

On the evolution of micropore widths and areas in the course of activation

Key Words - Carbonization, activation, micropore width and area

It is well known that in the course of activation the micropore volume W_0 of carbonaceous materials increases and its dependence on the degree of burn-off can be obtained easily from the traditional Dubinin-Radushkevich plot of the nitrogen or benzene adsorption isotherm.

During activation, the size of the micropores also tends to increase, although in a less predictable way than their volume, as shown below. For carbons with pore-widths L not exceeding 0.7-0.8 nm, the distribution of W with L , dW/dL , can be obtained from a series of adsorption and immersion experiments with molecules of known critical dimensions [1,2]. However, industrial carbons are usually characterized by relatively large micropores ($L > 0.8-1$ nm) and the assessment of their average pore-width rests largely on the so-called characteristic energy E_0 of Dubinin's theory, or its older equivalent, the structural constant B . The existence of a correlation between E_0 and B and pore dimensions has been postulated for many years, but only recently have quantitative relations been proposed [3-5]. Earlier correlations were based on the gyration radius of the micropores, for which experimental data was available, but later it appeared that the accessible pore-width L was a better concept. On the basis of a number of independent determinations [1,2], including the selective adsorption of caffeine from aqueous solutions [7], we suggest the following expression,

$$L \text{ (nm)} = 30/E_0 + 5705/E_0^3 + 0.028 E_0 - 1.49 \quad (1)$$

relating L , the average width of ideally slit-shaped pores, to the characteristic energy E_0 given in kJ/mol. Eqn (1) is in good agreement with an earlier expression [6], but it can be used over an extended range of pore-widths (from 0.45 to 2.5 nm, approximately), with an uncertainty of 5 to 10 per cent. For $L < 0.45-0.50$ nm ($E_0 > 35-37$ kJ/mol), the simple relation $L = 16.5/E_0$ applies.

Eqn(1) is a useful tool for the assessment of the average micropore sizes of industrial carbons on the basis of a single adsorption isotherm (C_6H_6 at 298 K, for example). It can also be used for the study of activation itself, where it provides useful information on the evolution of L , and on the influence of the starting material. This is illustrated by the study of different activation series obtained in our laboratory, and by the examination of earlier data of Dubinin et al. [8,9] for the activation of various carbons by CO_2 and H_2O near 800-900 °C.

As shown in figures 1 and 2, different patterns emerge for the change in L with the degree of burn-off. The limiting cases are illustrated by Dubinin's series D [9], a natural coal activated with H_2O , and our series C-87, obtained from soft wood (barbecue charcoal) activated with CO_2 at 850 °C. The former shows a rapid increase in L , followed by a plateau near 1.2-1.4 nm. For the carbons of series C-87, on the other hand, L

increases rapidly beyond a burn-off of 40 per cent. Intermediate cases, not shown for the sake of clarity, have also been observed.

There is no doubt that the precursor (sugar, wood, coal, etc.) has a direct influence on the microporosity of the final material, but the carbonization stage also plays a role (see figure 2). In the present example we investigated the result of H_2O activation at 900 °C, on carbons prepared from the same precursor (rubber), but carbonized under different conditions. The first carbon was obtained by carbonization at 600 °C (2 hours), without removing the light liquid fractions. The subsequent activation produced series FTC-A with a plateau for L , starting already at low degrees of burn-off (curve A). This profile is similar to that of Dubinin's series D. The second carbon was prepared by carbonization at 450 °C (2 hours), but with the removal

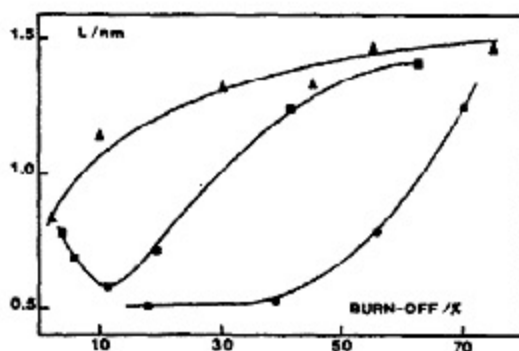


Figure 1. The variation of the average pore-width L with the burn-off for the carbons of series D (\blacktriangle), B (\blacksquare) and C-87 (\bullet).

