

Note

Microscopic investigation of the surface structure of carbon-silica adsorbents

I. Influence of the modifier used on the topography of carbon-silica adsorbents

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Electron microscopic methods have not been widely used for the direct determination of the properties of adsorbents. However, Grimaud *et al.*¹ used scanning electron microscopy (SEM) in comparative ultrastructural studies of three series of gels: Ultrogel, Sephadex G and Bio-Gel P. Unger and Gimpel² determined the particle sizes of commercial spherical silica packings of graduated pore size by means of sedimentation and compared them with results obtained by microscopy. Colin and Guiochon³ presented micrographs of particles of Spherosil coated with different percentages of pyrocarbon. Leboda⁴ investigated the porous structure of silica gels impregnated with various amounts of Co_3O_4 and carbon-silica adsorbents using SEM. Röchel *et al.*⁵ examined the structure of polyacrylamide gels by transmission electron microscopy (TEM).

In this work, it has been found that carbon deposited on the surface of silica gel by different methods and with different modifiers gave different microscopic pictures. Chromatographic data were obtained to supplement the microscopic investigations.

EXPERIMENTAL

Preparation of carbon-silica adsorbents

Two types of silica gel, A and B, for gas chromatography (GC) manufactured by Macherey, Nagel & Co. (Düren, F.R.G.) (particle size range 0.15–0.3 mm) were used. Wide-pore silica gel A was heated at 900°C for 4 h. The initial adsorbent A prepared in this way was more thermostable and had a stiffer skeleton than the original silica gel B at low temperatures. The specific surface area of the initial adsorbent A was 151 m²/g. The initial adsorbent A was modified in special equipment for obtaining Carbosils by a dynamic method⁶, in which a modifier was passed over the silica gel by a carrier gas (nitrogen) at 500°C. Two modifiers, *n*-amyl alcohol and dichloromethane, were used; the conditions of the modification process are given in Table I.

TABLE I
CONDITIONS FOR MODIFICATION OF SILICA GEL ADSORBENT A

Carbon-silica adsorbent	Modifier	Time of the process (h)	Flow-rate of nitrogen (cm ³ /min)
A ₁	CH ₂ Cl ₂	1	110
A ₂	C ₃ H ₁₁ OH	3	150
A ₃	CH ₂ Cl ₂	1	110
	C ₃ H ₁₁ OH	3	150
A ₄	C ₃ H ₁₁ OH	3	150
	CH ₂ Cl ₂	1	110

Adsorbents A₃ and A₄ were obtained by repeated modification of A₁ and A₂.

Narrow-pore silica gel B was modified by the static method, giving a specific surface area of 418 m²/g. A 15-g amount of silica gel B was dried at 200°C and then 1-octanol was pyrolysed out in a 0.2-l autoclave at 500°C for 7 h. Five carbon-silica adsorbents were obtained using different volumes of alcohol: B₁, 0.5 ml; B₂, 1 ml; B₃, 3 ml; B₄, 7 ml; and B₅, 15 ml.

Having been modified in the autoclave the adsorbents of type B were washed with dimethylformamide (using a Soxhlet apparatus) and acetone, then dried at 150–200°C in air.

Testing of the adsorbents

The specific surface areas of the adsorbents were measured by the nitrogen thermal desorption method⁷. The heats of adsorption of hexane, chloroform and benzene were calculated from the temperature dependence of the retention⁸. These measurements were carried out at 150–200°C on a Guide Model 183 gas chromatograph (G.D.R.) with a thermal conductivity detector, using 400 × 2.3 mm I.D. glass columns. Hydrogen purified on molecular sieve 4 A was used as the carrier gas.

For the examination of exterior surface of the initial silica gels and the modified carbon-silica adsorbents, TEM and SEM were used. The samples for investigation by SEM were covered with a gold conductivity layer by vapour process. A Cambridge S4-10 scanning electron microscope was used. For TEM a Tesla BS 613 was used. As samples platinum-carbon direct replicas were prepared. On the surface SiO₂ and carbon layer deposited by the pyrolyzing process of the carbon-silica adsorbent a C-Pt film was vapoured. Then the SiO₂ was solved in 20% HF and the film consisting of a C-Pt layer (from the replica) and a C-layer (from the pyrolyzing process) was washed and transferred to a grid covered with Formvar. Samples from the initial silica gel were prepared the same way, but because the initial silica gel was free of the carbon layer deposited by the pyrolyzing process the film consisted only of the C-Pt replica. In this way the changes of the surface during the pyrolyzing process can be investigated.

