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## Note

### A microscopic investigation of the surface of carbon-silica adsorbents

#### II. Relationships between the type of information obtainable about the surface and the microscopic techniques used for its examination

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In a previous paper<sup>1</sup> the replica technique was used for examination of the surface of complex carbon-silica adsorbents (Carbosils). The aim of the present study was to find the most appropriate technique of sample preparation for transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Two opposite Everhart-Thornley detectors were used for examination of the surface in SEM.

#### EXPERIMENTAL

The characteristics of the examined adsorbents are given in Table I. The preparation of the Carbosils was described previously<sup>1</sup>.

Samples for TEM were prepared using the carbon replica, carbon-platinum replica or direct carbon deposit technique. The replica technique depends on the evaporation of carbon or carbon and platinum onto the surface of the adsorbent, followed by treatment with a solution of silica in hydrofluoric acid. Because the

TABLE I

CONDITIONS FOR MODIFICATION OF SILICA GEL AND 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)	<i>S</i> (m <sup>2</sup> /g)	<i>C</i> (% w/w)	<i>L</i> (Å)
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	Dichloromethane	1	138.2	1.76	0.65
	Pentanol	3			
Carbosil A4	Pentanol	3	109.5	2.21	0.81
	Dichloromethane	1			

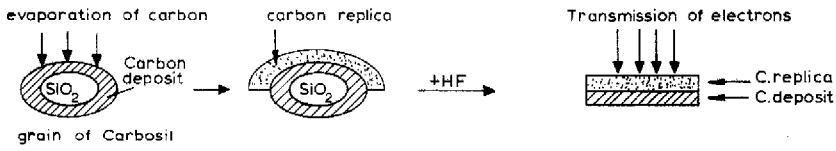


Fig. 1. Sample for TEM consisting of carbon replica and carbon deposit.

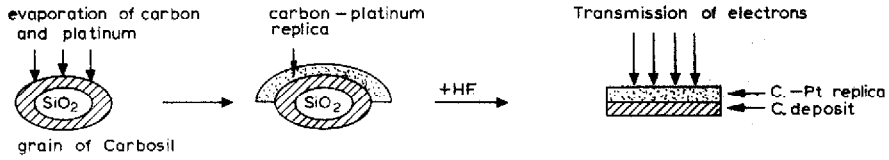


Fig. 2. Sample for TEM consisting of carbon-platinum replica and carbon deposit.

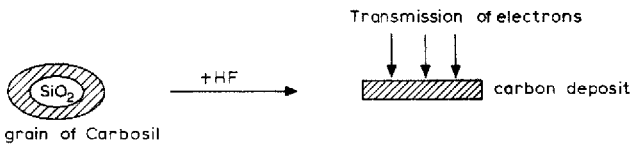


Fig. 3. Sample for TEM consisting of carbon deposit.

