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CHANGES IN THE MICROPORE STRUCTURE OF STRONGLY ACTIVATED CARBONS, INDUCED BY LARGE ADSORBATE MOLECULES

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Abstract—Adsorption of molecules with increasing sizes, by strongly activated carbons, is characterized by a restricted accessibility of the micropore system for relative pressures $p/p_0 < 10^{-3}$ approx. The adsorption capacity at low pressures increases with successive adsorption–desorption cycles. The adsorption of relatively small molecular probes, considered in the light of the generalized equation proposed by Stoeckli, suggests that substantial but largely reversible modifications are induced in the micropore system by the large adsorptives. This is also in agreement with the results obtained from the heats of immersion of a heterogeneous carbon into benzene and tertiobutyl-benzene, before and after treatment with tertiobutyl-benzene.

1. INTRODUCTION

The three-parameter equation recently proposed by Stoeckli[1–3], for adsorption by strongly activated carbons, gives information on the heterogeneity of the micropore system[3, 4]. It is an extension of the well-known equation of Dubinin and Radushkevich[5, 6] or D–R equation,

$$W = W_0 \exp\{-(B(T/\beta)^2 \log^2(p_0/p)\}, \quad (1)$$

where W_0 is the total volume of the micropores, and W represents the volume filled at relative pressure p/p_0 and temperature T. The specific parameters B (structural constant) and β (affinity, or similarity coefficient) depend respectively on the solid and on the adsorptive. The generalization proposed by Stoeckli is based on the observation that eqn (1) is followed over a large range of pressure and temperature in the case of adsorption by carbons with molecular-sieve properties, whereas strongly activated carbons show significant deviations from it. Postulating that, in the case of total accessibility of the micropore system, adsorption consists of a weighted sum of D–R equation, one obtains the generalized equation

$$W = W_0 \exp\{-B_0 y\} \exp\{y^2\Delta^2/2\} \cdot [1 - \mathrm{erf}(z)]/2. \quad (2)$$

The quantity $y = (T/\beta)^2 \log^2(p_0/p)$ is a generalized coordinate, $z = (y - B_0/\Delta^2)\Delta/\sqrt{2}$, and Δ is a measure of the spread of B around B_0, if one assumes a Gaussian distribution of the micropore volume W with B. Since B is related to an average pore-size[2, 5, 6], Δ reflects its spread.

Equation (2) is a possible generalization for adsorption by heterogeneous systems of micropores within the framework of Dubinin's theory for the filling of micropores[5, 6]. This equation describes the adsorption isotherms of type B, according to the classification of Rand[7], which show an upward curvature in the representation of ln W vs $\log^2(p_0/p)$ or y. This curvature gradually appears with increasing activation, as shown by Marsh and Rand[7, 8] for the case of CO_2 adsorbed at 195 K by polydivinylbenzene carbons.

These authors also report examples of downward, or type A deviations from linearity[7], occurring at relative pressures $p/p_0 < 10^{-2}$ (CO_2 adsorbed at 195 K by activated polyfurfuryl alcohol carbons). This type of deviation disappears with increasing activation (and increasing structural constant B), which suggests that it is connected with restricted entry at low pressure, suppressed by activation.

In the present paper we show that type A deviations can also be observed in the case of adsorption of larger molecules by strongly activated carbons, where small molecules (N_2, Ar, Kr, Xe, SF_6, N_2O and C_6H_6) lead to type B deviations. Moreover, the adsorptivity of the larger molecules gradually increases with the number of adsorption–desorption cycles. It seems that this particular effect has not received attention in the past.

2. EXPERIMENTAL

All adsorption measurements were carried out with a spring balance (Mc Bain type) and a "Mettler" microbalance. Pressures were measured with transducer gauges, covering the range from 10^{-4} to 10^3 mm Hg. The experimental procedure is described in detail elsewhere[9].

The enthalpies of immersion of carbon U-O2 in benzene and in tertiobutyl-benzene were measured by one of us (A.P.) at the School of Chemistry, University of Bristol U.K., with a calorimeter of the "Calvet" type.

The active carbons used in this study, series U and F and the molecular-sieve "Carbosieve", have been fully characterized previously[2–4, 6, 9–11].

