Correlation between crystal texture and microporous structure of carbon adsorbents

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A correlation of adsorption and X-ray data for a series of both initial and modified active carbons (AC) was performed. The AC were modified by thermal treatment and progressive activation. A linear correlation between the sizes of crystallites and micropore widths of AC was established. It was shown that the adsorption of water vapor results in an increase in the parameter L_a of crystallites of active carbons.

Key words: carbon adsorbents, X-ray diffraction, microcrystallites, micropores, adsorption, water vapor.

Carbon adsorbents have been studied for a long time using various physicochemical techniques; nevertheless their structure remains insufficiently clear. X-ray diffraction analysis of active carbons (AC) allows one to obtain information on that part of the structure of the adsorbent that retains a graphite-like structure. These are small regions, crystallites, that are surrounded by an amorphous phase.[1,2] Crystallites are relatively rigid formations, as compared to neighboring amorphous carbon,[3] that are improved in the course of thermal treatment both because of transformation of "non-ordered" carbon to a graphite-like state by removal of a fraction of CH_2 groups (more dense packing of layers arises) and because of substitution of CH_2 groups for C—C bonds; as a result, neighboring layers coalesce, and the diameter of the crystallite, L_a, increases.

In this work, a comparative analysis of changes in the structural sizes of crystallites and adsorption characteristics of AC that occur upon modification by thermal treatment and progressive activation is performed. The establishment of the relation between structural parameters of AC determined on the basis of both adsorption measurements and the X-ray diffraction method can extend the concept on the structure of AC.

Experimental

X-ray diffractograms were recorded on a DRON-3M diffractometer with CuKα radiation (Ni filter) using the reflection scheme from a sample that was previously crushed and rubbed in a round cuvette. The measurements were performed at ~20 °C. It should be noted that any binder that is commonly used for preparation of samples disturbs the true pattern of the interferential maximum (002). The samples of AC prepared without a binder or rubbed with ethanol (polar molecule) or cyclopentane (nonpolar molecule) give different profiles for the (002) maximum. Therefore, all samples were prepared without a binder.

Parameters of the microporous structure of AC, the limiting volume of adsorption space (W_0) and the characteristic energy of adsorption (E_0), were calculated from adsorption isotherms of nitrogen at 77 K with the equation of the theory of volume filling of micropores[4] using the γ/F-method for estimation of the surface of mesopores.[5] A micropore width, $2x_0$, for the slit-like model of pores was determined according to the Stoeckli generalized equation,[6] which connects the $2x_0$ value with characteristic energy of adsorption E_0.

The following samples of AC were studied: AC-**1** — industrial AC of AG-5 type; AC-**2** and AC-**3** — AC-1 which was thermally treated in an argon atmosphere at 1400 and 1600 °C, respectively; AC-**4** — industrial AC of SKT type; AC-**5**—AC-**9** — laboratory wood-based AC obtained by progressive activation; AC-**10**—AC-**13** — furfural-based AC of FAS type obtained by progressive activation; AC-**14** — laboratory AC based on brown coal; AC-**15** and AC-**16** — SKT thermally treated at 900 °C in an atmosphere of NH_3 and Ar, respectively; AC-**17** and AC-**18** — AC of SKT and AC-14 types, respectively, treated with concentrated HNO_3; AC-**19** — industrial molecular-sieve AC of MSC-4A type (Japan); AC-**20** — AC obtained from molybdenum carbide in a laboratory.

Results and Discussion

When AC are calcined at 900 °C in an argon atmosphere, the values of the relative intensities noise to signal ratio, $I^{Ph}{}_{002}/I_{10,}$, decrease, indicating improvement of the structure of the crystallites due to decrease in the fraction of "non-ordered" carbon. With rise in the temperature of thermal treatment, the size of the crystallites increases. An increase in L_a occurs, possibly as a result of stacking of neighboring layers because of the above-described reasons, whereas an increase in L_c can be explained by the joining up of the crystallites into columns at temperatures of 1400—1600 °C.[7] This can

