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Fractals in geometry of carbon black

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Abstract - The fractal dimension was evaluated on the bases of the experimental results on the adsorption of nitrogen, phenol, aerosol OT, CTAB and narrow fractions of polymers (polyethylene glycole and dextranes). The fractal dimension dependences on the oxidation duration were considered for two samples of carbon black.

INTRODUCTION

Dubinin has developed the method molecular probes for microporous activated carbons (refs. 1,2). This method is based on the geometrical relationship between the pore sizes of adsorbent and the sizes of the vapour molecules of the substances. Later this approach was used in studying the mesoporous structure for adsorbents of different chemical nature by analysis of the equilibrium adsorption isotherms for narrow fractions of polymer (refs. 3,4).
It is known that carbon black is characterized by the disordered structure. Carbon black particles consist of fused primary particles having a complex form and curved surface relief. It is difficult to describe such complex secondary structures of carbon black by the methods of Euclidean geometry. The method of fractal geometry developed recently opens wide opportunities for the description of geometric and mass parameters of disordered structures (refs. 5 - 9).

Adsorption measurements permit to estimate the main parameter of fractal geometry - fractal dimension (refs. 10 - 12). In adsorption measurements the adsorptives with molecules of different form and size act as an instrument of the fractal geometry. This paper presents the analysis of the surface fractal dimensions for oxidized carbon blacks using the adsorption of nitrogen, phenol, aerosol OT, CTAB and narrow fractions of polymers.

THEORY

Theoretical approach to the determination of the fractal dimension of the particle surface on the basis of the analysis of the cummulative distribution curve is connected with the interpretation of accessability characteristics of complex surface and curved relief of powder particles. The regularity found experimentally - dependence of the particle surface area on the size of the marker - was assumed as a basis of this approach. This regularity implies increasing the values of the surface area of the fine adsorbent being measured with lowering the molecular size of adsorbtives serving as the markers and underlies the method of determination of the surface fractality of powder of solids. At present the fractal conception is widely used for description of fractal geometry of structurized systems as a function of resolving power (resolution scale).

Therefore if a property of the system being measured depends on the meter sizes (resolving power) the system is characterized by fractal structure. The dependence of the surface being measured, y, on linear dimensions of the meter molecules, x, may be described by a power function (refs. 5, 6):

$$y = a\, x^{D_t - D_g(x)} \qquad (1)$$

where D_t - expected topological dimensions and D_g - dimension of fractals in the range of x-linear dimensions of meter molecules. In this case the dimension becomes a measure of a structure gradation when real properties of the structure or its geometric parameters are compared to topological properties of the system for a given parameter within certain scale interval. The dimension of the structurized fractal system differs from that of a topological system.

The value of the fractal exponent $D_t - D_g$, i.e. the excess dimension, may vary in different scale intervales in accordance with the change of the degree of the system disorder. Thus the fractal exponent defines the degree of a structural organization of the system, predetermined by geometric and statistical laws of the substructure formation. If in some scale interval the dependence $D_t - D_g$ on the scale is not found then $D_g = 0$. If the degree of gradation is constant in a wide scale interval, the fractal exponent $D_t - D_g = b = \text{const.}$, i.e. the system of fractals becomes self-similar. In the self-similar structure the resolution scale cannot be obtaind from the degree of the structurized organisation for any particular model. In the case of self-similarity the fractal relation becomes a power function of the following form:

$$y = a\, x^{b} \qquad (2)$$

For this structure the plot log y vs log x is represented by a straight line with the slope $b = D_t - D_g$. Real structurized systems possess self-similarity only in a limited region of x and are connected with the upper and lower limits of x.

The surface of a porous solid is considered to be fractal if the surface area of particles of the structurized system is characterized by $D_t - D_g(x)$ and if both the volume of a solid and the pore volume change along with the sample volume in the total scale interval. The fractal dimension (or fractality) $D_g(x)$ of the surface area of structurized system particles is determined by the nature as well as by the properties of a marker. The fractality of pores reveals itself only when the surface and the pore volume change in the same way as the dimension D, and the adsorbent volume - as the total volume of the material.

The direct analysis of the surface fractality comprises the determination of the dependence of number of molecules n_m in a monolayer on a molecule radius r, i.e. :

$$n_m = a\, r^{-D} \qquad (3)$$

Together with it there must be the chemical affinity of the surface for adsorbate molecules, expressed in almost complete absence of specific interaction with polar molecules of an adsorbate. For flexible chain molecules capable of arranging themselves along the adsorbent surface the surface fractality of a porous body is characterized by the topological dimension $D_t = 2$.

