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Note

Microscopic investigations of the surface structure of carbon–silica adsorbents

III. Heterogeneity of the carbon layer

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The influence of the heterogeneity of adsorbents on their chromatographic performance has been described[1,2]. Thus studies of the crystalline structure and crystal defects of adsorbents are very important. Bethge and Heydenreich[3] stated that the "microstructure" is related to the crystallographic structure and micromorphology of solids as well as to local inhomogeneities in the chemical composition. Based on the results of electron microscope studies, Kranaukhov[4] classified porous materials according to whether they had a corpuscular or spongy structure. Corpuscular systems are formed by particles of various shapes connected to one another. In this case, the pores represent the interstices between the particles. For spongy structures a system of channels and cavities is developed wherein individual particles cannot be distinguished. Sometimes both these two types are combined: particles of the corpuscular system may have internal spongy porosity, and large pores of the spongy system may involve small particles.

Dubinin[5] reported that fossil coals carbonized at temperatures of 500–900°C consist of an ordered part (carbon crystallites) and an amorphous part (high-carbon-number radicals). The structure of the crystallites resembles that of graphite, and they are irregularly spaced throughout the coal. The radicals are bound with carbon atoms. Carbonized organic materials generally contain crystallites 0.6–3 μm in diameter. The number of layers of carbon atoms in the crystallites increases from two to five with increasing diameter.

Boehm[6] distinguished three forms of carbon: graphite, diamond and black microcrystalline carbon. The last one, formally called amorphous, can be obtained by pyrolysis of organic materials. It consists of graphite-like layers of limited size stacked parallel to one another without ordering. Sometimes there is a considerable content of disorganized tetrahydrally bonded carbon, often cross-linking different layers. These defects cause a regular array of carbon bonds to be disturbed by forming free valences, which become sites of heterogeneity at the carbon surface.

TABLE I

CONDITIONS FOR MODIFICATION OF SILICA GEL AND THE SURFACE PROPERTIES OF
THE ADSORBENTS INVESTIGATED

S = Specific surface area; L = average layer thickness of deposited carbon; C = amount of carbon =
the loss of mass of carbosils during heat treatment in the air.

Adsorbent	Modifier	Time of pyrolysis (h)	S (m^2/g)	C $(\%, w/w)$	L $(\mathring{A})$
Initial silica gel	Unmodified	—	150.7	—	—
Carbosil A1	Dichloromethane	1	112.2	0.8	0.29
Carbosil A2	Pentanol	3	151.2	1.2	0.44
Carbosil A3	1. Dichloromethane	1			
	2. Pentanol	3	138.2	1.76	0.65
Carbosil A4	1. Pentanol	3			
	2. Dichloromethane	1	109.5	2.21	0.81

The aim of this study was to investigate the microstructure of the carbon layer formed by pyrolysis of pentanol or dichloromethane and a mixture of these two compounds.

EXPERIMENTAL

The silica adsorbents were prepared as described previously[7]. Different amounts of carbon were deposited on their surfaces by pyrolysis of dichloromethane and pentanol (Table I).