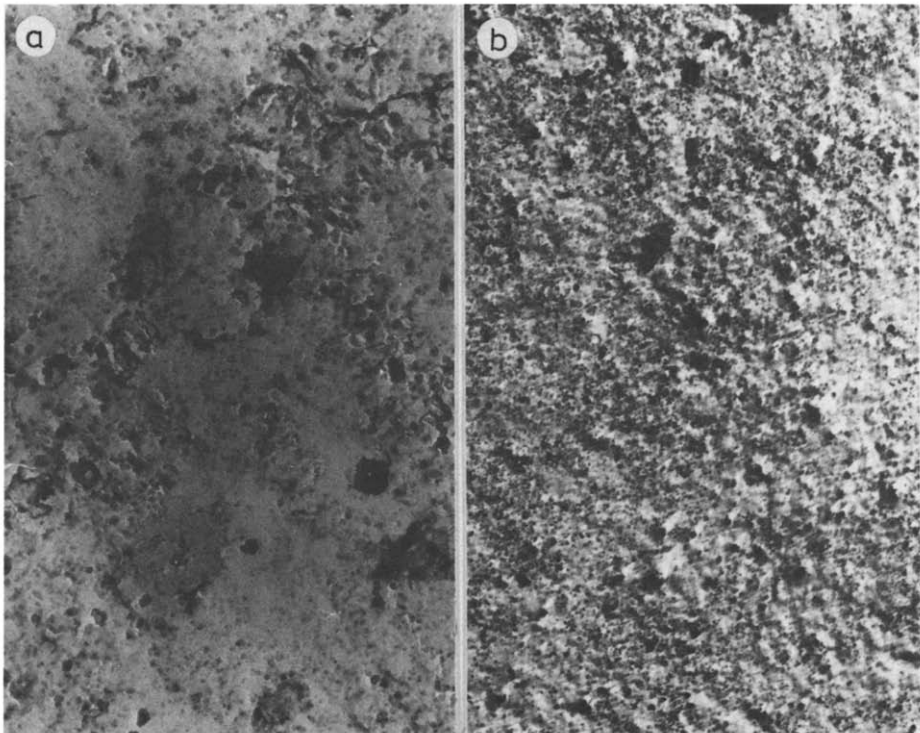


Fig. 4. Surface of initial silica gel examined by TEM, magnification  $\times 5000$ . Methods of preparation: a, carbon replica; b, carbon-platinum replica.

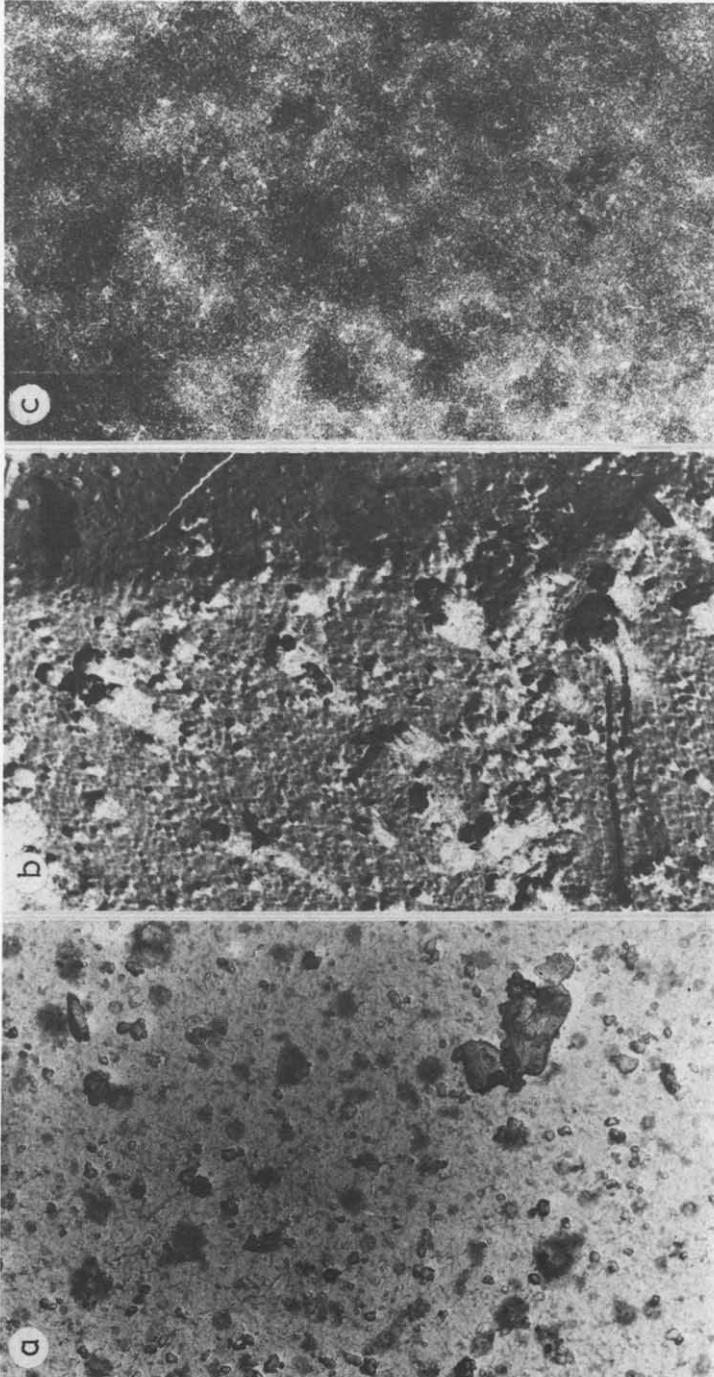


Fig. 5. Surface of Carbosil A1 (silica + dichloromethane). Details as in Fig. 4 except for part c which shows the film obtained by direct deposition of carbon.