EXPERIMENTAL

The objects of this study were samples of carbon black P 234 (ref. 14) and P 245 (ref. 15) oxidized with the atmospheric oxygen at 653 K and then treated in He stream at 1173 K for 3 h. This treatment almost completely eliminates oxygen containing groups from the surface of carbon black particles. After the thermal treatment the samples were cooled in the stream of inert gas and stored in a desiccator in the atmosphere of nitrogen up to the begining of the experiment. Oxidizing and thermal treatment of carbon black particles noticeably changes the topography and the energy of their surface.

Fig. 1 shows the projection of a stereomicrophotocopy of an isolated secondary particle of carbon black Vulcan 3 (ref. 16). Carbon black particle presents a unity of fused precursors (primary particles), on the surface of which precipitation of pyrocarbon took place. The structure of such a particle is characterized by a complex relief of the pore surface. Oxygen treatment of carbon black results in the burn-out of the carbon between crystallites, appearance of pores comparable to adsorptive molecule and increase in the surface area S (Table 1). Values of S were calculated from a common formula:

$$S = N_A \, n_m \, r^2 \qquad (4)$$

where N_A is the Avogadro number, n_m is the monolayer capacity, r is the adsorbtive molecule radius.

The following oligomers and polymers were used: polyethylene glycols with molecular weight MW 200, 620, 980, 3000, 5800, 6500, 22000 and 41500 and dextranes with MW 19200, 41300, 68800, 112000, 285000, 495000 and 2000000. The measurements of polymer adsorption carried out by static method from water solutions at room temperature. The static method for study of liquid phase adsorption was described in detail in (refs. 3, 4). The concentration change due to adsorption was determined using the differential liquid refractometer. The adsorption value n was calculated from static experiments as

$$n = m \, \Delta c \, / \, m_a \qquad (5)$$

where m and m_a are the masses of the polymer solution and the adsorbent, respectively, Δ c is the change in concentration of the polymer solution after adsorption.

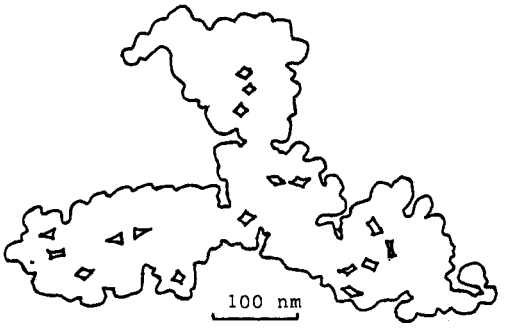

Fig. 1. Projection of an isolated particle of Vulcan carbon black

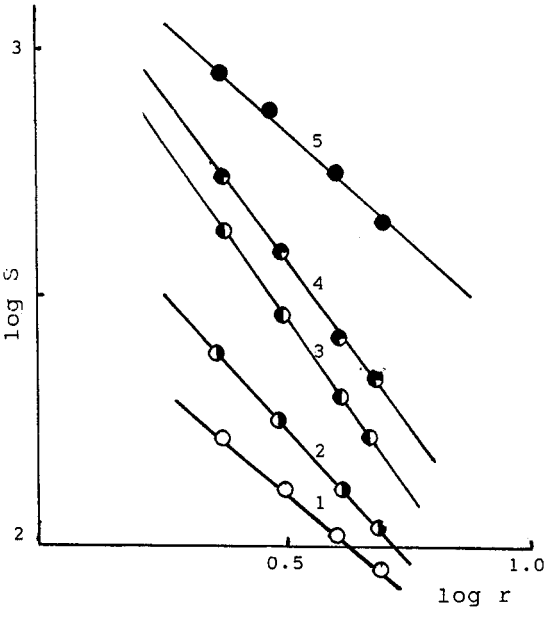

Fig. 2. Fractal analysis of the surface for carbon black P 245. Oxidation time: 10(1), 20(2), 40(3), 50(4) and 190(5) hours

RESULTS

Fig. 2 and Table 1 show that the dimension of fractals D is varied from 2.8 to 3.4. Depending on the duration of the treatment of carbon black particles a process of disordering of the pore structure of particles takes place first followed by a tendency to lowering the disorder in these structures. The linear character of log S / log r relation testifies to a self-semilarity of carbon black structures in the range of r from 0.23 to 0.48 nm (Fig. 2).

