACFs. In addition, activated carbon yields are relatively high for these materials (8-10), so the process could be economically viable if the final adsorbents do offer advantages over the traditional ones. The textural properties of ACFs obtained through physical activation with carbon dioxide and steam using several varieties of aramid fibers as feedstocks have already been reported in the literature (4-7,11-13). However, little attention has been paid to the analysis of their pore size distribution. Moreover, to the authors’ knowledge, no low relative pressure N₂ adsorption data on this type of materials has yet been reported. Obviously, a proper characterization of the porosity of these adsorbents is essential for their successful synthesis and application.
In this work, pyrolysis and physical activation with steam were carried out, using Nomex as starting material. Nomex (poly (m-phenylene isophthalamide)) is a particularly attractive precursor for obtaining very selective adsorbents, as it has been proved to yield fibrous adsorbents, whose porosity covers a narrow range in relation to other aramid fibers, making them promising molecular sieves (4, 7, 14). As for the use of steam as activating agent, it has been suggested that its utilization instead of carbon dioxide in the activation process of aramid fibers does not lead to a significant widening of the pore sizes (4), unlike the case of other carbonaceous materials (15, 16). In these conditions, steam is preferable to carbon dioxide from a practical point of view, due to its lower price and its higher reactivity towards carbon (lower temperatures can therefore be used for convenient activation rates, with the subsequent saving of energy).

The textural characterization of the samples has been focused in this work on the determination of their pore size distribution. With this aim, low relative pressure N\textsubscript{2} (77 K) as well as CO\textsubscript{2} (273 K) adsorption isotherms were measured in an attempt to elucidate pore size distributions indirectly by means of different calculation methods. Moreover, immersion calorimetry using adsorptive molecules of different size as molecular probes was employed to obtain a direct measurement of the amount of pores of different sizes. This technique has proved to be a useful tool for the characterization of microporous solids (16,17).

It is expected that these studies will help to predict in which separation processes these materials may be useful and whether it will be necessary to modify their textural characteristics with further treatments such as carbon chemical vapor deposition or other techniques to obtain valuable molecular sieve carbons.
2. Materials

The starting material was commercially available Nomex aramid fiber in a variety known as Crystalline Nomex (T450 2.2 dtex.). All treatments were carried out in a tubular quartz reactor. Batches of about 10 g of Nomex as received were pyrolyzed in argon (99.99990% pure by volume, flow rate: 50 cm$^3$ min$^{-1}$) up to 1073 K (heating rate: 10 K min$^{-1}$) and then cooled down to 1053 K and activated with a steam/argon mixture (720 cm$^3$ min$^{-1}$ / 50 cm$^3$ min$^{-1}$) for various periods of time to attain different burn-offs (BO), namely, 0, 10, 21, 42 and 63%.

3. Methods

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 analyzer, respectively. With the help of a ASAP 2010 apparatus, it is possible to measure N$_2$ adsorption isotherms starting from relative pressures around $10^{-6}$-$10^{-7}$, in order to obtain so-called “high resolution” N$_2$ adsorption isotherms. Samples were outgassed overnight under vacuum at 523 K prior to every adsorption experiment.

The heats of immersion of the samples into liquids with different minimal molecular dimensions such as dichloromethane (0.33 nm), benzene (0.37 nm) and cyclohexane (0.48 nm) were determined at 298 K with a Tian–Calvet differential microcalorimeter (Setaram, Model C80D). The samples (~0.1 g) were outgassed overnight under vacuum at 523 K. The experimental procedure to determine enthalpies of immersion has been described elsewhere (18).

The densities employed for adsorbed N$_2$ (77 K) and CO$_2$ (273 K) were 0.813 (bulk liquid) and 1.182 g cm$^{-3}$ (solid phase) (19), respectively. BET surface areas, $S_{BET}$, were
obtained by the standard BET method in the relative pressure range from $10^{-6}$ to 0.1 (20). Total porosity ($V_{p,(N_2)}$) was calculated from the gas volume adsorbed at $P/P^0=0.95$.