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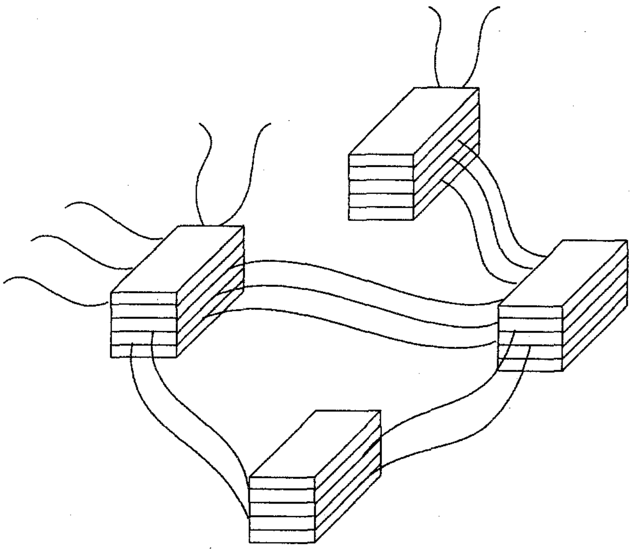

Fig. 1. "Fringed packet" model of active carbons.[1]

result in a change in the ratio between the basic and prismatic surfaces of carbon materials.[8] An increase in L_a and L_c with rise in the temperature of treatment is confirmed by the data presented in Table 1 for AC-1 calcined at 1400 °C (AC-2) and 1600 °C (AC-3). As seen from Table 1, an increase in the size of the crystallites is accompanied by an increase in the size of the micropores; the most pronounced changes are observed in the 1400—1600 °C range. One can suppose that an increase in crystallite sizes results, on the one hand, in a decrease in the number of small micropores because of their "closing" and, on the other hand, in the appearance of larger micropores. This assumption can be explained on the basis of a "fringe-packet" structure of AC[1] (Fig. 1).

Figure 2 presents the schemes of possible modes of the arrangement of crystallites: *a* corresponds to the structure of the initial sample, in which the distances between crystallites are the micropores; schemes *b* and *c* show the structure of AC after calcination at 1400 and 1600 °C.

During progressive vapor-gas activation of the wood-based ACs (AC-5 — AC-9) performed at 900 °C, no substantial changes in L_c are observed; initially L_c drops and then gradually rises. As a whole, L_a values increase during activation although not monotonically.

Table 1. X-ray structural parameters L_a and L_c for the initial and thermally treated AC-1

AY	L_a/nm	L_c/nm	Number of layers
Initial	2.10	1.82	5
Thermally treated at			
1400 °C	2.60	4.15	11(5+5+1)
1600 °C	3.00	7.15	23(11+11+1)

