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Evolution of microporosity during activation of carbon

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Various adsorption and immersion techniques and a recent model for micropore distributions have been used to assess quantitatively the evolution of the main properties of active carbon. The precursors used in this study were of vegetable and polymeric origin. One activation series based on natural coal was also included.

Keywords: microporosity; adsorption; coal

Although the precursor plays an important role in determining the structural properties of an active carbon, the carbonization (pyrolysis) and activation stages can still significantly influence these properties.

In this paper, these influences are examined quantitatively by applying different techniques developed in this laboratory[1-5], for the characterization of microporous carbons. By using combined adsorption and immersion techniques and a theoretical model based on the adsorption isotherm, quantitative information can be obtained on the development of the microporous structure (volume and pore-size distribution), the internal and external surface areas and the hydrophilic and hydrophobic character of carbons obtained by physical activation. These properties are closely related to the origin of the active carbons, and to the carbonization and activation stages.

From a structural point of view, active carbons are characterized by the volume W_0 and the width L of their micropores and by the external (non-microporous) surface area S_*. These parameters determine the general features of physical adsorption in the material. The chemistry of the surface can influence the selectivity of the adsorption process, but basically active carbons are hydrophobic.

The theoretical background for the structural characterization is traditionally based on Dubinin's theory and its developments[2-9]. The basic relationship is:

$$W = W_0 \exp[-(A/\beta E_0)^n] \qquad (1)$$

where W represents the volume filled at temperature T and relative pressure p/p_0, W_0 is the total volume of the micropores, $A = RT\ln(p_0/p)$ and n, E_0 and β are parameters of the system under investigation. For a variety of microporous carbons (in particular active carbons of industrial origin), the adsorption data can be fitted over a variable range of relative pressures to Equation (2) with exponent $n = 2$. This corresponds to the original equation of Dubinin and Raduchkevich (DR)[1]:

$$W = W_0 \exp[-B(T/\beta)^2 \log^2(p_0/p)] \qquad (2)$$

As shown elsewhere[1,4,7], the so-called characteristic energy E_0 (or the structural constant B of the DR equation) is related to the average width of the micropore system. It is also possible to obtain a good approximation for the micropore distribution by subjecting the adsorption isotherm to a theoretical treatment[2,4]. Its validity has been tested by direct determination of the distribution in the range 0.35–1.5 nm. The following empirical relation is suggested:

$$L(\text{nm}) = 10.8/(E_0 - 11.4) \qquad (3)$$

E_0 being given in kJ mol^{-1}. High resolution transmission electron microscopy (HRTEM) also provides independent evidence for the general pattern[2,10].

From the volume W_0 and the width L of the micropores, it is possible to estimate the real surface area of the walls S_{mi} (as opposed to the BET surface area), by assuming that the pores are ideally slit-shaped. This point is discussed by Ballerini *et al.*[5], where the technique based on the selective adsorption of caffein from aqueous solutions, monitored by immersion calorimetry, is also described. The external surface area S_* can be assessed by different techniques and a satisfactory agreement is usually obtained[1].

The number of hydrophilic centres a_0 responsible for the adsorption of water vapour by active carbons[10] can be determined either from the type III isotherm or more rapidly from immersion calorimetry[1,12]. The latter provides a good assessment for a_0, but the material should first be washed with HCl–H_2O to eliminate inorganic salts.

EXPERIMENTAL

This study was based on polymeric materials (rubber tyres, series FTC), natural coal (series CN) and materials of vegetable origin such as soft wood (BIO), barbecue charcoal (C-87), coconut shells (coco), olive stones (R), banana skins (UFC) and the skin of coffee beans (CAF). The emphasis was placed on the materials of vegetable origin and on the tyres, CN being investigated mainly to support evidence derived from data previously published[13] and re-examined here.

With the exception of series CN, carbonization was carried out under nitrogen in a quartz tube, with a rate of heating of 33°C min^{-1} (slow) or 200°C min^{-1} (fast). This was followed by a soaking time of 2 h at temperatures varying between 450 and 600°C. At the end of the carbonization process, the quartz tube was rapidly cooled to 100°C in approximately 15 min, still under nitrogen, and the sample weighed. We used standard batches of 40 g of dry precursor. The light fraction of the liquids

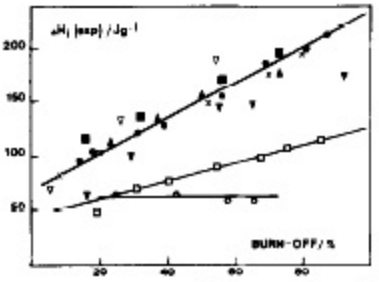

Figure 1 Variation of the enthalpy of immersion ΔH_i into benzene as a function of burn-off for active carbons FTC (□), CN (○), C-87 (●), BIO (▲), R (×), CAF-A (▼), UFC (▽) and coco (■)

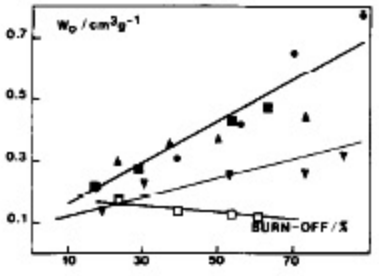

Figure 2 Variation of the microporous volume W_0 as a function of burn-off for active carbons C-87 (●), CAF-A (■), BIO (▲), FTC (▼) and CN (□)

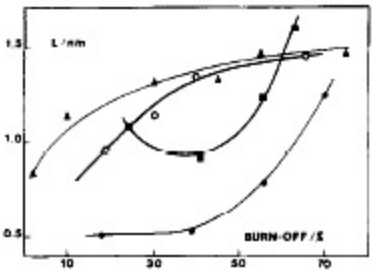

Figure 3 Variation of the average micropore-width L as a function of burn-off for active carbons D (▲), FTC (○), CN (■) and C-87 (●)

produced during this stage could either be distilled off, or kept in the reaction vessel to be pyrolysed. The total yield of carbon therefore varied between 20 and 40% of the initial mass.