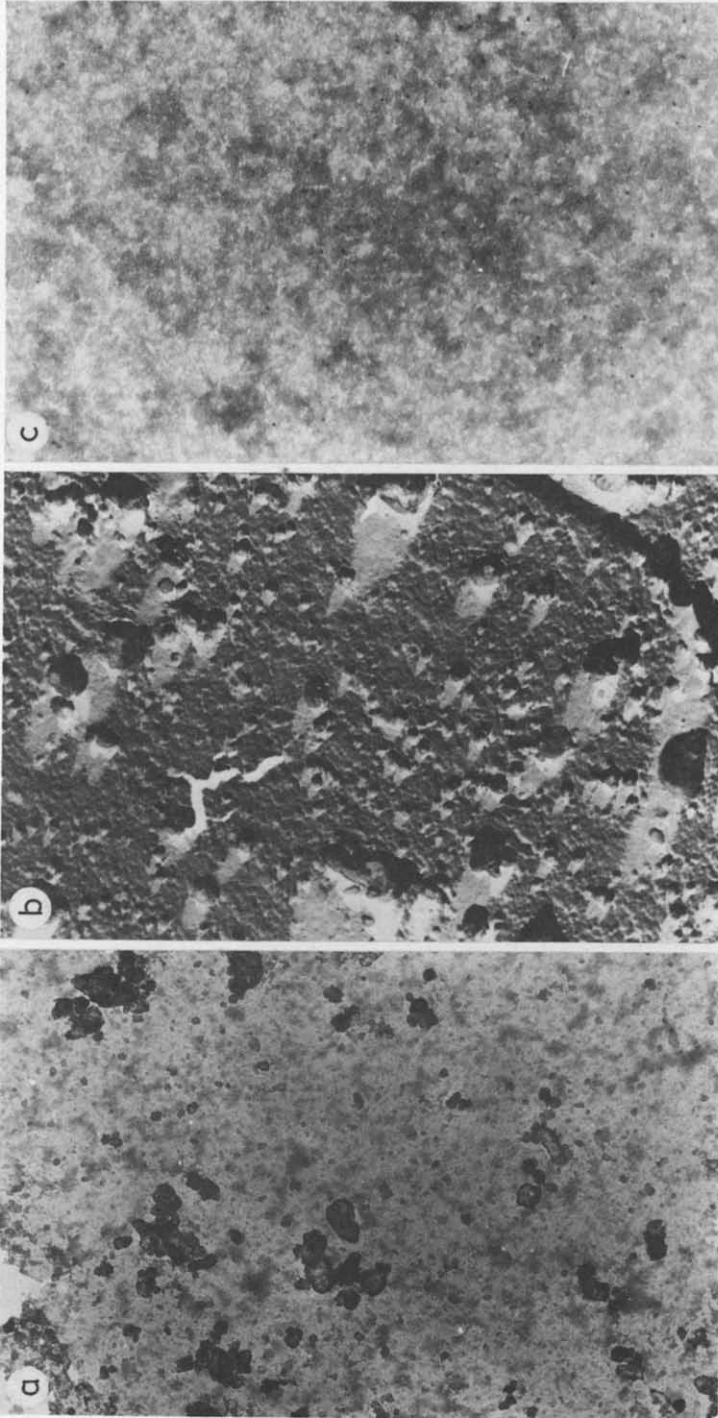


Fig. 6. Surface of Carboxil A2 (silica + pentanol). Details as in Fig. 5.