3. THE ADSORPTION OF VAPOURS OF RELATIVELY LARGE MOLECULES

Our systematic investigations were carried out with adsorptives of increasing molecular complexity, such as

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toluene, chlorobenzene, tertiobutyl-benzene and tri-methyl-phosphate[11]. They reveal a break-down in the applicability of the D–R eqn (1) at low pressures.

As illustrated by the classical plots of ln *W* vs $\log^2(p_0/p)$ of Figs. 1–3, one observes type *A* deviations for $\log^2(p_0/p) > 9$ or even less. It is found that adsorption is systematically smaller than predicted by the linear D–R branch, which is always followed at higher pressures. The variable uptake of larger molecules in the low pressure region can not be described in terms of a modified D–R equation, and it appears to be linked with structural modification in the micropore system itself.

As illustrated by Figs. 1 and 2, the phenomenon varies from one type of active carbon to the other. The general trend observed with our well characterized active carbons, is an increase in the adsorption capacity at the lower pressures, with increasing numbers of adsorption–desorption cycles. However, the limiting behaviour, reached after 3–4 cycles, may vary considerably from one type of carbon to the other. In the case of the molecular sieve (Fig. 2), the adsorption capacity for toluene, at low pressures, does not increase as much as in the more activated and heterogeneous carbon U–O2 (Fig. 1). Both carbons have been investigated by small angle scattering of *X*-rays[4] and by transmission electron microscopy at high resolution[10]. It appears, that the molecular sieve has a relatively dense structure, with homogeneous micropores. Carbon U–O2, on the other hand, appears to be less dense and it has a very heterogeneous micropore system, including some mesoporosity[11]. Typical micrographs of the structure[10] suggest that some exfoliation of the elementary aromatic sheets could take place in this carbon (*V*-shaped entrances to micropores).

As shown in Figs. 1 and 3, the increase in the adsorption capacity of large molecules by carbon U–O2 is largely reversible: the repetition of the adsorption–desorption cycles leads to the same pattern when the solid has been left *in vacuo* for 6–8 weeks.

The increase in the adsorption capacity at low presdures may be caused either by the gradual and reversible removal of constrictions leading into the micropores, or by more substantial modifications in the micropore system, under the influence of the adsorbate. The experimental evidence, given below, suggests that the latter mechanism takes place, in particular with the heterogeneous carbons of series F and U. Evidence for structural modifications in active carbons, on adsorption, is already provided by the work of Bangham *et al.*[12], and more recently by Dacey and Evans[13]. The latter experiments show that a reversible swelling can already occur in the micropore system, under the influence of molecules such as benzene. However, this swelling is only observed while the adsorbate is present. In our case, the occurrence of transitory but significant changes in the micropore structure, induced by larger molecules around the constrictions, is suggested by two independent experiments:

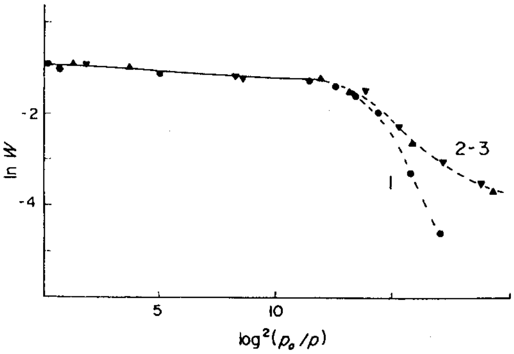

Fig. 2. The successive adsorptions of toluene vapours by the molecular-sieve "Carbosieve", at 293 K.

(1) The adsorption of simple molecular probes, before and after the adsorption–desorption cycles with the larger adsorbates.

As shown by the results of Table 1, obtained for carbon U–O2 and illustrated by Fig. 4, the adsorption of N_2 (78 K) and N_2O (293 K) reveals significant changes in parameters B_0 and Δ of the D–R–S eqn (2).

It appears, that after three adsorption–desorption cycles of tertiobutyl-benzene (Fig. 3), the average poresize in carbon U–O2 is shifted towards higher values (increase in B_0). At the same time, the heterogeneity increases, as shown by the increase in parameter Δ[2, 4]. This suggests that under the influence of the larger molecules, the pore-size distribution is slightly shifted

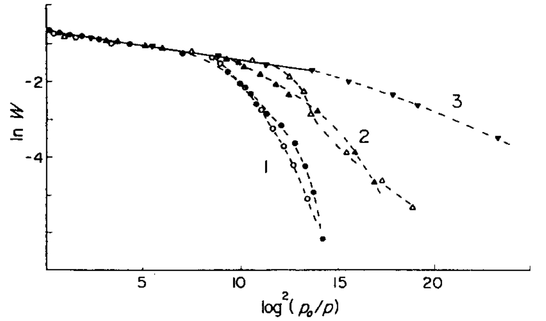

Fig. 1. Successive adsorptions of toluene vapours by carbon U–O2, at 293 K (1–3). The closed and open symbols correspond respectively to the initial series of adsorption–desorption experiments, and to its repetition 8 weeks later.