Table 1. Characteristics of oxidized samples of carbon black P 245 (in the brackets molecules radius, nm)

Oxidation duration, h	Mass loss,%	Specific surface area, S , m^2 g^{-1}				Fractal dimension, D
		nitrogen (0.23)	phenol (0.31)	CTAB (0.40)	aerosol OT (0.48)	
10	6	170	130	110	90	2.8
20	10	260	190	120	110	3.1
40	17	460	300	200	170	3.4
50	22	570	400	270	230	3.3
190	68	970	930	640	480	2.9

Fig. 3 illustrates the dependences of the maximum adsorption values n_{max} of water-soluble polymers (dextranes and polyethylene glycols) on hydrodynamic diameter ϕ of the coil of a flexible chain molecule. The hydrodynamic diameter was estimated from the Flory-Fox formula (ref. 17). The expression for the diameter of a coiled macromolecule will be the following:

$$\phi = (M^{1 + a} K / F)^{1/3} \qquad (6)$$

where K and a are the coefficients characterizing the interaction energy of polymer with the solvent. Flory constant F was assumed to be equal to 2.6×10^{21} $mole^{-1}$. Linear relations log n_{max} / log ϕ indicate the self-similarity of the structure of carbon black particles in the range of ϕ from 4 to 100 nm (Fig. 3).

Table 2 presents experimental values of the fractal dimension D for the surfaces of the oxidized samples of carbon black P 234. The mean mesopore diameter was calculated from the curves of differential distribution of pore volume. These distributions were found from the n_{max} dependences on the ϕ - values.

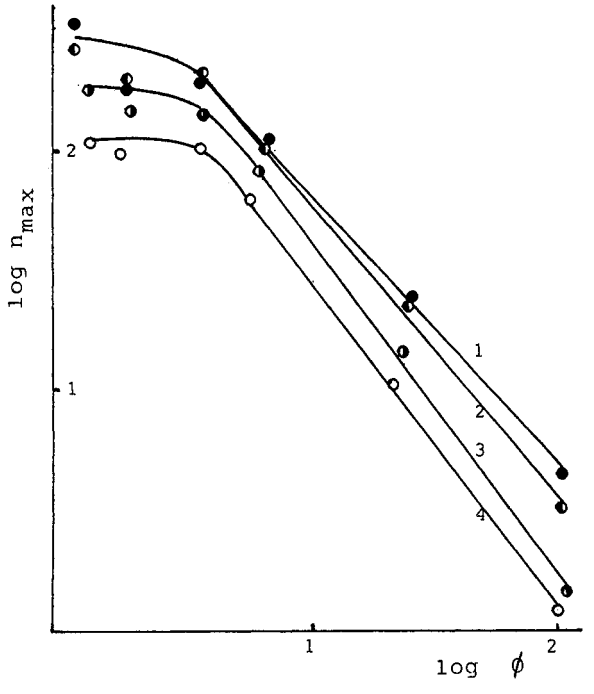

Fig. 3. Fractal analysis of the surface for carbon black P 234; n_{max} is maximum adsorption value, mg g^{-1}; ϕ is the macromolecule hydrodynamic diameter, nm; thermooxidative treatment duration: 40(1), 63(2), 20(3) and 5(4) hours

Table 2. Structural characteristics of the oxidizing samples of carbon black P 234; τ is the oxidation duration, S_{BET} is specific surface area, d is the mean mesopore diameter, D is the fractal dimension

Sample No.	τ, h	S_{BET}, m^2 g^{-1}	d, nm	D
1	0	150	24	2.8
2	20	220	25	2.6
3	40	280	22	2.5
4	63	400	21	2.0

It can be seen from Table 2 and Fig. 3 that all oxidized samples of carbon black P 234 are characterized by the fractal structure of surface. The oxidation causes the ordering of the surface structure owing to the burning of the disordered part of carbon particle.

Thus the structures of carbon black particles may be described within the frame work of fractal geometry. The value of the surface fractal dimension found for these particles testify to the change in the structure ordering in the process of thermooxidative treatment as well as to the self-affinity of these structures in certain scale intervals.
Further research on the fractality of carbon black structures by independent methods will lead to a better understanding of the influence of different factors on the structure formation in these systems.

CONCLUSION

The dependences of maximum adsorption values for carbon blacks on the macromolecular coil sizes of water soluble polymers allowed to evaluate the fractal dimension of adsorbent surface. The decrease of the fractal dimensions indicated the ordering of carbon black structure after the progressive oxidation.

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