Further insight into the textural evolution of the samples was gained through high resolution $\alpha_S$-analysis, based on the original $\alpha_S$ method proposed by Gregg and Sing (21a) and reviewed for the high resolution adsorption isotherms by Kaneko (22). In this procedure, the adsorption isotherm for a given porous solid is expressed as a function of the amount adsorbed on a macroporous or non porous reference adsorbent. To do this, a parameter ($\alpha_S$) is defined as the ratio of the amount adsorbed on the reference solid at each equilibrium relative pressure to the amount adsorbed at the relative pressure (0.4 for nitrogen) at which all the micropores are supposed to be already filled and the adsorbed amount is plotted as a function of $\alpha_S$. External surface areas ($S_{\text{ext}}(\alpha_S, N_2)$) are calculated from the slope of the linear segment of the $\alpha_S$ plot corresponding to $\alpha_S$ higher than 1. Total micropore volumes ($V_{\mu p}(\alpha_S, N_2)$) as well as ultramicropore volumes ($V_{\mu \mu p}(\alpha_S, N_2)$) are obtained from the y-axis intercepts of the linear portions of the $\alpha_S$ plots corresponding respectively to the highest $\alpha_S$ values and to $\alpha_S$ of around 0.5. Spheron 6 carbon black ($S_{BET}=108 \text{ m}^2\text{g}^{-1}$), which has been shown to be equivalent to other reference materials offered in the literature as suitable for active carbons (23), was used as non porous standard.

Pore size distributions (PSDs) from the nitrogen adsorption data were obtained through the application of non local density functional theory (NLDFT) procedure (24) using a software provided by the Micromeritics Instrument Corporation. The NLDFT method for deriving PSDs is based on the assumption that experimental isotherms can be expressed as the sum of contributions from ideal isotherms calculated for adsorbate molecules on pores of fixed shape and size, the weighing function being equivalent to the PSD. Fluid-fluid interactions are accounted for using one-center Lennard-Jones potentials. The pores are modeled as an array of semi-infinite, rigid slits and their walls as
energetically uniform graphite. An analogous NLDFT method implemented for carbon
dioxide (25), provided by Quantachrome, was used to obtain PSDs from the CO₂
adsorption data.

The accessible surface areas of the samples based on immersion calorimetry data were
determined with the method proposed by Denoyel et al. (26), using as a reference the areal
enthalpies of immersion of Vulcan 3 (S_{BET}= 82 m^2 g^{-1}).

4. Results and Discussion

4.1. Nitrogen adsorption isotherms, comparative plots and derived PSDs. Fig. 1
shows the high resolution N₂ adsorption isotherms obtained for the samples under study.
The adsorption isotherm of the pyrolyzed sample was not included in this figure because
this material has a very narrow porosity, which is not accessible to N₂ at 77 K. As for the
remaining samples, all their isotherms belong to type I according to the IUPAC
classification (27), although distinctions can be established between them based on the
widening of their knee as the burn-off increases. Whereas the isotherms of the low burn-off
samples exhibit quite a sharp knee, reflecting the predominance of narrow microporosity
(ultramicropores, i. e., pores with widths smaller than 0.7-0.8 nm), those corresponding to
high burn-off degrees have a more rounded knee pointing to a widening of microporosity
that even extends to mesoporosity in the sample activated to the highest burn-off, as shown
by the appearance of a very narrow hysteresis loop in its isotherm.

To take full advantage of the information provided by the high resolution isotherm,
the isotherms are represented on a semilogarithmic scale, as shown in Fig. 1b. Sing (21b)
and Kaneko (22) pointed out that the pore filling process could be divided into three or
Figure 1. Adsorption-desorption isotherms of N$_2$ at 77 K. Filled symbols, adsorption; empty symbols, desorption. (a) Conventional plots; (b) Semilogarithmic scale.
four stages: the filling of narrow micropores (ultramicropores), monolayer formation on
the wider micropores (supermicropores) and small mesopores, the filling of mesopores by
capillary condensation, and the filling of macropores by capillary condensation, which can
be ascribed, respectively, to relative pressure ranges of ca. $10^{-6} \text{-} 10^{-4}$, $10^{-4} \text{-} 10^{-2}$, $10^{-2} \text{-} 10^{-1}$, and 0.9-1. Unlike conventional activated carbons (28) but like other ACFs (20, 29), all the
samples in this work, even those activated to the highest BO, show a significant nitrogen
uptake below $p/p^0 = 10^{-5}$, indicating the presence of a large amount of ultramicropores.
However, the relative importance of the narrowest microporosity in the total porosity of the
samples diminishes as BO increases. While ACFs activated to low BOs (10%, 21%) adsorb a large percentage of their total nitrogen uptake below $p/p^0 = 10^{-4}$, the uptake at the
relative pressure range related to supermicropores ($10^{-4} \text{-} 10^{-2}$) acquires significance for the
ACFs activated to higher BOs (42%, 63 %), and even the appearance of a small amount of
mesoporosity in the sample activated to 63% BO is reflected in the corresponding pressure
range in its isotherm.