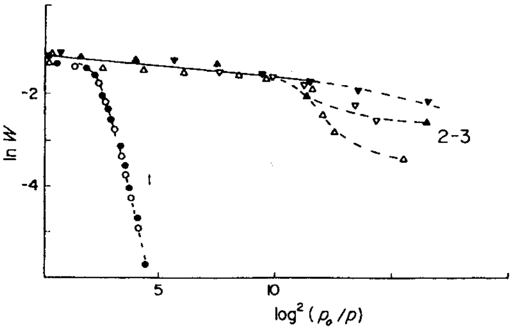

Fig. 3. The adsorption of tertiobutyl benzene by carbon U–O2, at 293 K. The conditions are the same as for toluene in Fig. 1.

Table 1. Properties of active carbon U-02, before and after treatment with tertiobutyl-benzene

	W_0 (cm^3/g)	$B_0.10^6$ (K^{-2})	$\Delta.10^6$ (K^{-2})	ΔH_i (J/g solid)	
				Benzene	t butyl – benzene
Initial carbon	0.46	0.90	0.19	117.3	114.3
After treatment	0.47	1.22	0.39	119.8	122.4

towards supermicropores. On the other hand, the total volume of the micropores W_0 is not modified in a significant way. These features, revealed by the use of molecular probes and the D–R–S eqn (2), do not appear clearly in the classical D–R representation obtained from the adsorption data of the larger molecules themselves.

(2) The determination of the enthalpies of immersion ΔH_i of the carbon, before and after treatment with tertiobutyl-benzene.

Table 1 gives the values of ΔH_i obtained for carbon U–O2 at 31°C, in benzene and tertiobutyl-benzene. In the case of benzene, for which the solid shows total accessibility in both cases, the enthalpy of immersion is slightly larger after the treatment. The increase of 2% is comparable with the increase in the micropore volume from 0.46 to 0.47 cm^3 (the error on W_0 is approx. ± 0.005 cm^3/g).

In the case of tertiobutyl-benzene, on the other hand, one observes a much larger difference (8J/g) between the treated and the initial solid. Since the final state of both samples is the same after immersion in tertiobutyl-benzene, the difference in ΔH_i may be ascribed to the work needed for the deformation of the micropore structure in the untreated sample. The structural modifications are likely to occur around the constrictions.

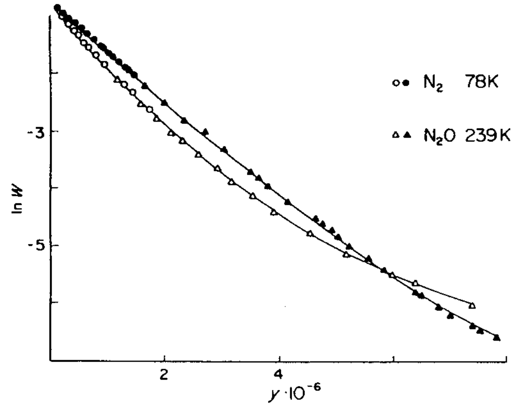

Fig. 4. Adsorption of N_2(78 K) and N_2O(293 K) by carbon U–O2 before (closed symbols) and after (open symbols) three adsorption-desorption cycles with tertiobutyl-benzene at 293 K. The data are represented in the logarithmic form of eqn (2).

The corresponding work is more important than the enthalpy change arising from the reversible swelling accompanying adsorption[13], and which is relatively small[14].

Our experiments also suggest that care has to be taken in the interpretation of heats of immersion, obtained from series of liquids and used for the determination of equivalent surface areas in certain microporous carbon. In the present example, very different values of ΔH_i are obtained with tertiobutyl-benzene, although the total micropore volume accessible to it has only increased by 2%. This problem will be investigated in detail later.

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