Samples for transmission electron microscopy were prepared by dissolving the silica in hydrofluoric acid according to the method described previously[8]. Because all the silica may not dissolve in the acid it possible that a small amount of it remains on the carbon layer. Finally, the thin carbon layer with a small amount of silica was examined by using a JEM 200 A transmission electron microscope at an acceleration voltage of 200 kV. The sample was cooled with nitrogen. The bright field (BF), dark field (DF) and selected area diffraction (SADP) techniques were used. In each experiment the sample orientation was perpendicular to that of the electron beam (goniometer position $x = 0$, $y = 0$). The results for four adsorbents (A1, A2, A3, A4) were recorded on 600 photoplates. Representative micrographs are illustrated.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the carbon layer deposited on adsorbent A1. Figs. 3 and 4 that deposited on adsorbent A2. The former layer was prepared by pyrolysis of dichloromethane, the latter by pyrolysis of pentanol. A magnification of 20 000 × (Figs. 1 and 3) revealed differences between these two samples. When a magnification of 100 000 × was used (Figs. 2 and 4), it was found that the carbon layer on adsorbents A1 and A2 consisted of small agglomerates, the microstructure of sample A2 being finer. Differences in the microstructure were also found for adsorbents A3 and A4. Fig. 5 shows the electron diffraction pattern obtained from the same area of the carbon layer as presented in Figs. 1 and 3. This kind of pattern is typical for non-
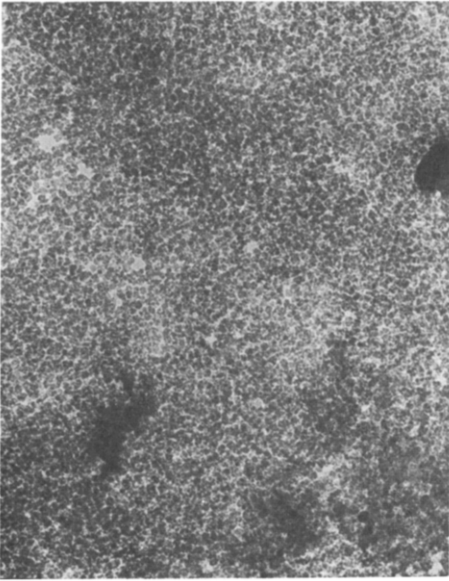
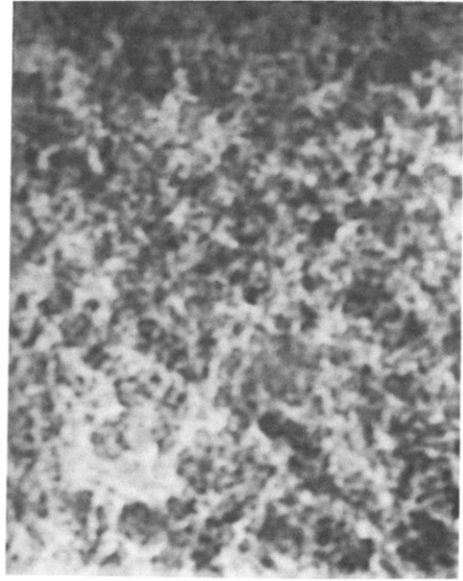Fig. 1. Carbon layer deposited on adsorbent A1 (magnification 20 000 ×).

Fig. 2. Carbon layer deposited on adsorbent A1 (magnification 100 000 ×).

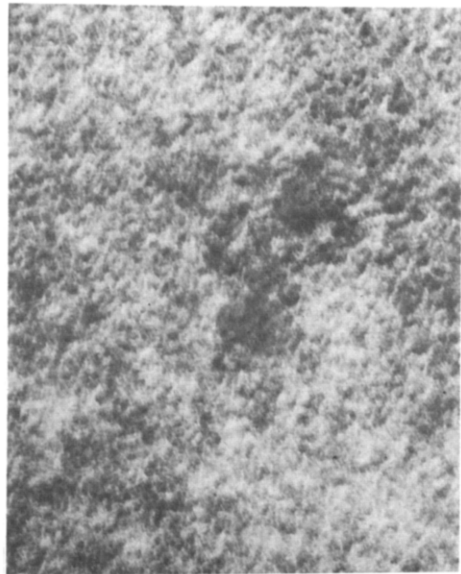Fig. 3. Carbon layer deposited on adsorbent A2 (magnification 20 000 ×).

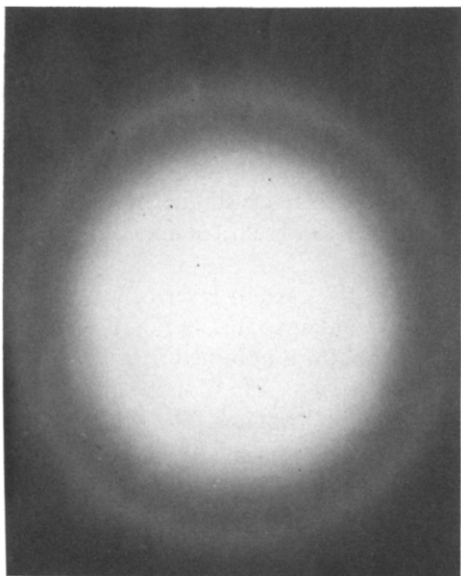Fig. 4. Carbon layer deposited on adsorbent A2 (magnification 100 000 ×).

