

THE PHYSICAL AND CHEMICAL CHARACTERIZATION OF A SULPHUR-IMPREGNATED ACTIVE CARBON, BY COMBINED ADSORPTION AND IMMERSION TECHNIQUES

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Abstract—A commercially available active carbon, impregnated with sulphur, has been characterized and compared to the original carbon by using adsorption and immersion techniques. The specific reaction of liquid CS₂ with sulphur, following the preadsorption of various amounts of n-nonane, shows that the accessibility of sulphur decreases rapidly. It is also found that the impregnated carbon becomes hydrophilic but, in the case of SO₂ adsorption, no change in adsorption capacity is detected.

Key Words—Active carbon, sulphur impregnation, structural and chemical properties, microporosity, adsorption, calorimetry.

1. INTRODUCTION

At the present time, activated carbons of low and medium activation can be characterized physically and chemically by the combination of adsorption and immersion techniques[1-4]. It has also been shown recently[5] that preadsorption of a heavy n-alkane (n-C₉H₂₀ or n-C₁₁H₂₄), followed by immersion into liquids with specific interactions, could be used to assess the distribution or accessibility of impregnating agents to hydrophilic centers.

Carbons impregnated with sulphur are used successfully for the removal of mercury from waste air streams[6-8]. In the present paper we describe the full characterization of a commercially available active carbon impregnated with sulphur (10%-15% in weight) and compare it with the starting material. The characterization described below is based on vapor adsorption and on immersion calorimetry (to obtain micropore distributions), and on the specific reaction of CS₂ with rhombic sulphur. The latter experiment is carried out for various degrees of prefilling with n-nonane, which blocks the micropores and does not react with carbon disulfide. This type of experiment provides information on the accessibility of sulphur in the presence of a preadsorbed organic compound.

2. THEORETICAL

Adsorption by microporous carbons is described by the equation of Dubinin and Astakhov[1-4]

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

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.

For a variety of activated carbons, as used here, $n = 2$ and eqn (1) becomes the classical eqn of Dubinin and Radushkevich (DR).

As shown elsewhere[1], the enthalpy of immersion Δh_i of an active carbon into a liquid whose vapor is adsorbed according to the DR equation, is given by

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

α and V_m are the thermal coefficient of expansion and the molar volume of the liquid, and h_i is the specific enthalpy (J m⁻²) of wetting the external surface area S_e .

In the case of CS₂, following the preadsorption of n-nonane, the enthalpy of immersion consists of two contributions: the first, given by eqn (2) corresponds to the filling of the remaining micropore volume $W' = (1 - \theta)W_0$. The second contribution arises from the specific interaction of rhombic sulphur with CS₂, ($h_s = 60 \pm 10$ J/g of sulphur). It follows that

$$-\Delta h_i = \beta E_0 (1 - \theta) W_0 (1 + \alpha T) \sqrt{\pi} / 2 V_m - h_i S_e - 60 m_s \quad (3)$$

where m_s represents the amount of sulphur (g/g carbon) accessible to CS₂. The situation is similar to the case of TEDA (triethylenediamine) detected by CH₃I[5].

The micropore distribution of the carbons can be obtained as described elsewhere, by molecular sieve experiments for the smaller pores (up to 1.0-1.2 nm) and/or by the use of the overall isotherm:

$$\Theta(A) = [a/(a + (A/\beta K_0)^3)]^3 \quad (4)$$

The isotherm is based on an integral transform assuming a D-A core with $n = 3$ [9-10] and an under-

Table 1. Main characteristics of carbons D47 and D47-S, derived from adsorption and immersion experiments. The surface of the micropores S_{mi} has been calculated from distribution (5), by assuming slit-shaped pores

Carbon	E_0 [kJ/mol]	K_0 [nm·kJ·mol ⁻¹]	W_0 [cm ³ /g]	S_p [m ² /g]	L [nm]	S_{mi} [m ² /g]	ν	a [nm ⁻³]
D47	21.50	23.0	0.402	12.1	1.08	742.5	2.011	1.387
D47-S	21.18	23.4	0.327	10.0	1.12	579.0	2.095	1.128

lying normalized distribution of the micropore width L

$$f(L) = 3L^{(\nu-1)} a^\nu \exp(-aL^3)/\Gamma(\nu) \quad (5)$$

where a and ν are adjustable parameters, and K_0 , given in nm·kJ·mol⁻¹, is related to E_0 [10] by:

$$K_0 = 10.8 + 123/(E_0 - 11.4) \quad (6)$$

3. EXPERIMENTAL

The original and impregnated carbons, D47 and D47-S have been supplied by Carbo-Tech, Essen (Germany). The relevant information is found in Table 1.