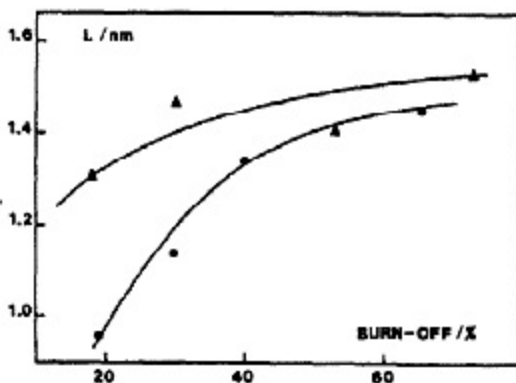


Figure 2. The variation of the average pore-width L with the burn-off for carbons FTC-A (\blacktriangle) and FTC-B (\bullet).

of the initial light fractions by distillation. The resulting series, FTC-B, shows a different profile, with a slower increase in the pore-width L (curve B). Although the development of the average micropore widths are different, series FTC-A and B show an almost identical increase in W_0 with the degree of burn-off. It follows that a study based on the increases of W_0 and E_0 (or B) alone would not reveal the differences between the two series (This was the case in Dubinin's earlier investigations, where the variation of the structural constant B did not suggest the differences shown in figure 1).

The combination of L with W_0 leads to the approximate area of the slit-shaped micropores, S_{mi} , given by [1]

$$S_{mi}(\text{m}^2/\text{g}) = 2 \cdot 10^3 \cdot W_0(\text{cm}^3/\text{g})/L(\text{nm}) \quad (2)$$

This area is a function of W_0 and L , and the examples shown in figures 1-2 suggest that the evolution of S_{mi} and S_{BET} will not be identical in the course of activation (The latter area is closely related to the monolayer equivalent of W_0). This point is illustrated by figure 3, which shows the variation of S_{BET} and S_{mi} of carbon C-87, as a function of the burn-off. The fact that at first S_{BET} is smaller than S_{mi} , can be explained by the limited pore-width L , which restricts the number of layers of adsorbate (C_6H_6 vapours at 298 K). The two areas are equal for a burn-off of approximately 60 %, where the average pore-width $L = 0.7-0.8$ nm (figure 1). Statistically, at this stage two layers of benzene can be adsorbed and both walls of the micropores are covered. For higher burn-offs, where L grows rapidly, the number of equivalent monolayers increases and S_{BET} no longer corresponds to the actual surface of the walls. It follows, that a good agreement would be found only for a series of carbons where L remains near 0.6-0.8 nm.

Further details, and in particular the influence of the precursor and its preparation on the microporous texture, will be published later.

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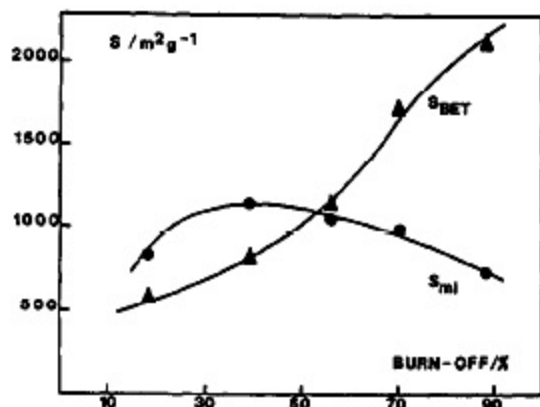


Figure 3. The evolution of the BET surface area (C_6H_6 ; 293 K) and of the true micropore surface S_{mi} for carbon C-87, as a function of burn-off.

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