RESULTS AND DISCUSSION

Using small electron magnifications of 200–1000× it can be established whether the modification of the initial silica gels to carbon-silica adsorbents changes the shape of the grains. As can be seen from the Figs. 1–3, the sharp edges and

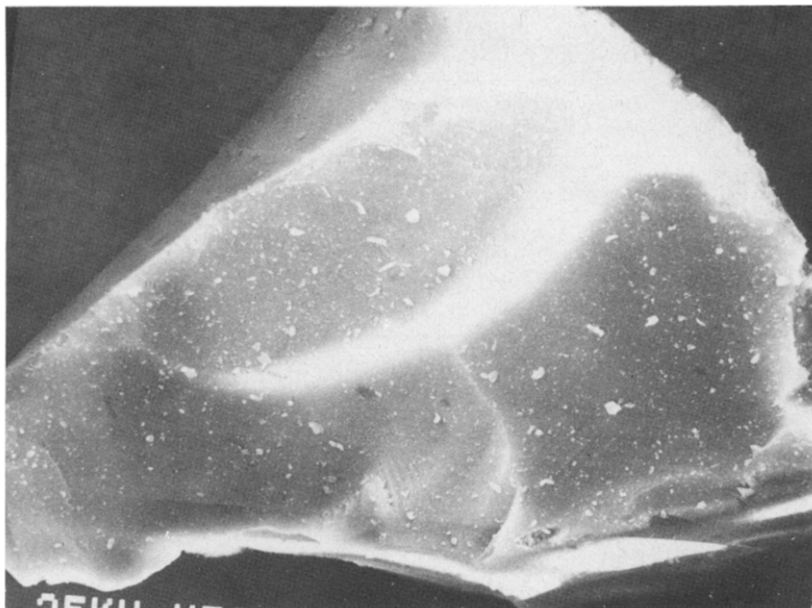


Fig. 1. Particle of initial silica gel adsorbent A (SEM, $\times 200$).



Fig. 2. Topography of carbon-silica adsorbent A₁ (SEM, $\times 1000$).

irregular shape caused during disintegration of the particles of the initial silica gel into smaller fractions (see Fig. 1) after pyrolyzing process (see Figs. 2 and 3) have been preserved.

Using a magnification of $6000\times$ it is possible to examine a larger unit surface



Fig. 3. Topography of carbon-silica adsorbent A₂ (SEM, $\times 1000$).

of the adsorbent studied. Fig. 4 shows the surface of the initial wide-pore silica gel and the detailed structure can be seen to some extent. Figs. 5-8 show the surface of carbon-silica adsorbents A₁, A₂, A₃ and A₄ respectively. The most disordered surface

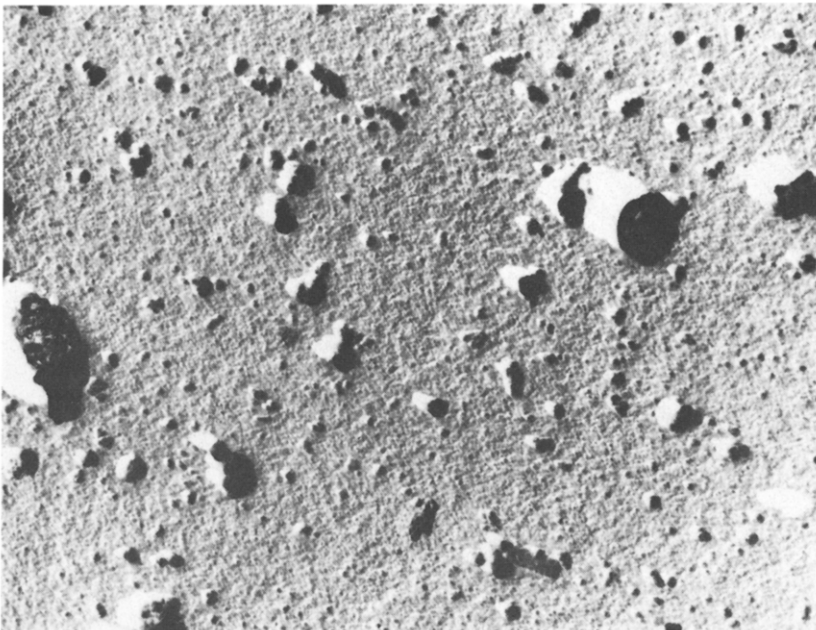


Fig. 4. Topography of initial silica gel adsorbent A (TEM, $\times 6000$).