Fig. 5. Electron diffraction pattern showing the amorphous character of the carbon layer on adsorbents A1 and A2.

Fig. 6. BF image of the carbon layer on adsorbent A1 (magnification 20 000 ×).
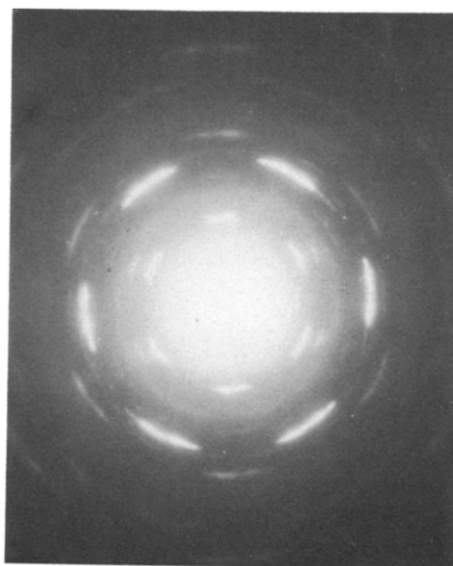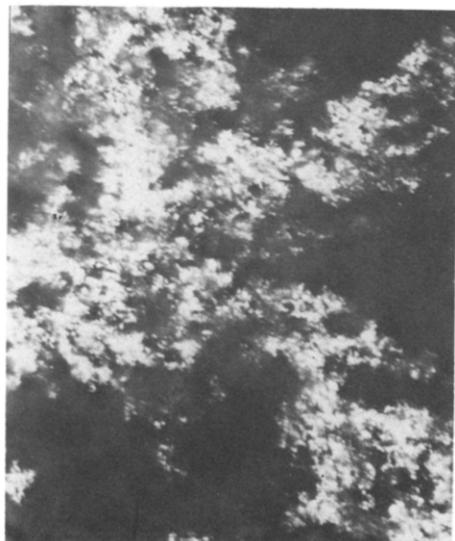

Fig. 7. DF image showing the distribution of crystallites in the area presented by the BF image (Fig. 6).

Fig. 8. Diffraction pattern obtained from the area shown in Fig. 6.

crystalline (amorphous) structures[9] and was observed in all the four samples.

According to the classification of the porosity types given by Kranaukov[4], the carbon layer on the adsorbents A1–A4 had corpuscular character. Dubinin[5] stated that such a system, also called polydisperse, can be regarded as a sign of inhomogeneity. This means that in the amorphous part of the carbon layer the homogeneity is disturbed by microporosity (microporous structure).

Figs. 6–18 show the regions of the carbon layer where crystallites were found. For observations of the crystalline phase, dark field (DF) and selected area diffraction (SADP) were used.

Figs. 6–8 show the crystalline phase found in the carbon layer of adsorbent A1. Fig. 6 shows that the carbon layer is amorphous, similar to that in Fig. 1, without features and crystallographic details. The diffraction pattern obtained from this area (Fig. 8) shows that small amounts of crystallites are present. Fig. 7 shows the distribution of crystallites in the area equal to that of the photoplates. The screen magnification was 20 000 ×, *i.e.*, 1 cm on the photoplates corresponds to about 0.5 μm; the size of each photoplate is 9 × 6 cm. Each photoplate provides information on an area of carbon layer equal to 13.5 μm^2. In the area mentioned above the concentration of crystallites is high (Fig. 7). Their sizes are $\leqslant$ 500 Å.