CS₂ has the following parameters: V_m (293 K) = 60.28 cm³ mol⁻¹, $\beta = 0.7$, $\alpha = 1.49 \cdot 10^{-3}$ K⁻¹, $h_i = -73$ mJ m⁻², and $h_s = 60 \pm 10$ J/g of sulphur. The latter value was obtained from the direct heats of immersion of small crystals of rhombic sulphur into CS₂.

The gravimetric and immersion techniques used in the present study are described in detail elsewhere [1.5]. Prior to its use, carbon D47 was outgassed for 12 hours in vacuo ($10^{-2} - 10^{-3}$ Pa), the final temperature being 400°C. In the case of carbon

D47-S, outgassing was carried out below 80°C, in order to avoid a loss of sulphur by sublimation. The amount of sulphur accessible after preadsorption of nonane was calculated from the enthalpies of immersion into CS₂. As described above, the total enthalpy of immersion corresponds to the physical process described by eqn (2) and to the enthalpy of reaction of CS₂ with rhombic sulphur.

Preadsorption of n-nonane was achieved by exposing the outgassed sample to the vapor of the liquid at room temperature. The exact amount of preadsorbed alkane was determined by weighing the sample in its ampule. The amount of micropore filling $\Theta = W/W_0$ was calculated using the molar volume of nonane at the working temperature of 293 K (178.73 cm³ mol⁻¹).

4. RESULTS AND DISCUSSION

The main characteristics of the carbon D47 and D47-S are given in Table 1. It appears that for D47-S the micropore volume is reduced by 0.075 cm³ g⁻¹. This corresponds to 15% in weight of sulphur if one assumes a density of 2.07 g cm⁻³ as for pure rhombic sulphur. This value is in good agreement with the average sulphur content given by the manufacturer. It also means that sulphur does not block off parts of the micropore system.

Figure 1 shows the good agreement that can be obtained between the experimental distribution (histograms) and the distribution (eqn (5)) obtained by fitting the extended adsorption data for C₄H₆ and N₂O

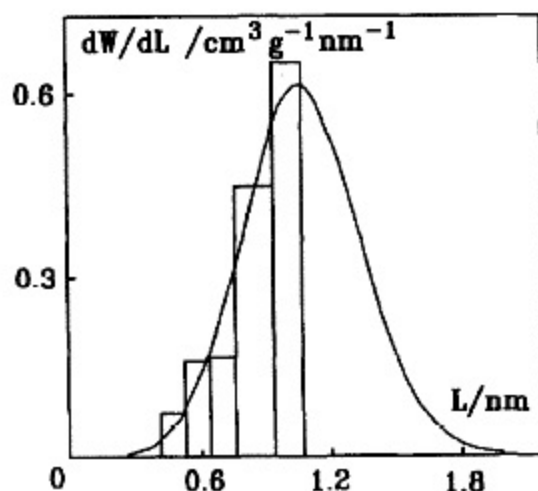


Fig. 1. The micropore distribution of carbon D47 (histogram and theoretical curve).

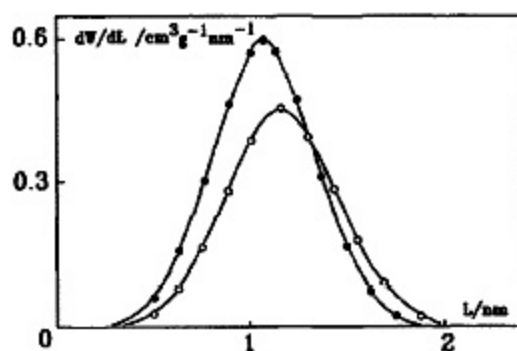


Fig. 2. The micropore distributions of carbons D47 (●) and D47-S (○), obtained from eqns (4) and (5).

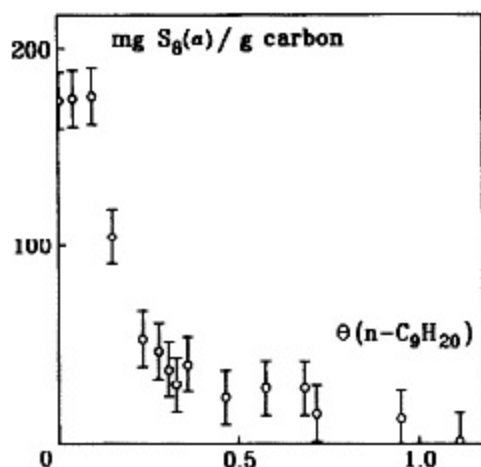


Fig. 3. The amount of sulphur accessible to CS_2 in carbon D47-S, as function of θ , the degree of filling with n-nonane.