Fig. 5. Topography of carbon-silica adsorbent A_1 (TEM, $\times 6000$).

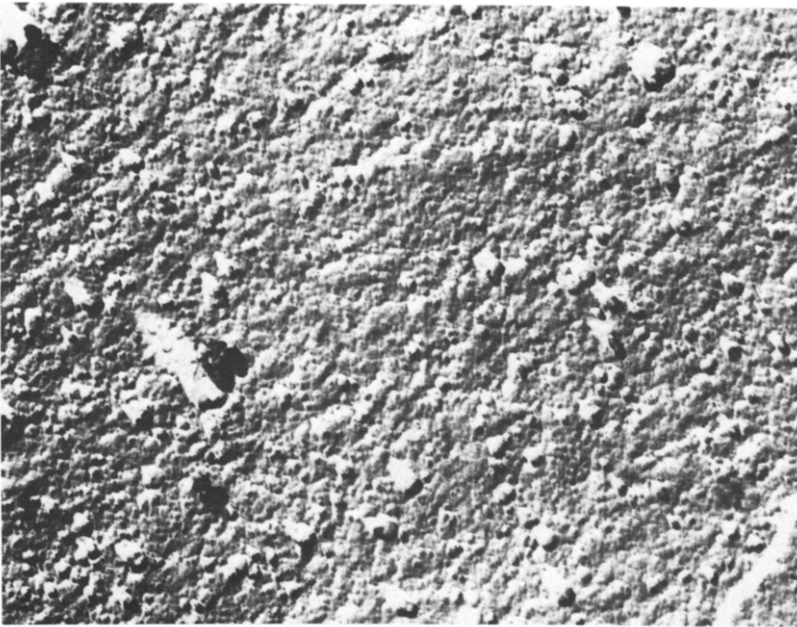


Fig. 6. Topography of carbon-silica adsorbent A_2 (TEM, $\times 6000$).

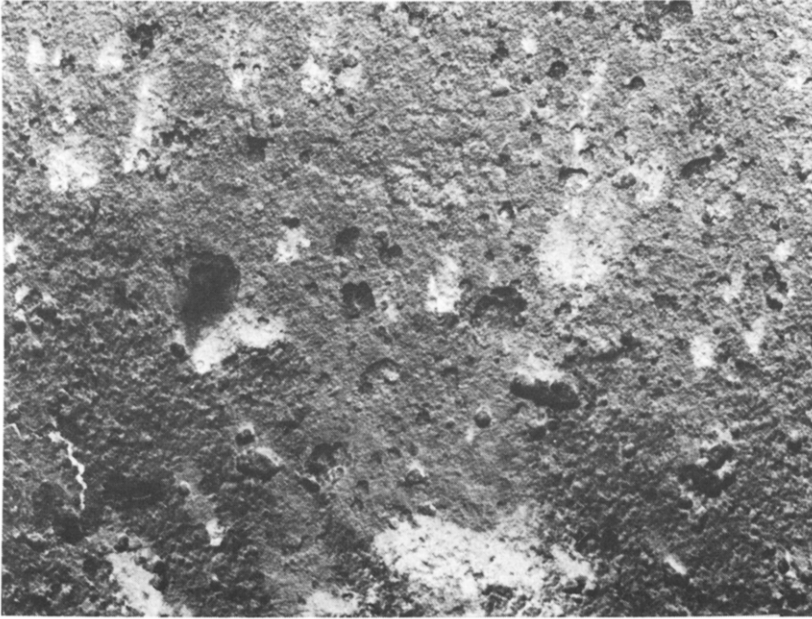


Fig. 7. Topography of carbon-silica adsorbent A_3 (TEM, $\times 6000$).