Physical activation was carried out on batches of 10 g of carbon (particle sizes 0.6–1.2 mm) in a reactor made of stainless steel, the gases being introduced through a porous glass plug at the bottom. We used either carbon dioxide or water vapour carried by a stream of pure nitrogen, at temperatures between 800 and 900°C. The degree of burn-off (mass loss) varied between 10 and 80%.

The properties of the resulting active carbons were determined from the adsorption isotherms of different vapours including benzene (293 K), measured gravimetrically, and by immersion calorimetry[1].

Samples of an earlier CEP series (soft wood) were also investigated by HRTEM, as described elsewhere[1–10].

RESULTS AND DISCUSSION

A first general observation, illustrated by *Figure 1*, is the variation of the enthalpy of immersion, ΔH_i, of the various active carbons into benzene, as a function of burn-off. It appears that a specific pattern is obtained, depending on the precursor and reflecting the ease of activation of the material. According to the general equation[1]:

$$\Delta H_i = -\beta E_0 W_0 (1+\alpha T)\sqrt{\pi/2 V_m} + h_i S_e$$

where α and V_m are the thermal expansion coefficient and the molar volume of the liquid and h_i is the enthalpy of wetting of the external surface area. The enthalpy of immersion reflects essentially the increase in W_0, and to a lesser extent the influence of the pore width L (an inverse function of E_0) and of the external surface area S_e. It appears that for the carbons of vegetable origin, W_0 dominates, whereas for series FTC the change in L tends to reduce the increase in ΔH_i. For series CN, the ease of activation is low because neither W_0 nor L vary greatly.

It is well known that the microporous volume W_0 generally increases in the course of activation[14,15], but, as confirmed here, the rate of increase depends on the precursor. This is clearly illustrated by *Figure 2*. We also think that W_0 is more realistic than S_{BET}, still quoted in many papers[14–16]. As far as the true surface area of the micropores S_{mi} is concerned, a good estimate can now be derived from W_0 and the average width L. The two areas, S_{BET} and S_{mi} have been compared and discussed elsewhere[17].

Our investigation shows that the variation of the average micropore width L with the degree of burn-off depends strongly on the precursor. This is illustrated by the examples of *Figure 3*, comparing the different series. As mentioned earlier[17], carbonization can influence to some extent the variation of L with the degree of burn-off.

As illustrated by *Figure 4*, the micropore distributions calculated from the adsorption isotherms[2,4,5] depend to some extent on the activation process, in agreement with the earlier work of Tomkow *et al.*[16]. It appears that for carbon C-87 activated with carbon dioxide to approximately 55% burn-off, an increase in temperature from 800 to 900°C leads to an increase in W_0 and in the average pore-width L. Water is more efficient (larger micropore volumes and sizes) and the distributions are wider. As a consequence, the molecular sieve properties of the carbon dioxide product are lost. A similar pattern is observed for the external surface area of these carbons

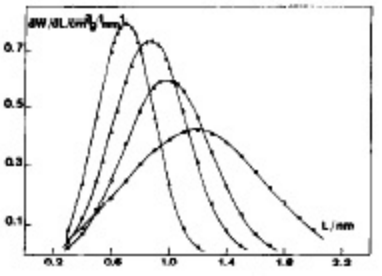

Figure 4 Variation of the micropore distribution dW/dL for the series of active carbons C-87 (burn-off 55%) activated at 800 and 900°C, with CO_2 (△, ▲) and H_2O (○, ●)

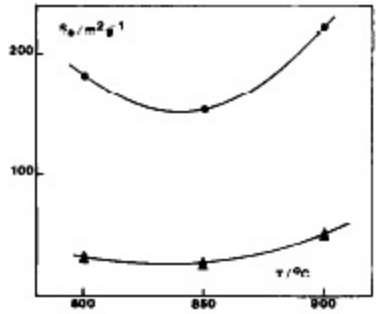

Figure 5 Variation of the external surface area as a function of the temperature for active carbons C-87 (burn-off 55%) activated with CO_2 (▲) and H_2O (●)

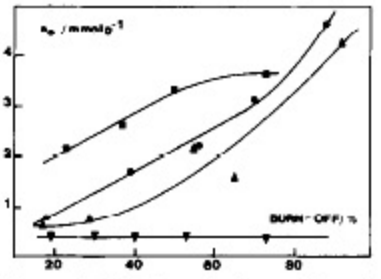

Figure 6 Variation of the number of hydrophilic centres a_0 as a function of burn-off for the series of active carbons C-87 (●), CAF-A (▲), BIO (■) and FTC (▼)

(*Figure 5*), S_e being much larger in the case of activation by water.

Figure 6 shows the evolution of a_0, the number of hydrophilic centres, in the course of activation. Our examples suggest that the precursor has a greater influence than the activation process itself, but it must be emphasized that the presence of mineral (mainly potassium and calcium) salts can also modify the overall behaviour of the carbon towards water.

These examples, based on test cases[1,3–5], show that it is now possible to obtain a quantitative assessment of some fundamental properties of active carbons, and to follow more closely the influence of the various stages involved in their preparation.

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