BET surface areas, $S_{BET}$, and total pore volumes, $V_p (N_2)$, for the activated samples
are given in Table 1. It can be seen that they increase systematically with the degree of
burn-off over the range covered by this series. The very low relative pressures from which
BET plots show linearity ($\sim 10^{-6} \text{-} 10^{-5}$) for all the samples are an indication of the highly
microporous nature of their texture (30).

<table>
<thead>
<tr>
<th>% BO</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_p (N_2)$ (cm$^3$ g$^{-1}$)</th>
<th>$S_{ext} (\alpha_s, N_2)$ (m$^2$ g$^{-1}$)</th>
<th>$V_{spp} (\alpha_s, N_2)$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{upp} (\alpha_s, N_2)$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{upp} (\alpha_s, N_2) / V_{spp} (\alpha_s, N_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>560</td>
<td>0.23</td>
<td>0.2</td>
<td>0.23</td>
<td>0.13</td>
<td>0.56</td>
</tr>
<tr>
<td>21</td>
<td>936</td>
<td>0.38</td>
<td>1.5</td>
<td>0.38</td>
<td>0.20</td>
<td>0.53</td>
</tr>
<tr>
<td>42</td>
<td>1329</td>
<td>0.56</td>
<td>2.7</td>
<td>0.56</td>
<td>0.18</td>
<td>0.32</td>
</tr>
<tr>
<td>63</td>
<td>1580</td>
<td>0.69</td>
<td>12.3</td>
<td>0.68</td>
<td>0.11</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Regarding the $\alpha_S$ plot analysis, Kaneko et al. (22) found that microporous carbons could show two upward swings from linearity below the downward bending due to saturated filling at higher $\alpha_S$, which they designated as filling swing (FS) and cooperative swing (CS), corresponding to $\alpha_S$ smaller and greater than 0.5, respectively. Both upward swings come from enhanced adsorbent-adsorbate interactions as a function of the pore size, and can be ascribed to different types of filling: primary micropore filling, which takes place in micropores whose width is less than two adsorbate molecular diameters, i.e., around 0.7-0.8 nm (ultramicropores (31)), for FS and cooperative adsorption in larger micropores (supermicropores) for CS.

The $\alpha_S$ plots derived from the $\text{N}_2$ adsorption data can be seen in Fig. 2. The two samples activated to the lowest BOs show mainly FS in the $0 < \alpha_S < 0.5$ range, with little evidence for CS, further confirming the view that ultramicropores are the dominant pores in these samples. On the other hand, the presence of both FS ($0 < \alpha_S < 0.5$) and CS ($0.5 < \alpha_S < 1$), in the two samples activated to the highest BOs is evidence of the existence of both ultramicropores and supermicropores. As burn-off increases, the FS, although still present, becomes less pronounced.

The textural parameters deduced from the application of the $\alpha_S$ method ($S_{\text{ext}}(\alpha_S, \text{N}_2)$, $V_{\mu p}(\alpha_S, \text{N}_2)$, $V_{\mu mp}(\alpha_S, \text{N}_2)$) are given in Table 1. A comparison of $V_p(\text{N}_2)$ and $V_{\mu p}(\alpha_S, \text{N}_2)$ shows that both parameters follow the same rising trend with increasing burn off. These values coincide in all samples as might be expected given that most of their porosity is restricted to microporosity. The very small discrepancy for the sample with the highest BO (63%) indicates that mesoporosity is barely developed, as mentioned above. A quantitative estimate of the relative importance of the ultramicroporosity in the microporosity of the ACFs studied can be made from the ratio between $V_{\mu mp}(\alpha_S, \text{N}_2)$ and $V_{\mu p}(\alpha_S, \text{N}_2)$ given in Table 1. The progressive weakening of the FS with increasing burn-off is reflected in the
Figure 2. $\alpha_s$ plots drawn from $N_2$ adsorption isotherms for the series of activated carbon fibers.