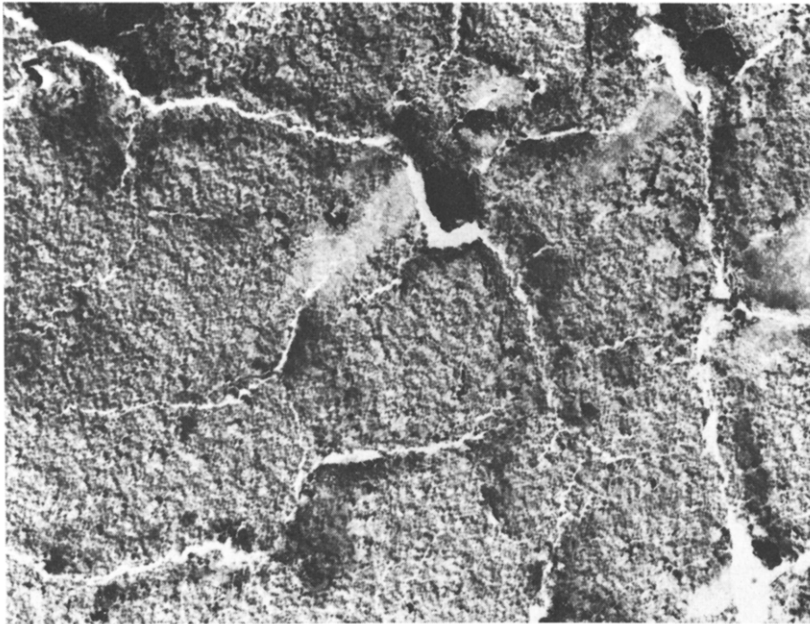


Fig. 8. Topography of carbon-silica adsorbent A_4 (TEM, $\times 6000$).

structure is shown by A_1 (Fig. 5), although it is not fully developed into a modified structure compared with that of the initial silica gel (Fig. 4). However, it can be seen that the structure of the surface of A_2 (Fig. 6) is distinctly ordered.

Fig. 7 shows the spatial character of the surface of carbon-silica adsorbent A_3 . The surface of adsorbent A_4 (Fig. 8) reveals a better ordered state of the carbon deposit than A_2 although dichloromethane was also used for modification of this adsorbent.

More detailed information about the surface of the adsorbents is given by a magnification of $18,000\times$. The spatial arrangement of the carbon deposit on adsorbent A_2 (Fig. 10) can be seen better than that on A_1 (Fig. 9). The most developed structure of the carbon deposit is shown by adsorbent A_4 (Fig. 12). The mosaic character of the surface of A_3 (Fig. 11) is confirmed by the dark spots.

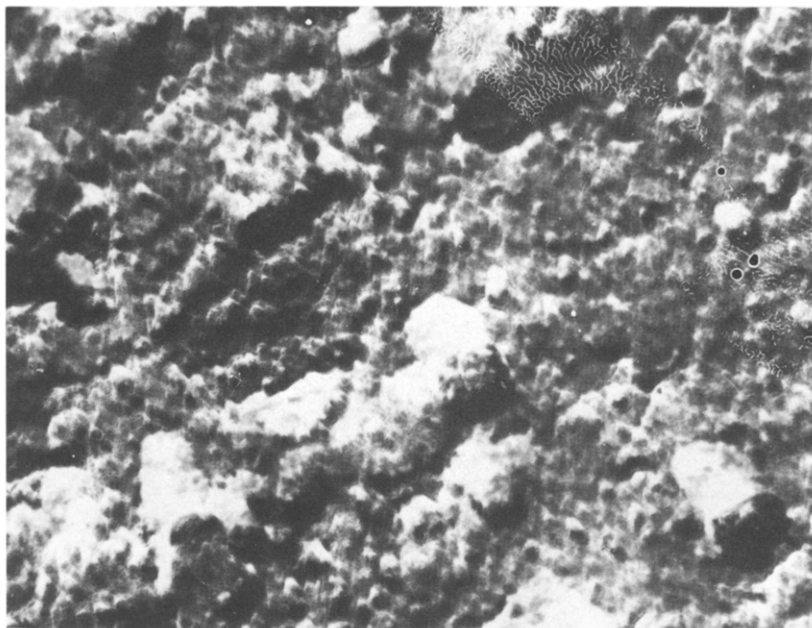


Fig. 9. Topography of carbon-silica adsorbent A_1 (TEM, $\times 18,000$).