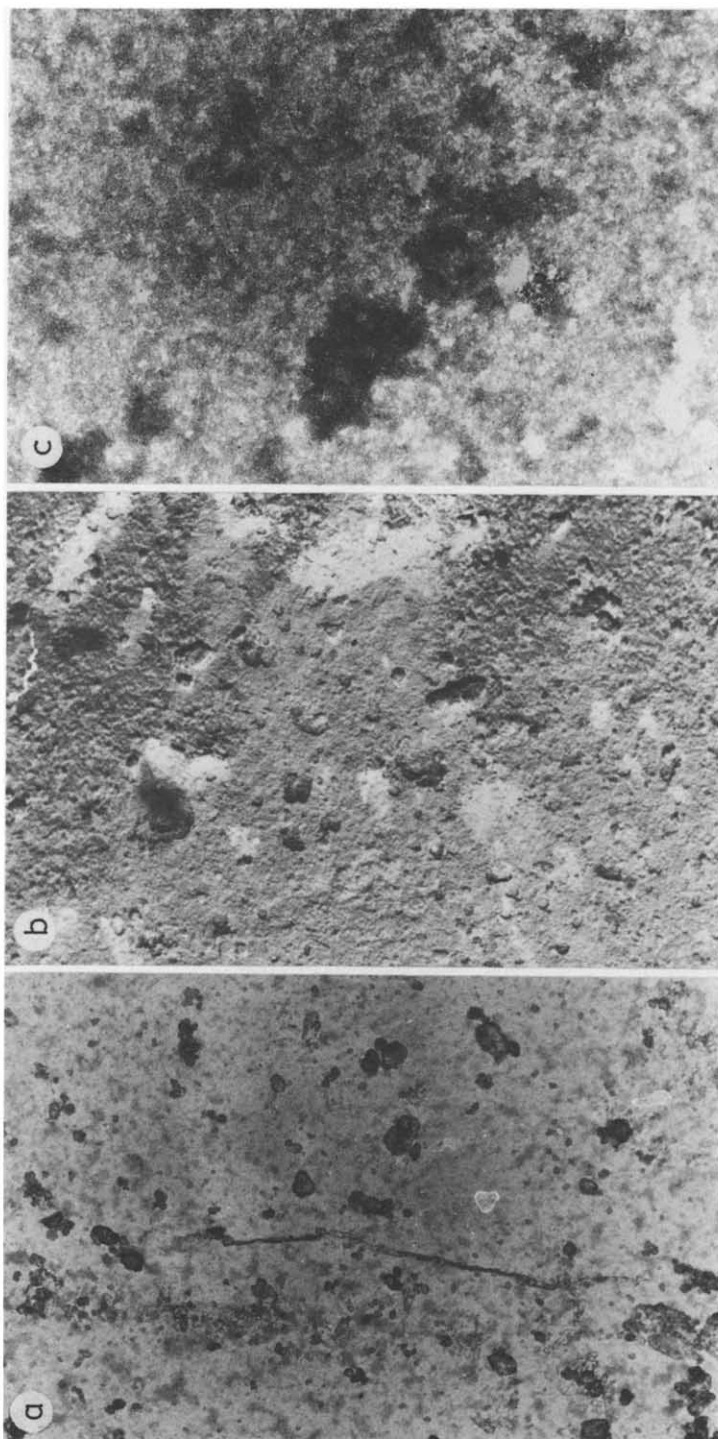


Fig. 7. Surface of Carbosil A3 (silica + dichloromethane + pentanol). Details as in Fig. 5.