A decreasing value of this ratio. The low value found for the sample activated to the highest BO again indicates that porosity has significantly widened in this sample.

As regards the PSDs, NLDFT distributions for all samples (Fig. 3) present maxima at around 0.6 nm with pore sizes under 1.6, 2.0, 3.2 and 7.0 nm, respectively, for the samples arranged in an increasing burn-off sequence. The PSDs reflect a widening in the micropore size distribution. This takes place in a restricted pore size range below 2.0 nm, i.e. in the microporosity range, for all the samples except the one activated at 63% BO.

However, it is known that the NLDFT method is not totally reliable as a tool for yielding PSDs as it has model-induced artifacts (31). The rigid parallel wall model used to build the theoretical adsorption isotherms exhibits strong packing effects which are not
present in real activated carbons. As a consequence, the resulting pore size distributions consistently show two minima at around 0.6 and 1 nm, corresponding to the transitions from pore widths accommodating one adsorbed layer to two, and two layers to three, respectively. This feature is confirmed in Fig. 3.

**Figure 3.** PSDs obtained from the N$_2$ adsorption isotherms through application of the NLDFT method.

**4.2. Carbon dioxide isotherms, Dubinin-Radushkevich plots and derived PSDs.** Carbon dioxide at 273 K and at subatmospheric pressures is known to cover only the microporosity range from around 0.3 nm to about 1.4 nm (25). On the other hand, a lower cut-off pore width of around 0.4 nm is generally assumed for nitrogen adsorption at 77 K owing to restricted diffusion. Thus, it has been suggested that the adsorption of these two
molecules should be used in a complementary way in order to characterize micro and mesoporosity more fully (33).

Fig. 4 shows the CO$_2$ adsorption isotherms for pyrolyzed and steam activated Nomex. Although the characterization by nitrogen adsorption at 77 K of the pyrolyzed sample was not possible, CO$_2$ adsorption at a higher temperature (273 K) serves as a useful tool for samples with narrow microporosity such as this one. At the early stages of activation, the CO$_2$ uptake increases over the entire relative pressure range covered, as can be confirmed by comparing the isotherms for the pyrolyzed and 10% BO activated samples. Although the total uptake at $P/P_0=0.03$ increases upon activation, a decrease in the uptake at low pressures is observed for further activated samples, reflecting the disappearance of some of the narrowest microporosity. Finally, the sample activated at the highest burn off even evidences a decrease in CO$_2$ total uptake, probably because high degrees of activation lead to the elimination of some of the pore walls in narrow micropores, thereby decreasing the amount of micropores enclosed in the range covered in these conditions.

The Dubinin-Radushkevich (DR) plots and textural parameters such as micropore volume ($V_{\mu p(DR, CO_2)}$) and adsorption energy $E_0$, calculated through the application of the DR equation to CO$_2$ adsorption data, are shown in Fig. 5 and Table 2 respectively. Straight lines typical of microporous solids were obtained. The plot is linear over the whole range of relative pressures measured for the pyrolysed sample as well as for that activated to 10% BO. The fact that the former required longer times to reach equilibrium reflects a certain molecular restriction to the access of CO$_2$ to the pores in these conditions. The range of linearity decreases for the rest of the samples. In fact, the sample activated to 63% BO shows two linear branches from which two different values of $V_{\mu p(DR, CO_2)}$ could have been calculated. This is further confirmation of the widening of micropore size distribution as the burn-off increases, resulting in different filling mechanisms for
micropores of different size. Concerning the trends for the different parameters derived from the DR method, $V_{\mu p}^{(DR, CO_2)}$ increases as $E_0$ decreases, indicating that the microporosity range covered, (ultramicroporosity), develops through the widening of the pores. However, the nitrogen adsorption data suggested that the development of microporosity as a whole in Nomex-derived ACFs mainly involves the creation of new micropores and/or the deepening of pre-existing ones, widening being a relatively minor contribution in comparison with ACFs derived from other precursors. It must been taken into account that nitrogen adsorption covers a wider range of porosity than carbon dioxide, thus offering a more general picture of textural evolution.

