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Pretreatment and physical activation of acetylene cokes

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Pretreatment of acetylene cokes at 450°C with a mixture of nitrogen, oxygen and water vapour creates a relatively large surface area and some initial microporosity, further developed by water activation at 800°C. For the same degree of burn-off, but without pretreatment, large micropores ($L > 2$–3 nm) are obtained and the external surface area remains small.

Keywords: acetylene cokes; activation; pretreatment

It is well known that the physical activation of coke by steam or carbon dioxide at ~800–900°C has little effect on this type of solid, and only a small degree of microporosity can be obtained. Chemical activation on the other hand can lead to better results, provided that specific treatments are applied.

The present paper reports the effect of a mixture of nitrogen, oxygen and water vapour at 450°C on a typical acetylene coke before steam activation at 800°C. This technique has already been applied to coal dust[1] and to carbon fibres[2]. It appears now that in the case of acetylene cokes this low-temperature treatment improves the yield of the subsequent physical activation, by creating some initial microporosity and a relatively large external surface area. Although the final porosity remains modest[3], compared with standard activated carbons[4], this technique suggests an interesting route for other precursors.

EXPERIMENTAL

This study was based on a typical acetylene coke of industrial origin. The starting material was crushed and sieved, the fraction 1–1.5 mm being used in all subsequent experiments. Pretreatment and steam activation were carried out on batches of 8 and 3 g in a stainless steel reactor to which the gas mixtures were introduced through a porous plug at the bottom. The equipment was the same as used previously[5]. The low-temperature treatment took place at 450°C, with a mixture of nitrogen and air (flow rates respectively 2.25 and 0.25 l min^{-1}, measured at room temperature), saturated with water vapour provided by a bath at 70°C ($p = 233.7$ mmHg). The treatment was applied for several hours, with mass losses up to 50% (see *Table 1*).

Physical activation was carried out mostly at 800°C, using a stream of nitrogen (flow rate 2.5 l min^{-1}, measured at room temperature), again containing water vapour produced at 70°C. With the original coke, activation was carried out at 900°C, to accelerate the process.

The properties of the samples were determined from the adsorption isotherms of CH_2Cl_2 at 293 K and by immersion calorimetry in water and CH_2Cl_2, at the same temperature. The structural characterization of microporous carbons is traditionally based on Dubinin's theory and its developments[4]. The basic relation is

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

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 specific parameters of the system under investigation. The case $n = 2$ corresponds to the classical equation of Dubinin and Radushkevich. As shown elsewhere, the so-called characteristic energy E_0 (kJ mol^{-1}) is related to the average micropore width L(nm) by[6]

$$L = 10.8/(E_0 - 11.4) \quad (2)$$

Moreover, if one assumes that the micropores are slit-shaped and open, the surface area of their walls ($m^2\ g^{-1}$) is given by the following approximation:

$$S_{mi} = 2 \times 10^3 W_0/L \quad (3)$$

where W_0 is in $cm^3\ g^{-1}$.

It has also been shown[4], that the enthalpy of immersion ($J\ g^{-1}$) of a microporous carbon in an organic liquid whose vapour follows Equation (1) is

$$\Delta h_i = -\beta E_0 W_0 \pi^{1/2}(1 + \alpha T)/2V_m + h_i S_e \quad (4)$$

where α and V_m are the thermal expansion coefficient and the molar volume of the liquid, and h_i is the specific enthalpy of wetting of the external (non-microporous)

Table 1 Main characteristics of samples

Sample Treatment	A 450°C, N_2–air–H_2O	B 450°C, N_2–air–H_2O	C 800°C, N_2–H_2O	D 800°C, N_2–H_2O	E 900°C, N_2–H_2O
Burn-off (wt%)	10	51	42	55	42
W_0 ($cm^3\ g^{-1}$)	0.05	0.09	0.17	0.21	0.13
E_0 (kJ mol^{-1})	28.0	25.7	21.3	19.0	14.4
L(nm)	0.65	0.75	1.10	1.4	> 3
S_{mi} ($m^2\ g^{-1}$)	154	240	304	295	50
S_e ($m^2\ g^{-1}$)	56	122	101	159	30
S_t ($m^2\ g^{-1}$)	210	362	405	454	80
$-\Delta h_i$ (CH_2Cl_2) ($J\ g^{-1}$)	26.3	48	60.4	75.0	21.0
$-\Delta h_i$ (H_2O) ($J\ g^{-1}$)	17.9	36.6	17.6	24.4	7.3
$-h_i$ (H_2O) ($J\ m^{-2}$)	0.085	0.101	0.043	0.053	0.091

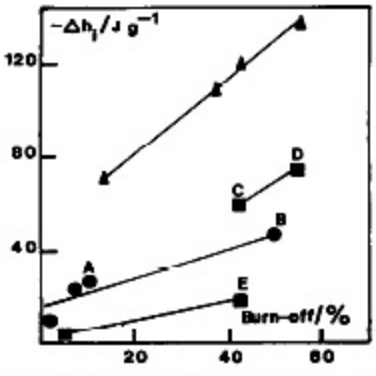

Figure 1 Enthalpies of immersion Δh_i of various carbons in CH_2Cl_2 at 293 K, as a function of degree of burn-off: ▲, activated carbons of series CAF; ●, ■, acetylene cokes (A–E as in *Table 1*)

surface S_e of the carbon. For dichloromethane, the standard adsorbent used here, $\beta = 0.66$, V_m (293 K) = 64.02 cm^3 mol^{-1}, $\alpha = 1.34 \times 10^{-3}$ K^{-1} and $h_i = 0.152$ J m^{-2}.

