Study by Gas-Chromatography of the Variation of the Adsorptive Properties of a Graphitized Carbon Black Upon Air Activation

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Introduction

Gas chromatography is of considerable interest studying adsorption at finite surface coverage, because it allows easily to measure the uptake over a wide range in temperature (1). This method provides a means to determine adsorption isotherms, London components of the surface free energy and equations of state. This method we have already used in a previous paper (2) in the case of several n-alkanes adsorbed on graphite and graphitized carbon blacks.

It is known that surface area and surface homogeneity of carbon blacks progressively change when they are activated in air. Thus, it has been reported (3) that graphitized carbon black, V3G, increases its surface area and surface heterogeneity with the above treatment, affecting these properties to the dispersion of Pt when these solids are used as supports for this metal (4,5).

In this communication we report how the benzene adsorption changes when increasing the B.O. of the V3G. Adsorption isotherms were obtained by gas-chromatography, together with other surface characteristics of the adsorbents.

Experimental

A graphitized carbon black (V3G) has been used in this work. This carbon was treated in a flow of dry air (100 $cm^3.min^{-1}$) at 873K and at different periods of time to obtaine several percentages of B.O. After that and in order to eliminate the oxygen surface complexes that might be fixed during the air treatment, the samples were heated in a flow of N_2 at 1173K for 2 h. Samples will be referred to as V3G followed by the total percentage of B.O. Sample V3G-77.7%(ox) is a sample without the N_2 treatment, thus some oxygen surface complexes will be left on it after the air treatment. When this sample was treated in N_2 at 1173K for 2 h it gave sample V3G-79.4%.

Nitrogen surface area (S_{N_2}) of all samples was obtained from the BET method applied to the adsorption isotherm at 77K. A value of 0.162 nm^2 was taken for the area occupied by a N_2 molecule at that temperature.

Chromatographic measurements were carried out in a Carlo Erba gas-chromatograph, model Fractovap 2350 using FID. N_2 was the carrier gas at a flow of 15 $cm^3.min^{-1}$. Before adsorption runs the column with the adsorbent was preconditioned at 473K for 12 h in N_2 flow. Benzene adsorption was performed at 333K injecting several amounts of the adsorbate. Adsorption isotherms were obtained by the peak maxima elution method (6). The data obtained were corrected for the sorption effect according to Conder's analysis (7). Details of the method are given elsewhere (2).

Results and Discussion

Adsorption isotherms of benzene at 333K on the adsorbents are depicted in Figure 1. As it is expected the benzene adsorption increases when increasing the percentage of B.O of the adsorbent. From these isotherms surface area of the adsorbents ($S_{C_6H_6}$) were obtained by applying
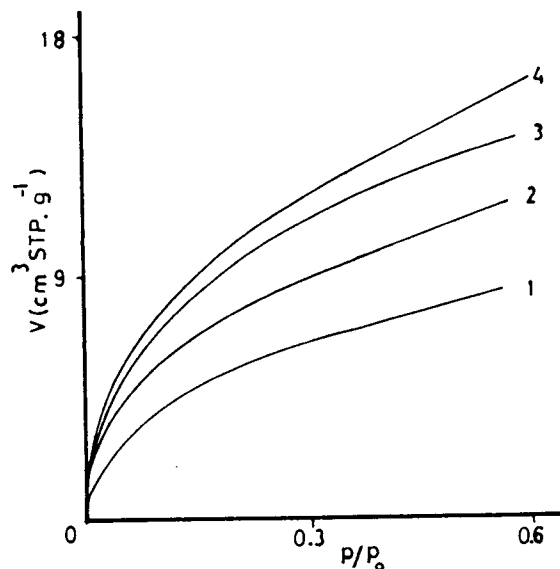

Figure 1. Adsorption isotherms of benzene at 333K on: 1, V3G; 2, V3G-28.2%; 3, V3G-50.1% and 4, V3G-79.4%.

the BET method. These values together with the S_{N_2} values are given in Table 1. The area occupied by a benzene molecule at 333K was obtained from the S_{N_2} value of V3G and the monolayer capacity obtained from the BET method applied to the benzene isotherm on that solid. The resulting value was $0.461 \ nm^2$. It is seen in Table 1 that $S_{C_6H_6}$ of samples increases with the percentage of B.O. of the V3G. This increase of $S_{C_6H_6}$ keeps a linear relationship with the %B.O., within the range here studied, giving the least square method applied to our data a correlation coefficient of 0.9998.

Table 1. Characteristics of the adsorbents

Adsorbents	S_{N_2} $m^2.g^{-1}$	$S_{C_6H_6}$ $m^2.g^{-1}$	γ_2^L $mJ.m^{-2}$	Π $mJ.m^{-2}$
V3G	62.1	62.1	86.3	1.7
V3G-28.2%	96.6	81.8	94.6	0.6
V3G-50.1%	126.1	97.8	96.0	0.4
V3G-79.4%	160.8	117.0	97.3	0.2
V3G-77.7%(ox)	–	115.8	108.4	–

London component of the surface free energy of the solid, γ_2^L, may be obtained from the adsorption data (2,8). These values are given in Table 1. It can be seen that the variation of this parameter with the %B.O. of the V3G does not present the same trend as the surface area. The relationship seems to be parabolic with the highest increase in γ_2^L up to a 28.2% B.O, and hereafter increasing γ_2^L slowly up to a 79.4% B.O. Therefore the surface heterogeneity of the V3G does not change with the B.O. as the surface area does.

From Table 1, if we compare the data obtained for V3G-79.4% and V3G-77.7%(ox) samples, it can be seem that the oxygen surface complexes introduced during the air treatment do not change the $S_{C_6H_6}$ value but essentially increase the γ_2^L value, that is the surface heterogeneity of the carbon.

Adsorption data also allow to obtain the equation of state, assuming that the gas adsorbed on the surface behaves as a two-dimensional gas (2). Thus, equations of state for the benzene-adsorbent systems were calculated, obtaining the surface pressure, Π, below which the adsorbate behaves as an ideal gas. These data are summarized in Table 1. It is seen that Π values decrease with the %B.O., following nearly the same trend that the γ_2^L values.

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