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ON THE CHARACTERIZATION OF CARBON BLACKS BY VARIOUS TECHNIQUES

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Abstract—It is shown how the use of various adsorption and calorimetric techniques can provide unambiguous information on the presence or the absence of porosity on the surface of carbon blacks. Dubinin's theory, its extension to immersion calorimetry, and gas-phase calorimetry can be applied successfully. As an example, the characterization of 6 porous and non-porous samples is described.

Key Words—Carbon black, microporosity, calorimetry, Dubinin equation.

1. INTRODUCTION

Carbon blacks[1] are characterized by their surface area but, depending on the origin of the solid and its treatment, one may find a variable degree of microporosity[2]. Its presence, which is not always obvious, can be revealed by a number of techniques currently applied to active carbons and based on Dubinin's theory[3]. In the present paper, we wish to illustrate these possibilities for a number of porous and non-porous blacks, and to cross-check them.

As shown below, BET treatment[4] alone and the value of its constant 'c' are not always sufficient to characterize the surface unambiguously. Moreover, even enthalpies of immersion combined with a standard enthalpy of wetting can be misleading in some cases. It follows that more refined approaches must be used. Provided that information is available for a suitable reference material, such as graphitized Vulcan 3, for example, the comparison of adsorption and immersion data obtained with the same adsorptive can provide important clues. This approach leads essentially to the value of the external (non-porous) surface area S_e and to the approximate micropore volume, if microporosity is present. The advantage of this technique lies in the fact that adsorption can be limited to relative pressures p/p_0 above 0.05, approximately, but the information is limited to the micropore volume alone. On the other hand, from adsorption data at low pressures (typically $10^{-6} < p/p_0 < 10^{-2}$) it is possible to gain more information on the micropore system, by applying Dubinin's theory and its extensions. Its fundamental relation is the Dubinin-Astakhov eqn[3]

$$N_a = N_{a0} \exp[-(A/\beta E_0)^n] \tag{1}$$

where N_a (mol/g) represents the amount adsorbed by the adsorbent at p/p_0 and at temperature T; N_{a0} is the limiting amount as p/p_0 tends to unit; $A = RT \ln(p_0/p)$ and n, E_0 and β are specific parameters of the system under investigation. The actual volume of the micropores is $W_0 = N_{a0} \cdot V_m$, when V_m is assumed to be close to the molar volume of the adsorbate in the liquid state. W_0 depends on the accessibility of the micropore system to molecules of different sizes. For a variety of active carbons $n = 2$, which corresponds to the classical equation of Dubinin and Radushkevich (D-R). From the linear section of a plot of $\ln(N_a)$ versus $(A/\beta)^2$, the classical D-R plot, one obtains, finally W_0 and E_0.

It has been shown that the so-called characteristic energy E_0, usually given in kJ/mol, is related to the average micropore width L by[5]

$$L \text{ (nm)} = 10.8/(E_0 - 11.4) \tag{2}$$

This relation is valid for pores smaller than 1.8-2.0 nm, and if one assumes locally slit-shaped and open micropores, their surface area is approximately

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

The parameters W_0 and E_0, obtained from the D-R eqn (1) for the adsorption of a given vapour, also appear in the enthalpy of immersion of the carbon into the corresponding liquid, Δh_i. As shown by Stoeckli, *et al.* [3,6], Dubinin's theory can be extended to immersion calorimetry, the fundamental relation being

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

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 surface of the carbon. If the second term on the right-hand side of eqn (4) is not too small, it is possible, in principle, to calculate S_e and to check for self-consistency, since the external surface area can also be derived from analysis of the adsorption isotherm. However, it must be pointed out that S_e and h_i are usually known within 10-15% only. Experience also shows that in the case of microporous carbon blacks, as opposed to active

Table 1. Standard analysis of the samples (BET and immersion calorimetry based on CH_2Cl_2 at 293 K)

Carbon black	S(BET) (m^2/g)	c(BET)	$\Delta h_i(CH_2Cl_2)$ (J/g)	S_i (m^2/g)
XYL-NE	112	16	20.0	131
XC-72	218	82	31	204
ACET-NE	180	28	23.8	156
T-5500	210	51	30	197
NG-2700	90	50	10.9	72
HOECHST	52	72	7.6	50

carbons[1], S_e obtained from eqn (4) is not always reliable.