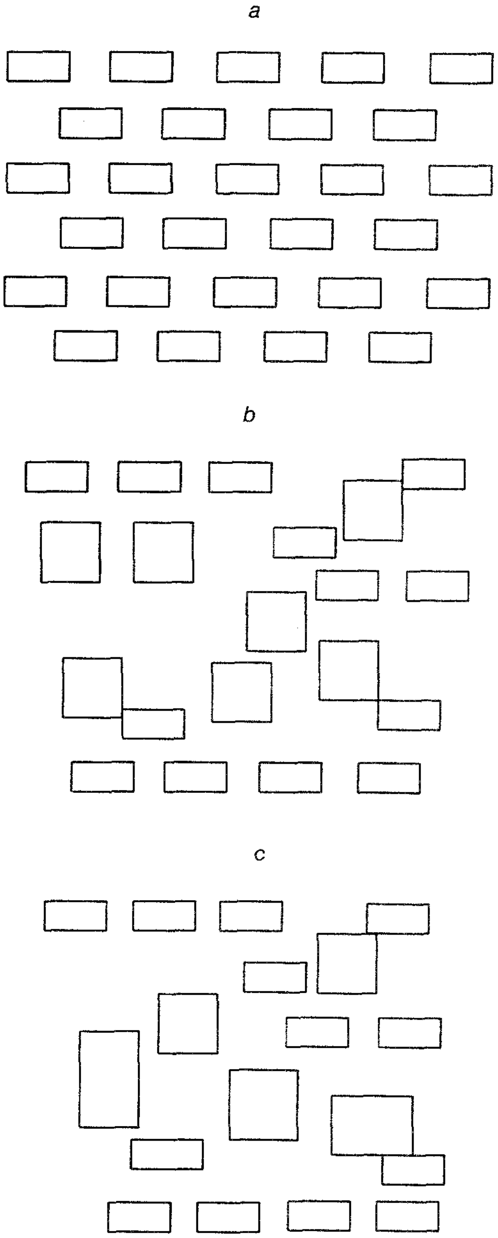

Fig. 2. Schemes of possible variants of the arrangement of crystallites: *a*, initial sample, *b* and *c*, structure of AC after calcination at 1400 and 1600 °C, respectively.

In the course of progressive activation of polymer-based AC of FAS type, the L_a value increases monotically, and the L_c value initially increases and then drops. A decrease in the L_c value can be explained by a gradual burning out of (002) layers rather than by joining of crystallites into columns, which is observed at higher temperatures in an inert gas atmosphere. Burning out of the layers is more likely than the distortion of prismatic faces, because the metallic bond between graphite layers is much weaker than the ionic bond between the edges of neighboring layers, which are formed owing to the

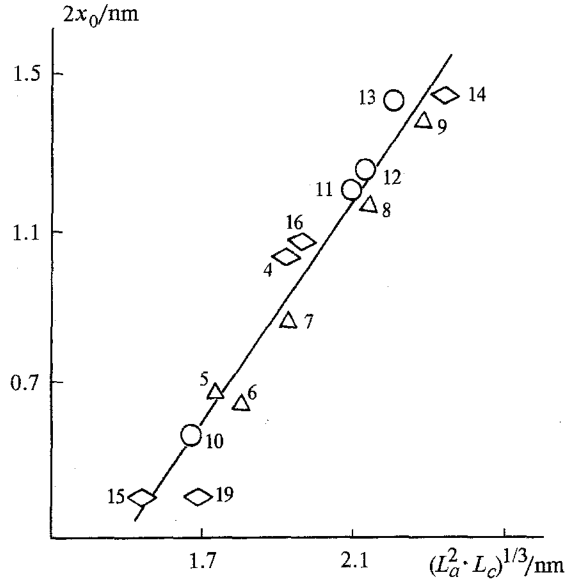

Fig. 3. Correlation between the averaged crystallite size and the micropore width for AC. Numbers correspond to the designations of AC studied.

Table 2. Comparison of X-ray structural parameters L_a and L_c (nm) with the limiting adsorption volume of micropores W_0 (cm^3/g) for AC from progressive activation

Sample	Parameters			
	L_a/nm	L_c/nm	$(L_a^2 \cdot L_c)^{1/3}$	W_0
5	0.98	2.36	1.76	0.26
6	0.61	3.14	1.82	0.31
7	0.87	2.88	1.94	0.43
8	0.94	3.30	2.17	0.53
9	1.14	3.30	2.32	0.53
10	0.98	2.40	1.78	0.32
11	1.17	2.80	2.09	0.59
12	0.89	3.30	2.13	0.60
13	0.75	3.70	2.17	0.67

Table 3. X-ray structural parameters L_a (nm) of AC dried at 100 °C, as well as that saturated with water vapor

Sample	L_a		Sample	L_a	
	100 °C	H_2O		100 °C	H_2O
4	2.20	2.45	**16**	2.36	2.90
14	2.64	3.37	**17**	2.76	2.88
15	2.80	3.30	**18**	2.93	3.37
			19	1.78	2.34

presence of radicals at side boundaries of crystallites.[9] Apparently, two competitive processes occur during the activation — burning out of the layers and their coalescence.