The data in Table II correlate relatively well with the appearance of the surfaces in the photographs. The carbon deposit on adsorbent A_2 does not, in fact, change the specific surface area compared with the initial silica gel, but it gives a completely different surface structure, which is reflected by the heats of adsorption. A more spatial arrangement of the carbon deposit on adsorbent A_2 in relation to A_1 is confirmed by the greater decrease in mass of A_2 , the higher heats of adsorption of the substances tested and its greater specific surface area.

From the data in Table II it appears that the carbon deposit formed as a result of pyrolysis of *n*-amyl alcohol is a better catalyst of dichloromethane carbonization (adsorbent A_4) than the deposit formed as a result of pyrolysis of dichloromethane (adsorbent A_3), which can be seen from the greater decrease in mass for sample A_4 than for A_3 .

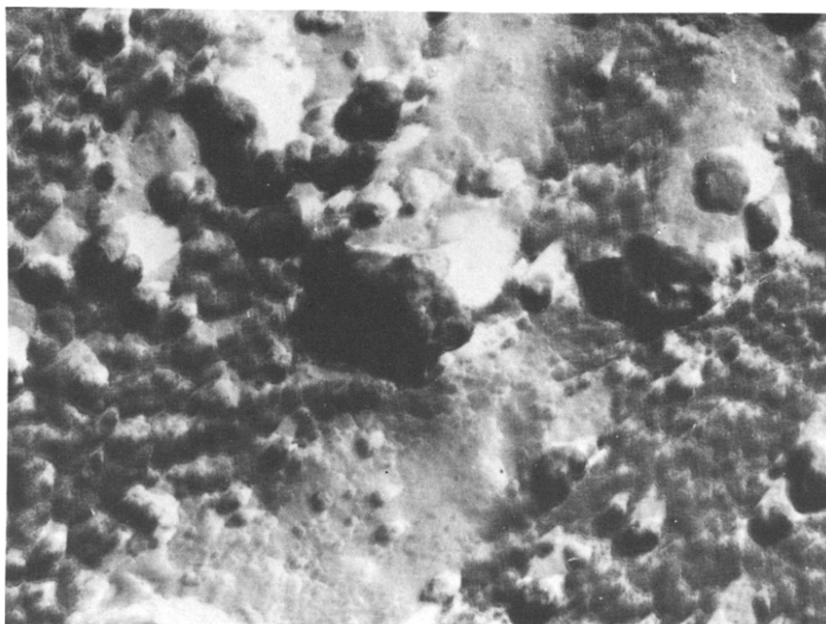


Fig. 10. Topography of carbon-silica adsorbent A₂ (TEM, ×18,000).

TABLE II

SURFACE PROPERTIES OF THE ADSORBENTS INVESTIGATED

S = specific surface area; *L_c* = average layer thickness of deposited carbon.

Adsorbent	<i>S</i> (m ² /g)	<i>C</i> (%, w/w)	<i>L_c</i> (Å)	Heat of adsorption (kcal/mole)		
				<i>n</i> -Hexane	Chloroform	Benzene
Initial gel (unmodified)	150.7	—	—	8.3	6.8	7.8
A ₁	121.2	0.8	0.29	6.9	6.1	7.2
A ₂	151.2	1.2	0.44	7.2	6.1	7.6
A ₃	138.2	1.76	0.65	6.8	6.6	8.7
A ₄	109.5	2.21	0.81	8.7	7.0	9.1

From the specific surface areas of the adsorbents, the blocking action of dichloromethane molecules and the action of *n*-amyl alcohol molecules, the development of the surfaces of the adsorbents can be seen distinctly. Adsorbent A₂ has a specific surface area of 151.2 m²/g, but that of A₄, after deposition of the deposit formed from dichloromethane on its surface is only 109.5 m²/g. However, for adsorbents A₂ and A₃ the specific surface area increases from 121.2 to 138.2 m²/g. Fig. 13 shows the surface initial gel B.

Figs. 14 and 15 show the surfaces of carbon-silica adsorbents obtained from narrow-pore silica gel. A distinct correlation was observed between structural changes and the amount of the carbon deposited on the surface. With increasing amounts of carbon a greater number of dark spots appeared on the photographs.