As shown earlier[5], the combination of adsorption and immersion techniques gives a good insight into the development of microporosity, in particular when series of homologues are considered. In this case, the enthalpy of immersion alone provides useful information.

Immersion in water, on the other hand, provides information on the hydrophilic or hydrophobic character of the carbon surface, as illustrated below. The various experimental procedures are described in detail elsewhere[4,7,8].

RESULTS AND DISCUSSION

As shown earlier[5,9], the variation of the enthalpy of immersion Δh_i (CH_2Cl_2) with the mass loss (burn-off) of a carbon is a good indicator of the development of microporosity and surface area in the course of activation. This is illustrated in *Figure 1* for a carbon obtained from the skin of coffee beans and activated with steam at ~850°C (series CAF). The absolute values of Δh_i and their rate of increase with degree of burn-off reflect the good activatability of the material (between 15 and 65%, the micropore volume increases from 0.20 to 0.45 cm^3 g^{-1}). In the case of acetylene coke, on the other hand, direct activation with steam at 900°C is not very efficient, as suggested by the enthalpies of immersion in CH_2Cl_2. The full characterization of the solid at 42% burnoff (sample E in *Table 1*) reveals a small micropore volume with $W_0 = 0.13$ cm^3 g^{-1} and an external surface area $S_e = 30$ m^2 g^{-1}. The total surface area S_t obtained from the selective adsorption of caffeine[10,11] is 80 m^2 g^{-1}, which means that the surface area of the micropore walls is ~50 m^2 g^{-1}. The low value of E_0 also suggests the presence of large micropores ($L > 2$–3 nm).

At ≳350°C, variable concentrations of oxygen in nitrogen react with carbons. The controlled reaction of activated carbons with air has been examined by a number of workers[12–15]. As shown by Tomkov *et al.*[16], at ~400°C oxygen can also produce some porosity in a xylitic coke, but in the present acetylene coke, matter is simply removed without creating any significant porosity (virtually no change in Δh_i, which remains in the range 0.5–2 J g^{-1}). On the other hand, at the same temperature water vapour does not react significantly with carbons, the activation energy being too high. It is therefore interesting to find that at 450°C a mixture of oxygen and water vapour in a stream of nitrogen can induce the development of significant external area and some microporosity in the acetylene coke. This low-temperature treatment also creates favourable conditions for subsequent activation by steam at ~800°C. The mechanism here is probably of the same type as reported some years ago by Bonnetain[17], who examined the combustion of graphite in oxygen at 653°C and its partial inhibition by water vapour. The resulting BET surface area of the sample was larger when water was present.

As shown in *Figure 1*, the enthalpies of immersion Δh_i (CH_2Cl_2) after treatment of the coke at 450°C are higher than for direct activation at 900°C. Samples A and B, corresponding to weight losses of 10 and 51%, were fully characterized by the combination of adsorption and immersion techniques at 293 K. The data shown in *Table 1* indicate the presence of small micropore systems (0.05 and 0.09 cm^3 g^{-1}) but relatively large external surface areas (56 and 122 m^2 g^{-1} respectively). The average micropore widths are similar, ~0.7 nm.

The subsequent activation of samples A and B with steam at 800°C for 5 h produces carbons C and D, with weight losses of 42 and 55%. These solids were also fully characterized by adsorption and immersion (*Table 1*). It appears that the classical activation process leads to significant widening of the micropores as their volume increases. On the other hand, the external surface area increases by only 40 m^2 g^{-1}. These features are typical of water activation, which destroys the smaller micropores as the degree of burn-off increases[5].

Samples C and D differ considerably from sample E, described above and obtained by direct water activation of the acetylene coke. This indicates major differences in the mechanisms of the treatments at 450 and 800°C, probably related to the action of oxygen during the first stage.

It is also of interest to point out the differences in the specific enthalpies of immersion in water, Δh_i (H_2O)/S_t, for the two series of carbons, the values for samples A and B being twice those for samples C and D. The latter are typical of steam-activated carbons, and for the reference series CAF, one obtains 0.030–0.055 J m^{-2}. The hydrophilic character of the surface treated at 450°C confirms the observation of Tomkov *et al.*[16] that xylitic coke activated with oxygen at 400°C contains a far greater concentration of oxygen complexes than the samples resulting from CO_2 or water activation.

Although the mechanism is not yet fully understood, the treatment at 450°C with nitrogen, steam and oxygen appears to be very useful when dealing with hard carbons. It may also play an important role, as an intermediate stage, in the preparation of activated carbons based on specific precursors. This possibility is being investigated and results will be presented in due course.

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