(293 K) to eqn (4) (curve). For K_a , we used the values calculated from E_a , given in Table 1.

The comparison of the distributions (Fig. 2) shows that the average pore-width of the carbon impregnated with sulphur is slightly larger than in the original carbon. This suggests that sulphur tends to occupy the smaller pores. A different behavior has been observed in the case of TEDA, which was found to occupy the larger pores and the external surface area[5].

In a second set of experiments, the amount of sulphur available at different degrees of nonane prefilling was obtained from the enthalpy of immersion into CS_2 , using eqn (3). Figure 3 shows the variation of the available amount of sulphur as a function of the degree of prefilling. The sharp decrease observed in the range $0 < \theta < 0.2$ tends to confirm that the sulphur is probably located in the smaller pores, which are filled first by n-nonane.

The effect of the impregnating agent can also be studied through the adsorption of water and SO_2 . Fig-

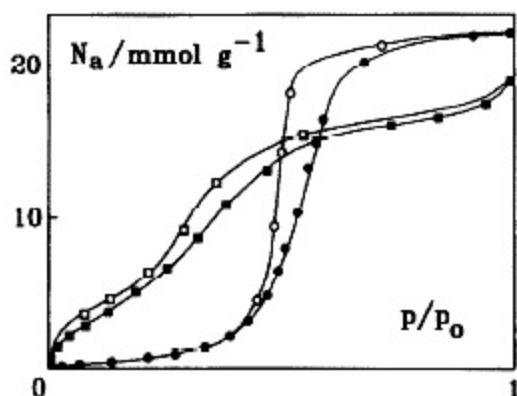


Fig. 4. Water adsorption at 293 K by carbon D47 before (●) and after (○) impregnation with sulphur (open symbols refer to desorption).

Table 2. Experimental enthalpies of immersion of microporous carbons into benzene and water (values of Δh_i in J g^{-1} of carbon)

Carbon	$\Delta h_i(\text{C}_6\text{H}_6)$	$\Delta h_i(\text{H}_2\text{O})$
D47	119.4	40.4
D47-S	96.3	81.6

ure 4 shows the adsorption of water by carbon D47, before and after impregnation with sulphur. For the original carbon, one observes a typical adsorption isotherm of type V, as described by Dubinin and Serpinsky[11-13]. In the case of the impregnated carbon, on the other hand, the water isotherm is of type IV. The displacement of the water adsorption isotherm towards lower values of relative pressure after impregnation reflects the large change observed for the immersion into H_2O (Table 2). This means that new hydrophilic centers have been introduced with sulphur. If one assumes that the type IV isotherm results from a Langmuir and a type V isotherm, we obtain the following numbers of primary centers: a_L (Langmuir) = 3.7 mmol/g and a_v (type V) = 2.8 mmol/g. For the original carbon D47, we obtain $a_v = 0.85$ mmol/g. The comparison between the total number of hydrophilic sites on carbon D47-S ($a_L + a_v = 6.5$ mmol/g) and D47 ($a_v = 0.85$ mmol/g) and the enthalpies of immersion into water (Table 2) suggests that the two types of sites found on the impregnated carbon are not equivalent.

SO_2 adsorption on active carbons is a subject frequently encountered in the specialized literature[14-16], because air pollution by sulphur dioxide emissions has become a serious problem in industry. The presence of certain oxygenated groups on the surface of the carbon can greatly influence the adsorption of SO_2 [17-19]. Figure 5 shows, however, that the presence of sulphur does not influence the adsorption of sulphur dioxide, except for the total capacity. The DR plots are also found to be similar.

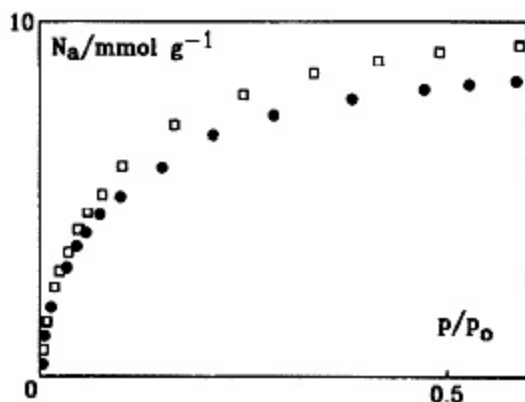


Fig. 5. The adsorption of SO_2 by carbon D47, before (□) and after (●) impregnation with sulphur.

It appears from the present study, and from earlier investigations[5], that the combination of immersion and preadsorption techniques can be very useful for the characterization of impregnated active carbons.

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