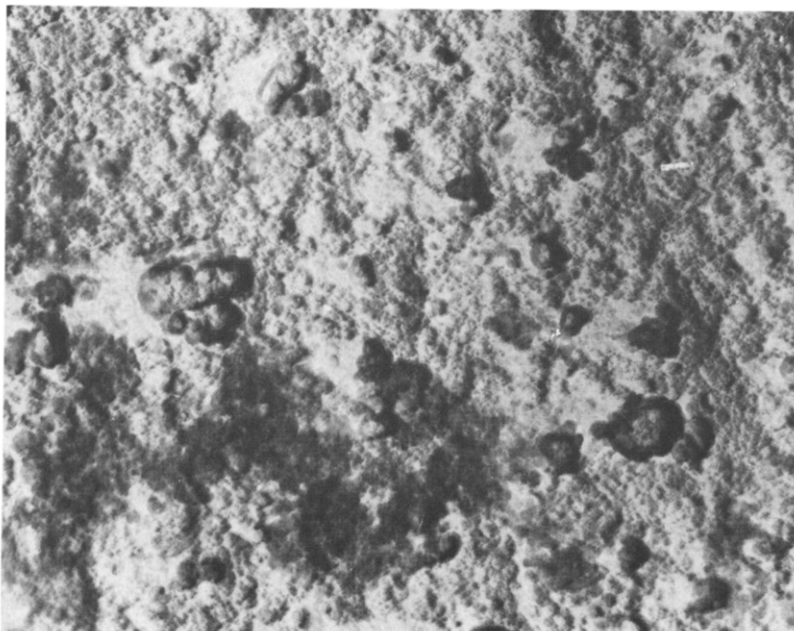


Fig. 11. Topography of carbon-silica adsorbent A₃ (TEM, × 18,000).

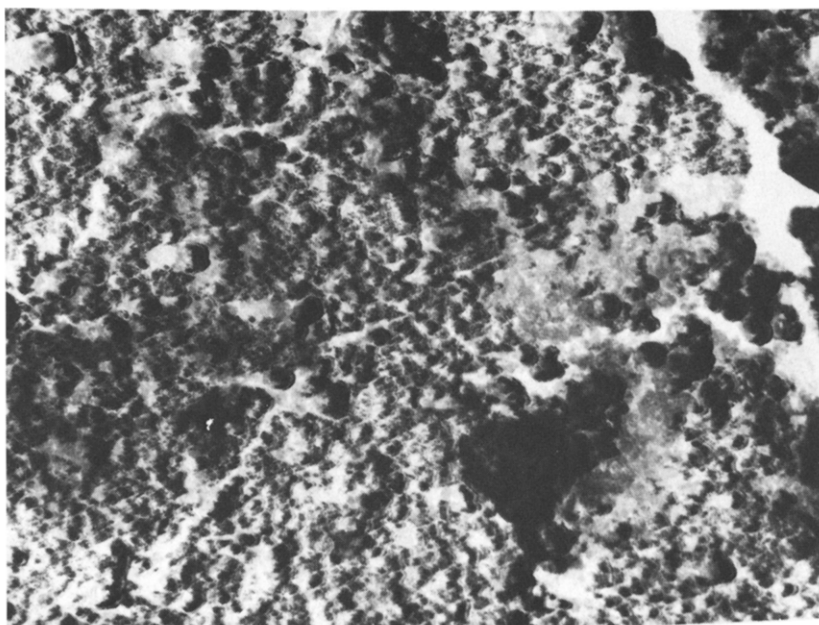


Fig. 12. Topography of carbon-silica adsorbent A₄ (TEM, × 18,000).