Like eqn (1), eqn (4) has also been used to obtain the volumes W_0 filled by molecules of different sizes. The two approaches are in agreement, but immersion calorimetry requires less time than the determination of the corresponding isotherms. These techniques lead to the corresponding micropore distribution of a carbon[5], dW/dL versus L, as shown below. It appears therefore, that Dubinin's theory provides a useful framework for the study of microporosity in carbons in general.

Independent information on the state of the carbon surface is also provided by vapor-phase calorimetry[7,8]. The differential heat of adsorption q^{diff} and its variation with the amount adsorbed clearly shows the presence or the absence of microporosity, as observed for active carbons. The integral heat of adsorption is also related to the enthalpy of immersion, Δh_i, the difference being equal to the enthalpy of condensation of the adsorbed gas. This provides again a test for self-consistency between the different and independent experimental techniques.

2. EXPERIMENTAL

We used 6 carbon blacks of different origins (Tables 1–3) and a sample of graphitized Vulcan 3. The latter (courtesy of J. Lahaye, Mulhouse) was used as a primary reference, since it is well known that the carbon blacks of these series are non-porous. The BET surface areas obtained from N_2 (77 K) and C_6H_6 (293 K) are 73.1 and 71.2 m^2/g, respectively, assuming molecular surface areas of 16.2 and $43 \cdot 10^{-20}$ m^2.

Carbon blacks T-5500, XC-72, NG-2700 and Hoechst are of industrial origin, whereas samples XYL and ACET-NE were produced in our laboratory from the combustion of xylene and acetylene in oxygen.

The adsorption and immersion techniques and gas-phase calorimetry are described in detail elsewhere[3,4]. Prior to their use, all carbons were outgassed for 12 hours *in vaccuo* (10^{-4} mmHg), the final temperature being near 450°C. In the case of the gas calorimeter, the sample was outgassed again *in situ*, at room temperature. The five samples were investigated at 293 K, using CH_2Cl_2 in the liquid and the vapor states. This adsorptive is convenient, in view of its vapor pressure (348.9 mmHg at 293 K) and its molecular dimensions (nearly spherical, with a diameter close to 0.35 nm). It has already been used extensively for the study of active carbons. Its main physical properties, used in connection with eqns (1) and (4), are $\beta = 0.66$, $V_m = 64.02$ cm^3/mol, $\alpha = 1.34 \cdot 10^{-3}$ K^{-1} and $h_i = 0.15$ J/m^2. The latter is an average obtained from immersion experiments carried out with carbons of known surface areas.

Based on a value of $43 \cdot 10^{-20}$ m^2 for benzene adsorbed on non-porous carbon blacks, the molecular surface area of CH_2Cl_2 is $29 \cdot 10^{-20}$ m^2, against $24.5 \cdot 10^{-20}$ m^2 calculated[4] from the liquid density at 293 K.

In the case of samples XC-72, Hoechst and NG-2700, the adsorption isotherms of C_6H_6 (293 K) were also determined, in order to compare these solids with Vulcan 3, the primary reference[2]. From the comparison plots, shown in Fig. 1, it appears that Hoechst and NG-2700 are non-porous and consequently either one can be used as an internal reference. Sample XC-72 appears to be microporous, as found earlier[5,8].

3. RESULTS AND DISCUSSION

Table 1 shows the results obtained from the standard BET analysis of the CH_2Cl_2 isotherms and from immersion into the same liquid. It appears that the surface areas S(BET) *and* S_i, the value obtained by dividing $-\Delta h_i(CH_2Cl_2)$ by 0.15 J/m^2, are relatively close (0.15 J/m^2 is an average obtained in this laboratory with different non-porous carbons). The 'c' values of the BET model[4] are also similar, and therefore one might conclude that, like sample Hoechst and NG-2700, the various blacks are non-porous. However, the comparison of the CH_2Cl_2 isotherms with the corresponding data for sample Hoechst shows that all other samples present some degree of microporosity (Fig. 2). From the linear sections and the extrapolated intercepts of the comparison plots, one obtains the external surface areas S_e and the pore volumes V_p

Table 2. Non-porous surface area S_e and pore volumes V_p obtained from the comparison plots of the CH_2Cl_2 (293 K) isotherms with sample Hoechst

Carbon black	XYL-NE	XC-72	ACET-NE	T-5500	NG-2700
S_e (m^2/g)	96	145	141	118	95
V_p (cm^3/g)	0.006	0.038	0.016	0.035	–

Table 3. Characteristics of the carbon blacks obtained from eqns (1)-(3) and from the decomposition of the adsorption isotherm (S_e)