If one takes the value $(L_a^2 L_c)^{1/3}$ (*i.e.*, the size of an "equivalent" disk with $L_a = L_c$, whose volume is equal to the volume of this crystallite) as the effective size of a crystallite, then, as seen in Fig. 3, good correlation between the averaged crystal size and the micropore width is observed for a series of FAS type AC (AC-10 — AC-13) during progressive activation as well as for a series of wood-based AC (AC-5 — AC-9). In addition, it should be noted that in each series (AC-5 — AC-9 and AC-10 — AC-13) a more accurate correlation is observed than in the average for all samples AC-5 — AC-13. This can be due to different mutual arrangement of crystallites and, as a consequence, to different shape of micropores. This, in turn, can affect the determination of the average size of a slit micropore (x_0) from the correlation between x_0 and characteristic energy of adsorption E_0. AC, which underwent high-temperature treatment in an inert atmosphere accompanied by essential transformation of crystallites and a sharp increase in the parameter L_c, do not fall into the correlation obtained, although the initial AC-1 does fall into the correlation as well as AC-4 and AC-14 (Fig. 3).

It is noteworthy that in the studied series of AC from progressive activation (AC-5 — AC-9 and AC-10 — AC-13), an increase in the effective size of crystallites is accompanied not only by an increase in the average size of micropores, but also in their volume (Table 2).

X-ray diffraction study of a number of samples of AC of various origins showed that after adsorption of water vapor, an increase in the "diameter" of the microcrystallites, L_a, was always observed. For example, Table 3 presents L_a values for some AC measured after preliminary drying at 100 °C followed by saturation with water vapor. One can suggest that the arrangement of side carbon chains becomes ordered when water vapor is adsorbed. The presence of a peak in the region of 4.6 ° does not contradict this suggestion: this peak was observed for some AC, and usually it appears when the carbon chains are ordered.[10]

Diffractograms obtained for carbide AC-20, as an example, also provide evidence of the ordering of AC structure upon adsorption of water vapor. Fig. 4 presents the reflections (10) for the samples of AC-20 both dried and saturated with water vapors. The separation of (10) and (101) maxima as well as an increase in the intensity of the reflection (10) after the saturation of the sample with water give evidence for the improvement of the crystal structure due to the ordering of carbon chains on prismatic faces. This indirectly explains the reason for an increase in L_a. Possibly, on the edges of graphite planes, the reactions involving radicals occur, and as a result, the layers are "flattened". Deficiency of water at the surface of some AC is known to cause the formation of anhydrides of carboxylic acids[3] which can arrange between neighboring layers and cause deformation of the lateral regions of carbon layers. In the presence of water molecules, a carboxylic anhydride transforms to coupled carboxylic groups, and this can result in the "flattening" of carbon layers.

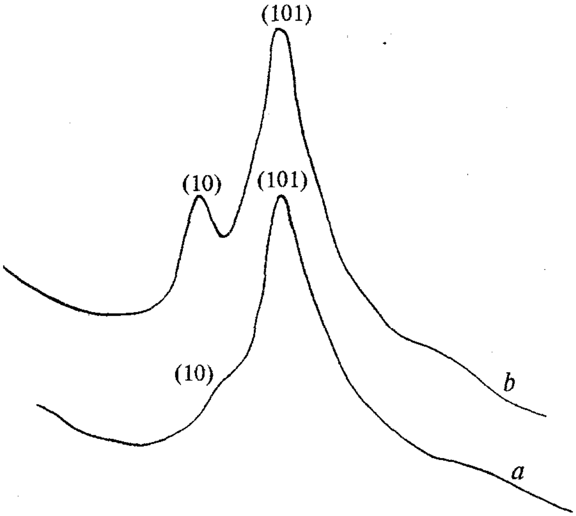

Fig. 4. Reflections (10) and (101) for dried AC-20 sample (*a*) and that saturated with water vapor (*b*).

In the work[11] devoted to the simulation of adsorption complexes of water at the graphite surface, it was shown that relative to the surface of the (1010) face with quinone and phenol functional groups water molecules arranged in the plane, which is parallel to graphite layers, *i.e.*, lengthen them. It should also result in the substantial increase in L_a observed in this work when water vapor was adsorbed.

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