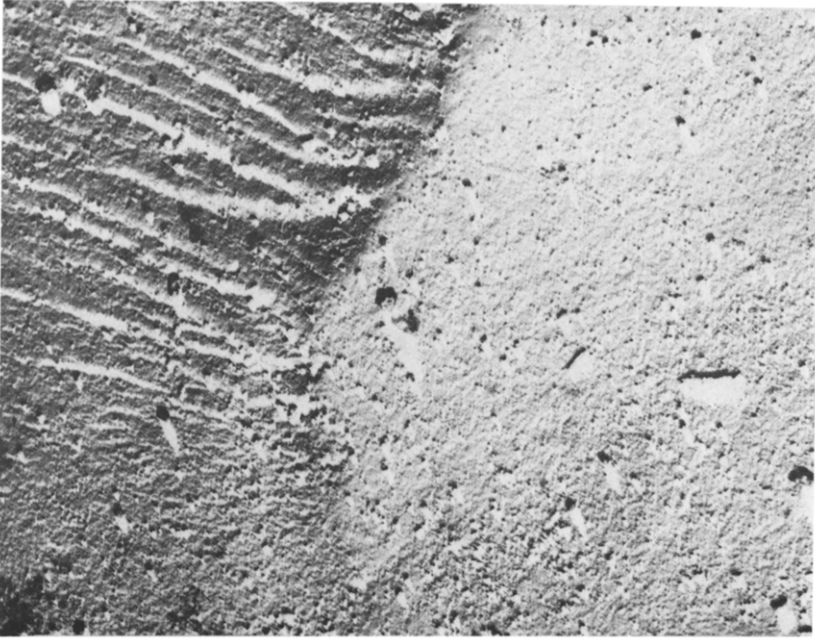


Fig. 13. Topography of initial silica gel adsorbent B (TEM, $\times 6000$).

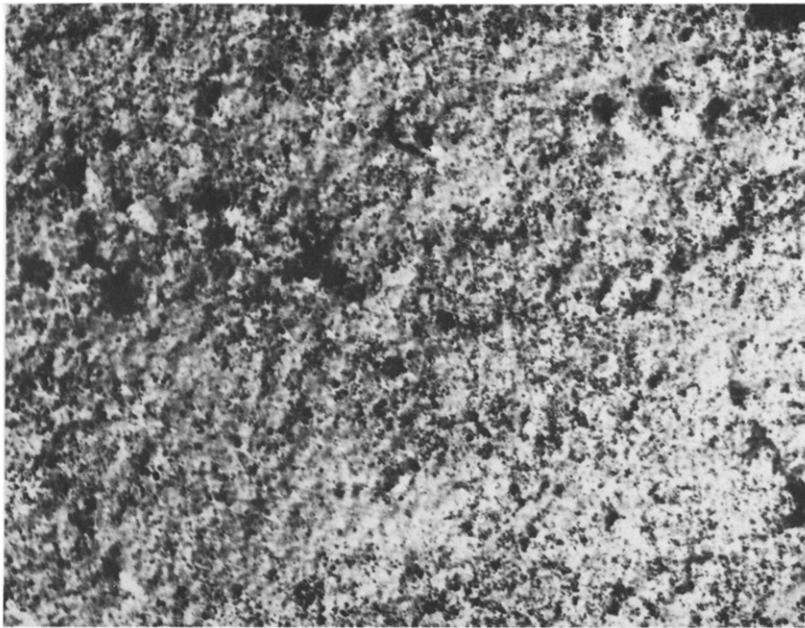


Fig. 14. Topography of carbon-silica adsorbent B₃ (TEM, $\times 6000$).

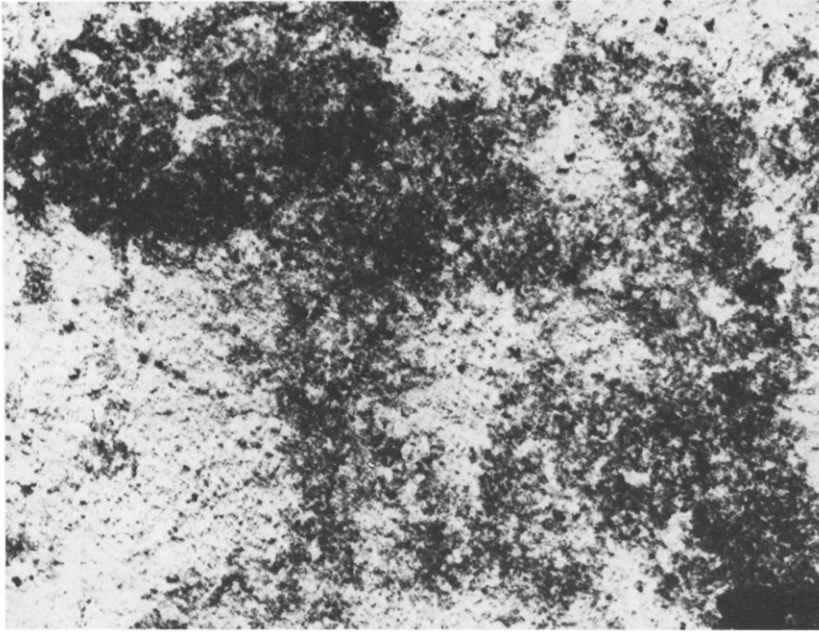


Fig. 15. Topography of carbon-silica adsorbent B₅ (TEM, × 6000).