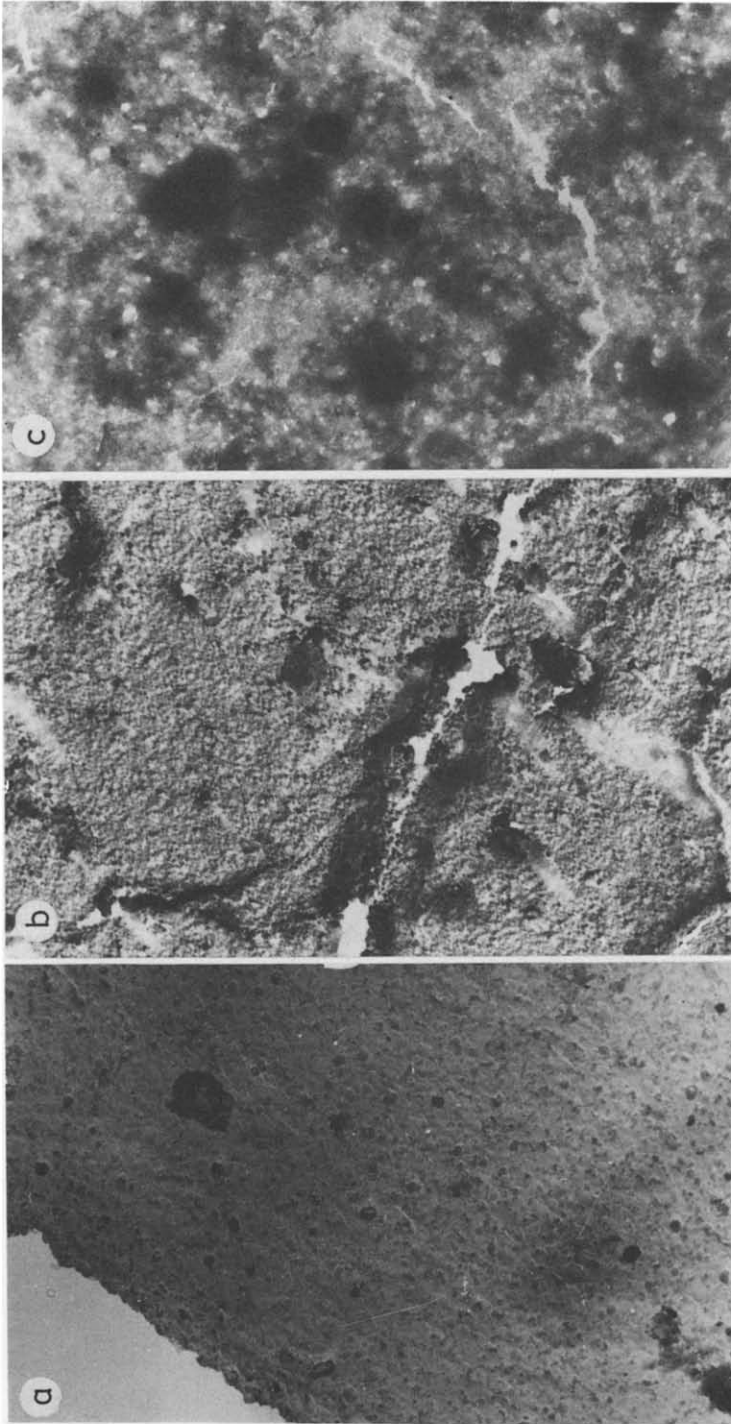


Fig. 8. Surface of Carbosil A4 (silica + pentanol + dichloromethane). Details as in Fig. 5.



Fig. 9.

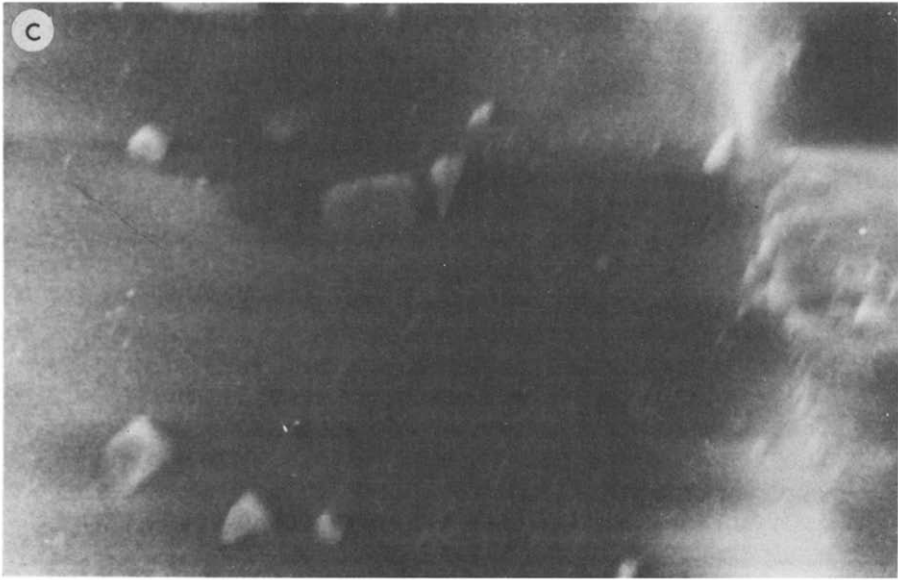


Fig. 9. Surface of the initial silica gel observed by SEM, magnification  $\times 1000$ . A two detector system with opposite Everhart-Thornley detectors was employed. BSE = Backscattered electrons; SE = secondary electrons. a, A + B, BSE image with material contrast; b, A - B, BSE image with imaging artifacts; c, A + B, SE image with material contrast; d, A - B, SE image with topographic contrast.