**Figure 4.** Adsorption isotherms of CO$_2$ at 273 K on carbonized Nomex and ACFs prepared from it by steam activation.
Figure 5. DR plots obtained from the CO$_2$ adsorption data.

Table 2 Textural parameters calculated through the application of the DR equation to CO$_2$ adsorption data at 273 K.

<table>
<thead>
<tr>
<th>% BO</th>
<th>$V_{\text{app}}$ (DR, CO$_2$) (cm$^3$ g$^{-1}$)</th>
<th>$E_0$ (KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.16</td>
<td>27.5</td>
</tr>
<tr>
<td>10</td>
<td>0.22</td>
<td>25.7</td>
</tr>
<tr>
<td>21</td>
<td>0.26</td>
<td>20.7</td>
</tr>
<tr>
<td>42</td>
<td>0.29</td>
<td>23.1</td>
</tr>
<tr>
<td>63</td>
<td>0.38</td>
<td>19.5</td>
</tr>
</tbody>
</table>
The comparison of \( V_{\mu p} (\alpha_s, N_2) \) determined by \( N_2 \) adsorption (through the \( \alpha_S \) method) with \( V_{\mu p} (DR, CO_2) \) determined by \( CO_2 \) adsorption (through the DR method) can provide useful information about the texture of the samples (32). The already discussed results from applying the \( \alpha_S \) method to \( N_2 \) adsorption were found to be equivalent to those derived from the application of the DR method to the same data (not shown to avoid duplication), which is why they are used here. When comparing \( V_{\mu p} (\alpha_s, N_2) \) with \( V_{\mu p} (DR, CO_2) \), three different situations typically arise as pores widen. The first situation, in which \( V_{\mu p} (\alpha_s, N_2) < V_{\mu p} (DR, CO_2) \), appears for the pyrolyzed sample. This situation usually occurs in molecular sieve carbons, carbonized materials or activated carbons with a very low burn-off (30). If, as already mentioned, carbon dioxide adsorption in these conditions starts from the smallest pore widths, around 0.3 nm, while nitrogen adsorption is restricted to pores wider than 0.4 nm, the volume of micropores with widths between 0.3 and 0.4 nm can be roughly estimated by subtracting \( V_{\mu p} (\alpha_s, N_2) \) from \( V_{\mu p} (DR, CO_2) \). In the case of the pyrolyzed sample studied in this work, no nitrogen at all was adsorbed, i.e., \( V_{\mu p} (\alpha_s, N_2) = 0 \), reflecting the fact that all the pores belong to the pore width interval, which is optimum for the separation of gas mixtures such as \( CO_2(0.33 \text{ nm})/CH_4(0.38 \text{ nm}) \) and \( O_2(0.346 \text{ nm})/N_2(0.364 \text{ nm}) \) (14). Consequently, the pyrolyzed sample could in principle serve as a good molecular sieve, at least from the point of view of selectivity. The usual argument against the use of simply pyrolyzed carbonaceous materials as molecular sieves is their low adsorption capacity. However, this is not the case here, as the micropore volume of the sample \( (V_{\mu p} (DR, CO_2) = 0.16 \text{ cm}^3 \text{ g}^{-1}) \) is well inside the range of those exhibited by commercial and non-commercial carbon molecular sieves in the literature (34, 35). Moreover, the densities used in the literature for \( CO_2 \) adsorbed at 273 K are typically lower than the one used in this work and consequently the values calculated for micropore volumes are “inflated” in relation with ours.
The second situation, $V_{μp}(α_s, N_2) \sim V_{μp}(DR, CO_2)$, arises for the sample activated to 10% BO and is the usual situation for some molecular sieves and activated carbons with a low or intermediate burn-off. As micropore volumes derived from nitrogen and carbon dioxide adsorption isotherms are practically identical for the 10% BO sample, all the porosity is restricted to microporosity, as in the first situation, but in this case the pores must have widened. If there are any pores left in the 0.3-0.4 nm range, only filled by CO$_2$ adsorption, in order that both volumes become equal, some development of microporosity must have occurred beyond the pore widths of 1.4 nm, covered exclusively by N$_2$.

The third situation, when $V_{μp}(α_s, N_2) > V_{μp}(DR, CO_2)$, is found for the remaining samples and implies the continued development of porosity beyond the upper limit of 1.4 nm covered by CO$_2$ adsorption. This is typical of activated carbons with a relatively high burn-off.