The carbon layer on sample A1 was obtained by pyrolysis of dichloromethane in a very simple reaction:

$$CH_2Cl_2 \xrightarrow{500°C} C + 2\ HCl \tag{1}$$

According to Leboda[10], the IR spectra of many carbon-silica adsorbents obtained by pyrolysis of dichloromethane show that homogeneous carbon is obtained in this
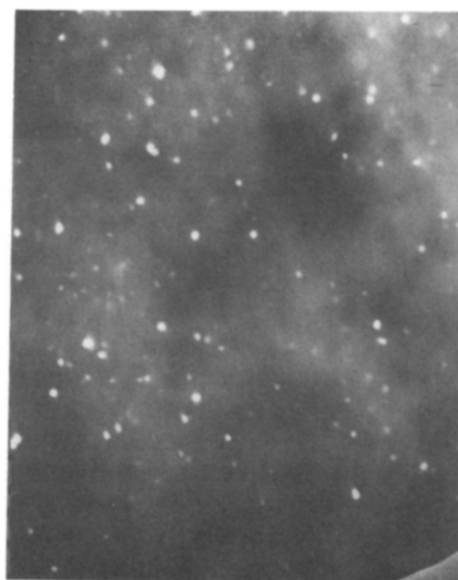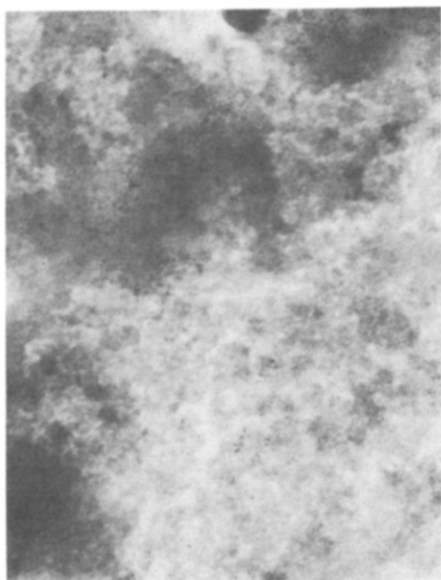

Fig. 9. BF image of the carbon layer on adsorbent A2 (magnification 20 000 ×).

Fig. 10. DF image showing the distribution of crystallites in the area presented by the BF image (Fig. 9).
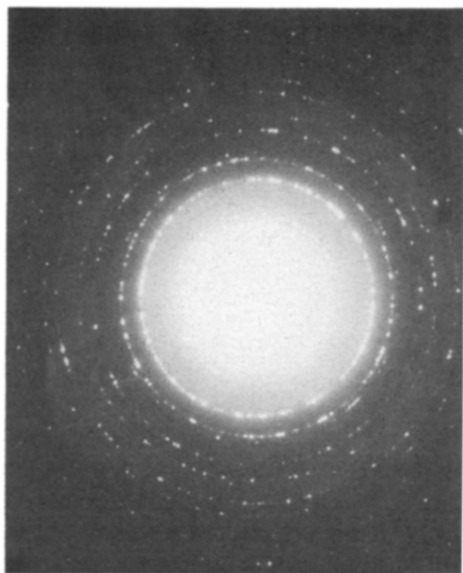
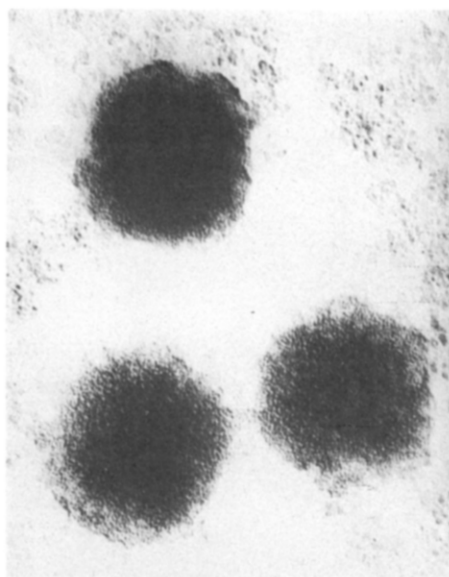Fig. 11. Diffraction pattern obtained from the area shown in Fig. 9.

Fig. 12. BF image showing the carbon layer on adsorbent A4.

reaction. However, the adsorption energy, E, for n-hexane on these carbosils showed three clear maxima[10]. Therefore, it has been suggested that the carbon layer obtained in reaction 1 consists of energetically non-equivalent carbon particles (agglomerates), etc. The results presented here show that the carbon layer obtained in reaction 1 is mostly amorphous and consists of agglomerates of about 200–300 Å (Fig. 6) and of a small amount of crystallites of < 500 Å (Figs. 7, 8). Furthermore the considerably complicated shape of the adsorption energy curves obtained by a chromatographic method[10] was caused by the fact that microcrystalline areas are present in amorphous geometrically non-equivalent carbon layers.