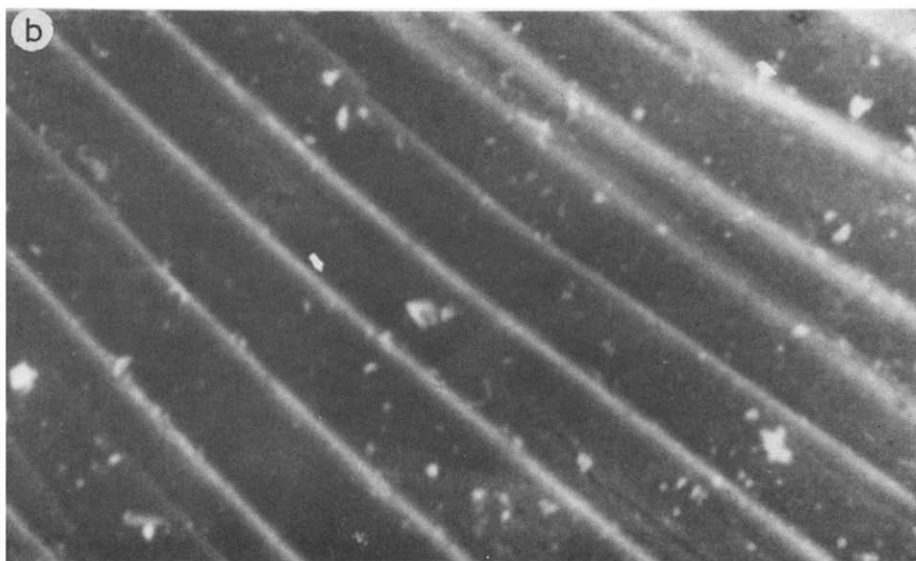
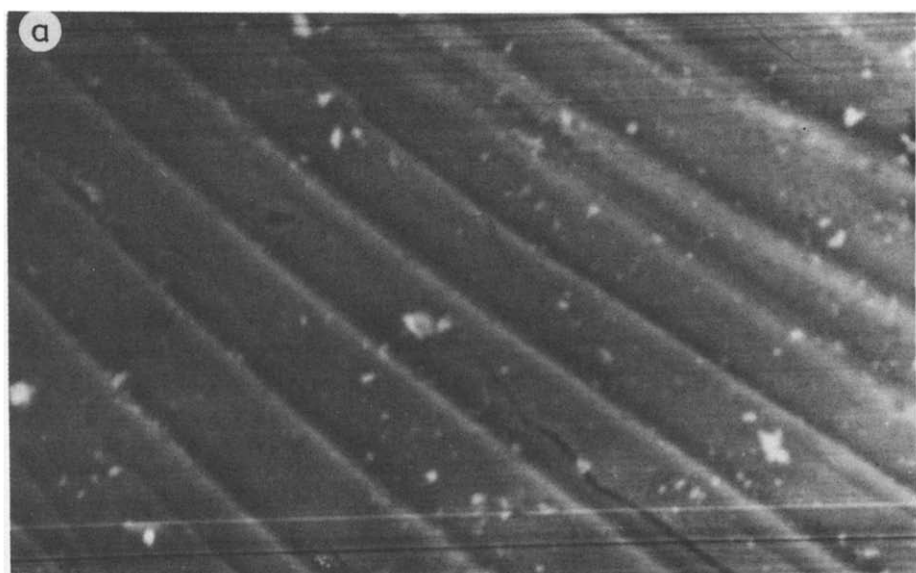


Fig. 10.