As for the possible use of the activated samples studied in this work, their rather small and uniform pore sizes make them promising CMS precursors through carbon chemical vapor deposition (36). Nevertheless, the sample activated to the highest burn-off shows mainly wide micropores, as shown above by the low $V_{μp}(α_s, N_2)$ to $V_{μp}(α_s, N_2)$ ratio, which even extends to mesopores (from the small hysteresis loop found in its isotherm). This makes its possible application even as a precursor of carbon molecular sieves doubtful. Moreover, such a high burn-off is hardly admissible from a practical point of view due to excessive carbon consumption.

Incremental pore volume plots calculated from CO$_2$ adsorption (NLDFT method) for all the samples are shown in Fig. 6. As the calculation procedure is analogous to that applied to nitrogen adsorption data, an artificial minimum at around 0.6-0.7 nm, related to the ideal transition from one to two layers of adsorbate, is also found systematically. The next transition from two to three layers is not appreciated in the relative pressure range.
extending to atmospheric pressure (25). The PSDs are represented up to the limit of sensitivity of CO\textsubscript{2} adsorption, in these conditions fixed at 1 nm, as theoretical isotherms for solids with pores greater than 1 nm are linearly dependent and, consequently, these pores cannot be distinguished.

![PSDs obtained from the CO\textsubscript{2} adsorption isotherms through application of the NLDFT method.](image)

**Figure 6.** PSDs obtained from the CO\textsubscript{2} adsorption isotherms through application of the NLDFT method.

As can be seen in Fig. 6, the pyrolyzed sample shows maxima at 0.35 and 0.50 nm which are also present in the activated samples. But as burn-off increases, the former disappears while the latter is gradually hidden, already at 10% BO, by the appearance of another maximum at 0.6 nm. For the most activated samples, the maximum for the PSDs occurs at 0.82 nm. Consequently, in the porosity range covered by CO\textsubscript{2} adsorption, widening of the pores can also be appreciated, as samples would have maxima for their
PSDs at around 0.35 and 0.50 nm (0% BO), 0.50-0.60 nm (10% BO), 0.60 nm (21% and 42% BO) and 0.82 nm (63% BO).

4.3. Immersion calorimetry measurements. As calculation methods based on data from a single isotherm do not seem to be totally reliable, it was thought advisable to employ adsorptive molecules of different sizes as molecular probes to assess the different stages of micropore filling in a direct way (37) through immersion calorimetry experiments.

A comparison of the different proportionality factors between the heats of immersion and surface areas obtained for a number of reference materials is given in Table 3. As can be seen, the values of specific surface areas derived from immersion data may vary significantly depending on the choice of the reference material. For example, the surface area of a material derived from its heat of immersion into C₆H₆ using Spheron 6 would be almost twice the value obtained using Reference1. As Spheron 6 is an extreme case, with the highest ratio of heat of immersion to surface area, Vulcan 3 was finally chosen as the reference to calculate specific surface areas derived from the immersion calorimetry data measured in this work.

Table 4 shows the experimental enthalpies of immersion in the various organic liquids studied of all the samples except for the one activated to the highest burn-off together with the calculated accessible surface areas. This sample (63 % BO) was useful for setting an upper limit for developing of exclusively microporosity through activation, but it has been excluded from further analysis because it is not of interest for possible application as a molecular sieve carbon.

The samples activated to low BOs (0 and 10 % BO) show surface areas accessible to dichloromethane higher than those accessible to benzene. However, the rest of the
samples show the opposite trend. This change in the activation series could be explained in terms of an evolution of the surface chemistry of the pyrolyzed sample, as activation takes place by way of the loss of surface functional groups, the appetite for polar molecules such as dichloromethane decreasing. Nevertheless, generally speaking, chemical factors are not thought to be important in an adsorption process like this (11, 40, 41).