Carbon black	W_0 (cm^3/g)	E_0 (kJ/mol)	L (nm)	S_{mi} (m^2/g)	S_e (m^2/g)	S_{tot} (m^2/g)
XYL-NE	0.017	24.7	0.8	43	90	133
XC-72	0.061	23.5	0.9	137	123	260
ACET-NE	0.031	23.1	0.9	66	127	193
T-5500	0.104	19.5	1.3	160	80	240
NG-2700	(0.052)	11.4	—	—	90	90
HOECHST	(0.032)	9.6	—	—	52	52

of these solids (see Table 2). At this stage, it must be pointed out that the values of V_p are relatively inaccurate, since small variations in the linear section of the comparison plot can lead to relatively large differences in the ordinate. Moreover, the comparison plot does not provide information on the actual pore sizes and therefore the following approach, based on Dubinin's theory, is recommended.

From the classical D-R plots[3,4] applied to the low-pressure domain of the adsorption isotherms, one obtains parameters W_0 and E_0 given in Table 3. Linear sections are found in the various D-R plots but, in the case of Hoechst and NG-2700, the low values of E_0 exclude the presence of microporosity. This is suggested by experience gained from the study of active carbons. In this case, the linearity of the plots indicates rather an adsorption process of the Dubinin-Radushkevich-Kaganer type[9,10], sometimes observed with open surfaces. Under these conditions, the limiting amounts should correspond to extrapolated monolayer capacities, but in the present case they are not very accurate (73 and 119 m^2/g, respectively).

As expected, it appears that the micropore volume W_0 is different from the volumes V_p derived from the comparison plots, but the latter is only indicative. On the other hand, from eqns (2)-(4), one obtains the average micropore widths L and the surface areas S_{mi} and S_e of the microporous carbon blacks. Inspection of Tables 2 and 3 shows that the value of S_e obtained from the comparison plots (Table 2) and from the decomposition of the isotherm[1] (Table 3) are in good agreement. On the other hand, the values of S_e obtained from eqn (4) are systematically smaller, in particular for T-5500 (only 28 m^2/g). The total surface area of the microporous samples, S_{tot} are relatively close to S(BET) and S_t, but this is fortuitous and misleading, since their meanings are different.

In the case of sample XC-72 (Fig. 3), the presence of microporosity is also revealed independently by molecular sieve experiments carried out with probes of different sizes[3,5,8].

On the basis of the total surface areas S_t of the carbon blacks, one obtains the specific heats of immersion into water at 293 K. The corresponding values in J/m^2 are: 0.044 (XYL-NE), 0.036 (XC-72),

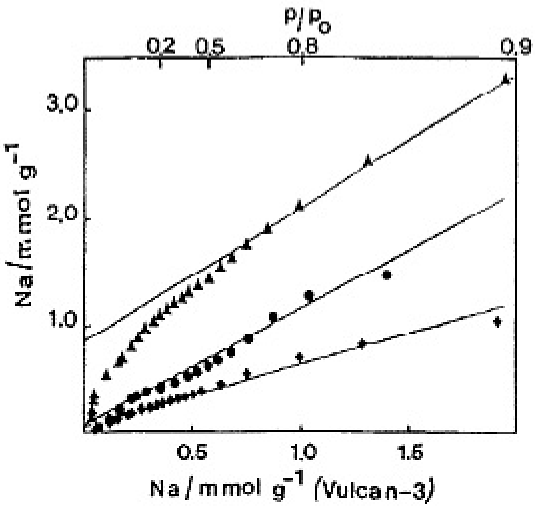

Fig. 1. Comparison plots for the C_6H_6 isotherms of carbon blacks XC-72 (▲), NG-2700 (●), and Hoechst (◆). Vulcan-3 is the reference material.

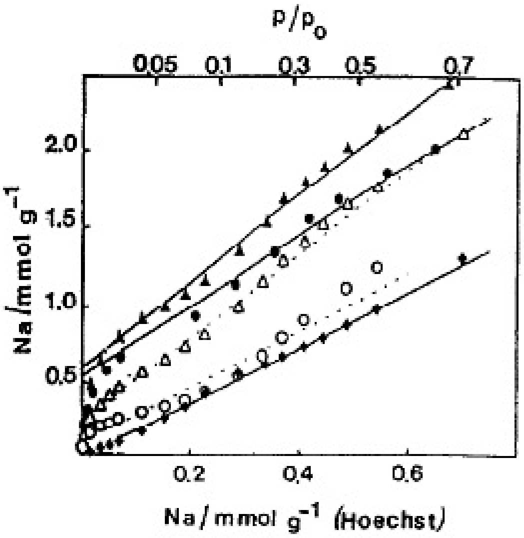

Fig. 2. Comparison plots for the CH_2Cl_2 (293 K) isotherms of XC-72 (▲), T-5500 (●), ACET-NE (△), XYL-NE (○), and NG-2700 (◆). The reference material is sample Hoechst.