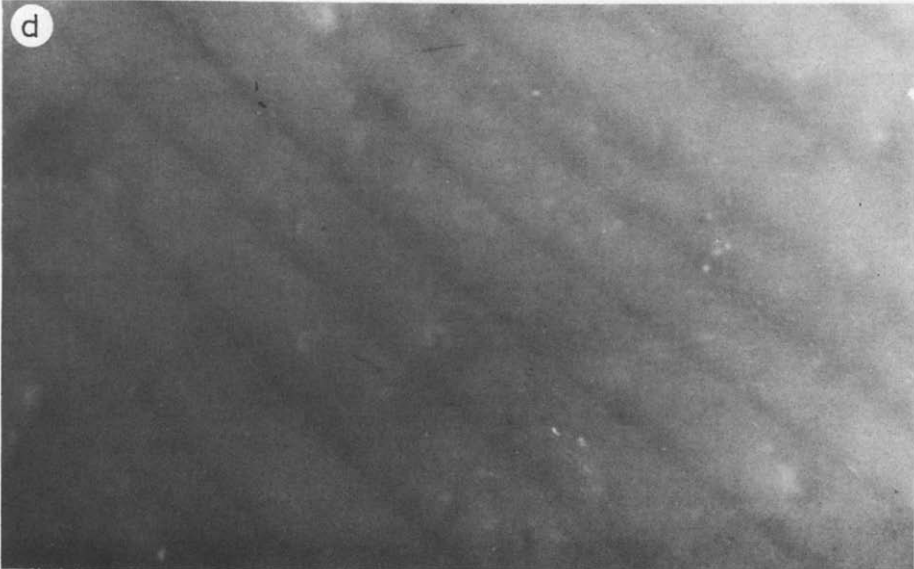
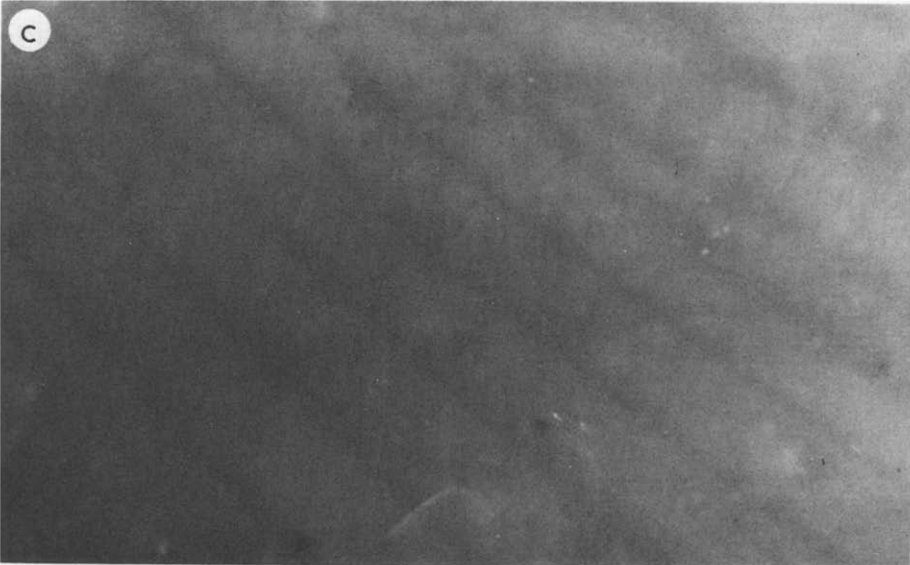


Fig. 10. Surface of Carbosil observed by SEM. Details as in Fig. 9.

carbon-silica adsorbent consists of silica and a deposited layer of carbon by dissolving silica in hydrofluoric acid the following samples were examined by TEM: carbon replica together with a carbon deposit (Fig. 1), carbon-platinum replica together with a carbon deposit (Fig. 2) and a carbon deposit alone (Fig. 3). The TEM micrographs were obtained using a TESLA BS 613 apparatus, magnification  $\times 5000$ .

For SEM, the initial silica gel and one of the Carbonsils were chosen. Uncovered samples and those covered by a conductive layer of gold layer were examined. The micrographs were obtained by a SEM apparatus Type MR 1000 equipped in a two-detector system with two opposite Everhart-Thornley detectors<sup>2</sup>, magnification  $\times 1000$ . Parts a of Figs. 4-8 show the surfaces of samples prepared by the carbon replica technique, parts b show the surfaces of samples prepared by the carbon-platinum replica technique and parts c show the film of carbon deposited directly on the silica gel by pyrolysis. The pictures are formed by the electrons transmitted through the layer of the evaporated carbon and carbon deposit (a), or the evaporated carbon-platinum and carbon deposit (b) and directly through the carbon deposit (c). It is seen that the pictures of the surface of each adsorbent are different and depend on the method of preparation. The micrographs in Figs. 4-8a are not very informative because the contrast is poor. In Figs. 4-8b the details of the surface are more visible. A comparison of the pictures for the initial silica gel (Figs. 4b) with those for adsorbents A1-A4 (Figs. 5-8b) indicates that during pyrolysis topographic changes take place. By use of the carbon-platinum replica technique it is possible to observe these topographic changes, but it is not possible to detect the carbon deposit. The morphology of carbon deposit can be examined using the electron diffraction technique<sup>3</sup>.