Figs. 9–11 show the carbon layer on adsorbent A2. It should be noted that the mechanism of formation of the carbon deposit on the silica gel surface during dichloromethane decomposition is totally different from that during alcohol pyrolysis. In reaction 1 carbon is formed due to thermal decomposition of dichloromethane, while alcohol pyrolysis is preceded by adsorption and chemisorption of alcohol molecules on the surface of the carrier. The IR spectrum shows that the adsorbents obtained by pyrolysis of alcohols have a very complicted chemical structure, but chromatographic experiments have shown that they are energetically homogenous[10].

The bright field image (Fig. 9) shows that the carbon layer on adsorbent A2 consists of agglomerates, but, in comparison to adsorbent A1 (Fig. 6), the microstructure of carbon is finer. The dark field image (Fig. 10) and SADP (Fig. 11) show crystallites to be present in sample A2. The size of the crystallites in sample A2 is similar to that in sample A1, but their distribution in the former over the same area of the photoplate is rarer (smaller concentration of crystals).

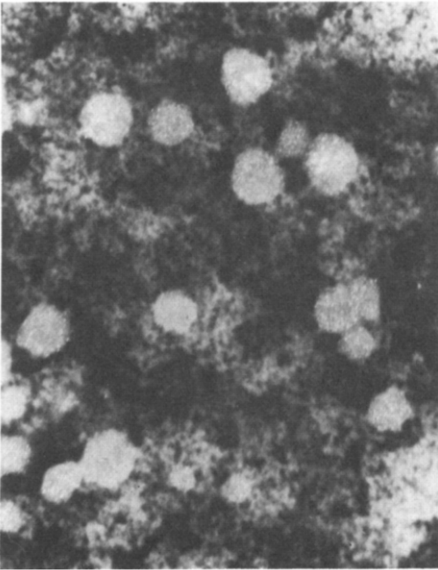Figs. 12–15 show the carbon layer on adsorbent A4 which was prepared by

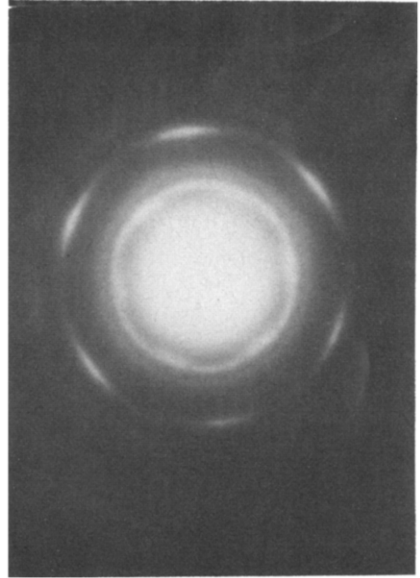Fig. 13. DF image showing the crystalline character of the agglomerates.

Fig. 14. Diffraction pattern corresponding to Fig. 12.

Fig. 15. Morphology of a single crystal which very often occurs in the carbon layer on adsorbent A2 (magnification 20 000 ×).
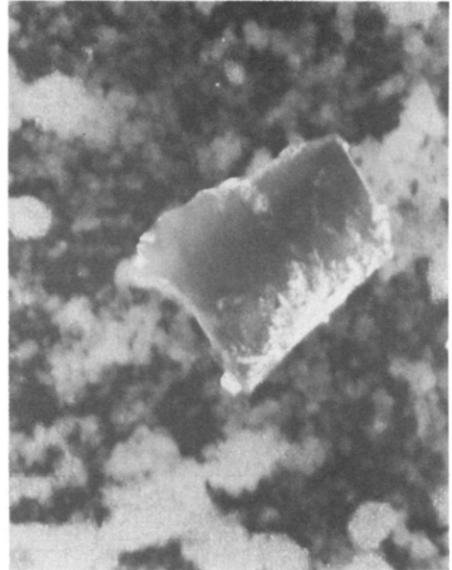
Fig. 16. Morphology of a single crystal which very often occurs in the carbon layer on adsorbent A4 (magnification 20 000 ×).