Table 3. Ratios between the enthalpy of immersion at 298 K into the three liquids used in this work and the BET surface area for different reference materials.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Ratio (mJ m⁻²)</th>
<th>Reference1 ⁹⁴ (50 m² g⁻¹)</th>
<th>Vulcan 3G  ⁹⁵ (62 m² g⁻¹)</th>
<th>Vulcan 3  ⁹⁶ (82 m² g⁻¹)</th>
<th>Spheron 6 ② (108 m² g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>63</td>
<td>113</td>
<td>134</td>
<td>170</td>
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<tr>
<td>C₆H₆</td>
<td>76</td>
<td>114</td>
<td>111</td>
<td>148</td>
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</tr>
<tr>
<td>C₆H₁₂</td>
<td>60</td>
<td>104</td>
<td>104</td>
<td>101</td>
<td></td>
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</tbody>
</table>

⁹⁴ Calculated from data in ref. 38.
⁹⁵ Calculated from data in ref. 39.
② This work.

Table 4. Experimental enthalpies of immersion at 298 K into different liquids and surface areas derived from them and from N₂ adsorption at 77 K.

<table>
<thead>
<tr>
<th>% BO</th>
<th>-ΔH_imm (J g⁻¹)</th>
<th>Surface areas (m² g⁻¹)</th>
<th>S_BET (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₂Cl₂ C₆H₆ C₆H₁₂</td>
<td>CH₂Cl₂ C₆H₆ C₆H₁₂</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>45.3 11.0 10.0</td>
<td>338 100 96</td>
<td>-⁹⁴</td>
</tr>
<tr>
<td>10</td>
<td>92.1 65.9 47.6</td>
<td>687 600 460</td>
<td>560</td>
</tr>
<tr>
<td>21</td>
<td>123.1 122.4 81.6</td>
<td>918 1116 787</td>
<td>936</td>
</tr>
<tr>
<td>42</td>
<td>138.1 146.7 107.6</td>
<td>1029 1337 1038</td>
<td>1329</td>
</tr>
</tbody>
</table>

⁹⁴ Only geometrical surface
Surface areas accessible to benzene are systematically higher than the corresponding BET surface areas. As the minimal dimensions of nitrogen (0.36 nm) and benzene (0.37 nm) are nearly the same, both molecules should have access to similar microporosity ranges. It has been asserted (26) that differences such as this arise from the underestimation of the actual surface area of microporous carbons whose pores have widths similar to one adsorbate molecule by the calculation of BET surface area. This underestimation occurs because one molecule is only considered to be in contact with only one planar surface. In the immersion method, the interaction of the molecule with both walls of the pore is taken into account giving higher, more realistic values. Accordingly, the biggest differences between the surface areas derived from nitrogen and benzene adsorption would appear in the samples with the narrowest porosities that are accessible to both molecules. This trend can be verified in the series studied as the differences between the two surface areas decrease with increasing burn-off, differences barely being noticeable in the sample activated to 42% BO. It was previously shown in discussing parameters calculated by the $\alpha_S$ method that the contribution of ultramicropores to the microporosity of this sample is smaller than for the samples activated to lower BOs. At 42% BO, the microporosity has widened to the point that almost all the pores can accommodate more than one molecule of nitrogen, so that the hypothesis of the BET surface is acceptable in this case.

For the next probe molecule, cyclohexane, the values for accessible surface areas are lower than the BET surface areas for all the samples except the pyrolyzed one, indicating a molecular sieve effect. The different sizes of nitrogen (0.36 nm) and cyclohexane (0.48 nm) molecules justify the differences as the bigger molecules will have access to a smaller range of microporosity in the samples. However, for the pyrolyzed sample, the surface area accessible to cyclohexane is higher than the BET surface area.
(assuming this to be the geometrical area). The porosity in this sample is probably so narrow that the leading factor is the underestimation of the area calculated from $\text{N}_2$ adsorption which, at 77 K, has restricted diffusion limitations in the pores of molecular dimensions. As a result, the difference in the size of the two molecules is counterbalanced.

5. Summary

It can be deduced from the different analyses performed that the microporosity developed in the samples studied through activation is mainly restricted to pores between one and two molecular diameters (of $\text{N}_2$ or $\text{C}_6\text{H}_6$), i.e. ultramicropores. Nevertheless, there is a qualitative change between the two samples activated to lower burn-offs (0 and 10 %) and the other samples. Ultramicropores are the dominant micropores in the former while supermicropores gain significance in the latter.

The absolute values for specific surface areas derived from immersion calorimetry measurements are highly dependent on the reference material chosen. This must be taken into account when comparing with other values in the literature or with BET ($\text{N}_2$) surface areas.

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References