The aim of the SEM examination was to determine how the method of prep-

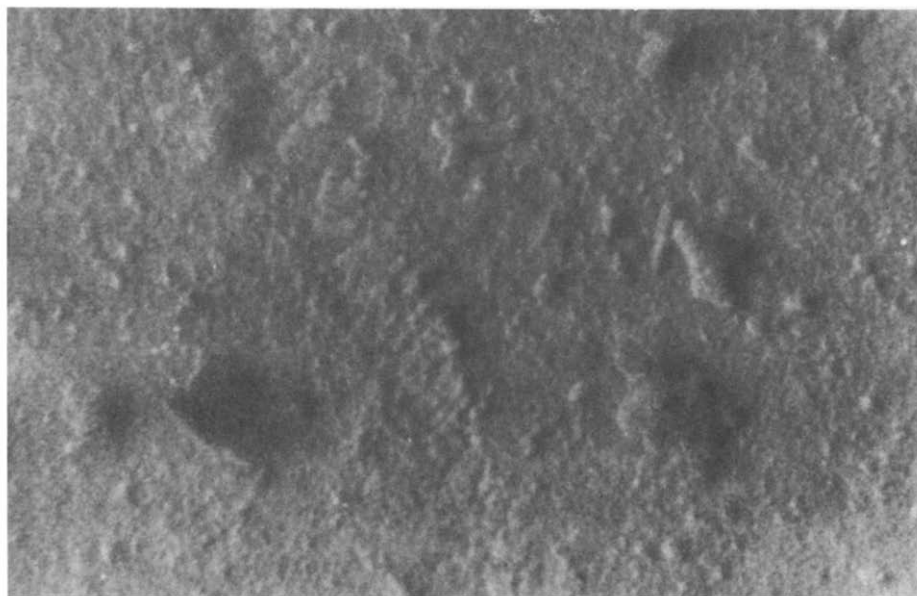


Fig. 11. Surface of the initial silica gel covered by a gold layer, as observed by SEM; magnification  $\times 1000$ .



Fig. 12. Surface of Carbosil covered by a gold layer, as observed by SEM; magnification  $\times 1000$ .

variation of the samples and the system of detection influence the information obtained from the surface of the adsorbent. Figs. 9 and 10 show the SEM pictures observed for the same place on the sample obtained by use of different detection modes. Fig. 9 depicts the surface of silica gel without a gold layer. The typical charge effect for uncovered inorganic materials was observed. Topographic details could not be detected, the contrast and the resolution being poor because the brightness of the edges was strong. Fig. 10 depicts the surface of Carbosil, where the silica gel is covered by a layer of carbon which eliminates the charge effect. The lack of this effect is proof that a carbon deposit is present on the silica surface.

Figs. 11 and 12 present the same silica gel and Carbosil but covered by a gold layer. Although this layer eliminates the charge effect, it is still impossible to distinguish carbon from silica gel.

## CONCLUSIONS

(1) By using different techniques of sample preparation for TEM, different features of the sample surface can be observed.

(2) The carbon-platinum replica technique of sample preparation is the most appropriate for TEM examination of the surface of Carbosils.

(3) The direct deposition of carbon is suitable for morphological examination, *e.g.*, by electron diffraction.

(4) By elimination of the charge effect it can be concluded that carbon is present on the surface of the silica gel, but distinction between carbon and silica by SEM is not possible. This is because the coefficients of the backscattered electrons for carbon and for silica are similar.

One of the most characteristic chromatographic parameters is the specific sur-

face area, which according to Guillemin<sup>4</sup> should not be neglected. The pore diameter is directly related to the specific surface area. By use of the replica technique, which gives an impression of the surface, a relationship between the microscopic picture and the pore diameter can also be found.

Carbosil A2 had the highest value of the surface area (Fig. 6b) and Carbosil A4 the lowest one (Fig. 8b). The value of the pore structure (Fig. 6b and Fig. 8b) seems to be opposite to the value of the surface of these two adsorbents. The Carbosils had increasing amounts of carbon (% w/w, see Table I) on their surfaces (Figs. 5–8c). Fig. 5c shows the film of carbon deposit on Carbosil A1 (0.8% w/w) which seems to be homogeneous, while Fig. 8c shows the corresponding film for Carbosil A4 where the process of carbon agglomeration takes place (2.21% w/w).

Further investigations will be undertaken in order to determine to what extent the different methods of preparation of the carbon–silica adsorbents influence the morphology of the carbon deposit and its crystalline structure.

#### ACKNOWLEDGEMENT

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#### REFERENCES

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