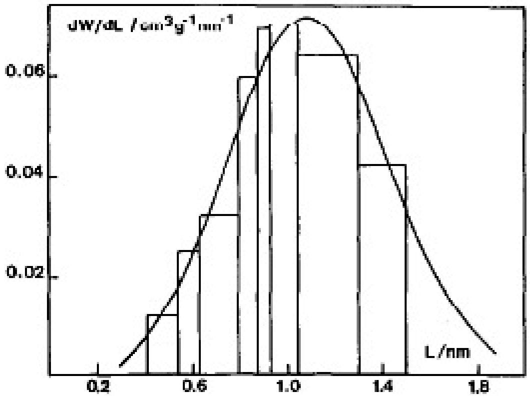

Fig. 3. The micropore distribution of carbon black XC-72 obtained from molecular-sieve experiments.

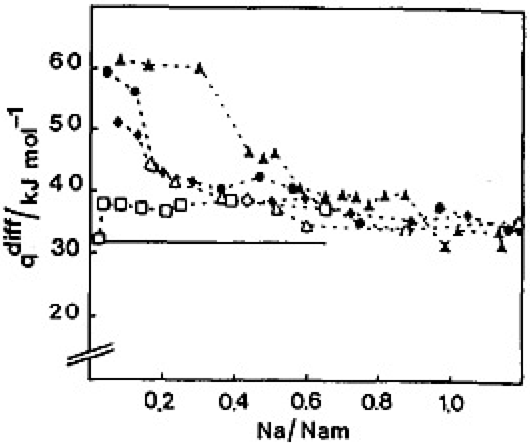

Fig. 4. The differential heats of adsorption q^{diff} of CH_2Cl_2 (293 K) vapour on samples XC-72 (▲), T-5500 (●), ACET-NE (◆), XYL-NE (△) and NG-2700 (□).

0.061 (ACET-NE), 0.039 (T-5500), 0.029 (NG-2700), 0.063 (Hoechst).

Finally, the differential heat of adsorption of CH_2Cl_2 vapours at 293 K (Fig. 4) also suggest the presence of microporosity in samples XYL-NE, XC-72, ACET-NE and T-5500. The relatively high values of 50-60 kJ/mol correspond to the adsorption of the same vapour by typical active carbons[7] and the drop in the differential heat of adsorption is in good agreement with the expected filling of the micropore system W_0. In the case of sample NG-2700, on the other hand, q^{diff} remains close to 40 kJ/mole, the value reached for the other blacks when the micropores are filled. Moreover, the enthalpy of immersion into dichloromethane calculated from the integral heat of adsorption is equal to 9.9 J/g, compared to an experimental value of 10.9 J/g (Table 1). This indicates consistency between the different experiments.

The data presented here illustrate the degree of information that can be obtained, depending on the techniques used. It is obvious that they are not needed simultaneously, unless a check for self-consistency is required, or the carbon under investigation presents unusual difficulties. However, it appears that Dubinin's theory provides the safest way to characterize a porous carbon black.

REFERENCES

1. J. B. Donnet, R. C. Bansal, and M. J. Wang, *Carbon Black*, Marcel Dekker, New York (1993).
2. P. J. M. Carrott, R. A. Roberts, and K. S. W. Sing, *Carbon* **25**, 59 (1987).
3. J. B. Donnet, R. C. Bansal, and H. F. Stoeckli, *Active Carbon*, Marcel Dekker, New York (1988).
4. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London (1982).
5. H. F. Stoeckli, P. Rebstein, and L. Ballerini, *Carbon* **28**, 907 (1990).
6. H. F. Stoeckli and F. Kraehenbuehl, *Carbon* **19**, 353 (1981).
7. H. F. Stoeckli, D. Huguenin, and A. Greppi, *J. Chem. Soc. Faraday Trans.* **89**, 2055 (1993).
8. H. F. Stoeckli, D. Huguenin, and A. Laederach, *Chimia* **47**, 211 (1993).
9. M. G. Kaganer, *Zh. Fiz. Khim.* **33**, 2202 (1959).
10. W. Rudzinski and D. H. Everett, *Adsorption of Gases on Heterogeneous Surfaces*, Academic Press, London (1992).