pyrolysis first of pentanol and then of dichloromethane. The BF image (Fig. 12) shows that the carbon layer consists of agglomerates of a few μm in size. These agglomerates have their own microstructure. DF (Fig. 13) and SADP (Fig. 14) show the crystalline character of the agglomerates. In contrast to adsorbent A4, adsorbent A3 was prepared by pyrolysis first of dichloromethane and then of pentanol. The fact that for adsorbent A3 no similar pictures were obtained is surprising. It can be supposed that crystallites formed upon pyrolysis of the alcohol act as nuclei for the growth of carbon crystalites formed upon thermal decomposition of dichloromethane. These results confirm our previous study, where the replica method was used[7].

Figs. 15 and 16 show the characteristic objects found in each of the four samples. The diffraction patterns formed from the area of these objects (Fig. 17) shows their crystalline structure with hexagonal symmetry. Andrews et al.[11] reported that a single crystal in the electron beam will give rise to a more or less regular and ideally symmetrical arrangement of spots, each of which has a different value of (hkl)*. Spots which are equidistant from the centre and diametrically opposite are associated with the same set of crystal planes and are indexed as (hkl) and $(\bar{h}\bar{k}\bar{l})$. They are single crystal type spot patterns. It is quite possible that these objects represent one of the crystalline forms of silica, since a similar diffraction pattern was obtained for silica gel heated at 600°C. The method of sample preparation involves the dissolution of silica gel in hydrofluoric acid. However, during pyrolysis in the autoclave, amorphous silica may change to a crystalline form. As amorphous silica is easier to dissolve in hydrofluoric acid than its crystalline forms, some of the latter may remain attracted to the carbon layer.
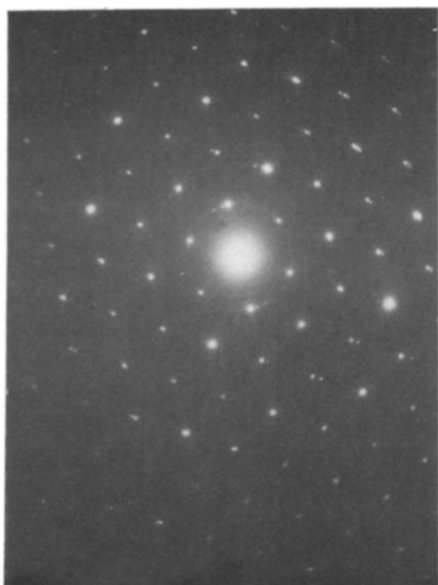

Fig. 17. Diffraction pattern corresponding to Fig. 15.

* The set of Miller indices which are reciprocal intercepts in units of cell of crystal. If the plane cuts one of the axes on the negative side of the origin the corresponding Miller indices are negative $(\bar{h}\bar{k}\bar{l})$.

At present it is not possible to solve the problem of the crystal structure of the objects examined. Examination of the adsorbents by means of X-ray diffraction does not reveal the diffraction lines corresponding to the Bragg reflections, because of the low sensitivity of this method. Moreover, as the effect of radiation damage was very strong, the measurements had to be made very quickly and could be made only for one position of the goniometer ($x = 0$, $y = 0$). In this way, diffraction patterns were obtained for accidentally crystallographic directions.

CONCLUSIONS

(1) The carbon layer deposited on the adsorbents A1–A4 consists mainly of amorphous carbon.

(2) In each of the four samples, crystallites were found to occupy only a small part of the carbon layer.

(3) In general, two types of crystallites were distinguished; (a) large ones, about 10–50 μm in size, gave a diffraction pattern with three-fold symmetry (Fig. 17) and are considered to be a crystalline form of silica; (b) small ones, about 500 Å in size, considered to be a graphite-like form of carbon.

The heterogeneous character of the carbon layer revealed by the electron microscope studies confirmed the earlier chromatographic results obtained for carbon–silica adsorbents[7,10]. Moreover, the electron microscope experiments allow us to conclude that both the chemical and crystallographic structure of the carrier (pure or partially carbonized silica) affect the character of the deposited carbon layer.

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