Also, there is a smaller spatial development of this type of surface and the structure of the carbon deposit differs from that of adsorbents obtained by the dynamic method. This probably results from the fact that in the static method the molecules of the modifying substance have a greater possibility of penetrating the surface of the initial silica gel.

CONCLUSIONS

We conclude that the modification of silica gel to carbon-silica adsorbents does not change of the shape of the grains. The carbon-silica adsorbents obtained as a result of *n*-amyl alcohol pyrolysis have a better ordered and more spatially developed structure of the carbon deposit than those obtained by dichloromethane pyrolysis. The carbon deposit formed by *n*-amyl alcohol pyrolysis is a better catalyst of carbonization than the deposit formed by dichloromethane pyrolysis. The structure of the carbon deposit on carbon-silica adsorbents obtained by the static method is characterized by a weaker spatial development than that obtained by the dynamic method.

Attention must be drawn to two important problems in this type of investigation: the reproducibility of preparation of the adsorbent and the reproducibility and reliability of the photomicrographs obtained. The question of the reproducibility of the preparation of composite adsorbents has been discussed elsewhere^{6,8}. The photographs presented here are the most representative of the adsorbents examined in the area of microscopy. They were selected from several prints for each single sample.

Table II gives the average layer thickness (L_c) of the carbon deposited on the surface of the initial adsorbents. The L_c values have been calculated from a simple equation:

$$L_c = \frac{\% C}{d \cdot S \cdot 100\%}$$

where d is the density of the pyrolytic carbon (1.8 g/cm³) and S is the surface area of the initial adsorbent. The L_c values in Table II are much smaller than the average size of a carbon atom (1.4 Å), which means that the surface of the examined adsorbents is mosaic-like. This is in accordance with the photomicrographs. It should be noted that the data presented here should be treated as approximate, because the actual density d for particular carbon deposit is not known, nor is the thickness of the monolayer of the deposited carbon.

The correlations obtained between the content of carbon (depending on the method of adsorbent preparation) and the photomicrographs of individual samples confirm the reliability of the results. However, we believe that the traditional microscopic techniques (TEM and SEM) may be inadequate to give a complete picture of the surfaces of composite adsorbents. Perhaps the technique proposed by Volbert and Reimer⁹ them will permit a greater differentiation of the structures of particular elements (carbon deposit and silica) on the surfaces of composite adsorbents. Examination of the topography of adsorbents in relation to the parameters of the process used for the preparation of the adsorbents is crucial from the point of view of chromatography^{8,10}. With composite carbon-silica adsorbents this is interesting because, as Colin and Guiochon³ and Bebris *et al.*¹¹ demonstrated, these adsorbents may become widely used in high-performance liquid chromatography.

REFERENCES

- 1 E. Grimaud, J. C. Lecoq, E. Boschetti and M. Corgier, *J. Chromatogr.*, 166 (1978) 37.
- 2 K. K. Unger and M. G. Gimpel, *J. Chromatogr.*, 180 (1979) 93.
- 3 H. Colin and G. Guiochon, *J. Chromatogr.*, 126 (1976) 43.
- 4 R. Leboda, *Chem. Anal. (Warsaw)*, 25 (1980) 539.
- 5 R. Röchel, R. L. Steere and E. F. Erbe, *J. Chromatogr.*, 166 (1978) 564.
- 6 R. Leboda, *Inz. Chem.*, (Wroclaw), 3,2 (1982) 343.
- 7 F. M. Nelson and F. T. Eggersten, *Anal. Chem.*, 30 (1958) 1387.
- 8 R. Leboda, *Chromatographia*, 14 (1981) 524.
- 9 B. Volbert and L. Reimer, in A. O'Hare (Editor), *Scanning Electron Microscopy*, Vol. IV, SEM Inc., Chicago, 1980, pp. 1-10.
- 10 R. Leboda, *J. Chromatogr.*, 178 (1979) 369.
- 11 N. K. Bebris, A. V. Kiselev, Yu. S. Nikitin, I. I. Frolov, L. V. Tarasov and Ya. I. Yashin, *Chromatographia*, 4 (1978) 206.