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POLISH DIATOMACEOUS SUPPORTS FOR GAS CHROMATOGRAPHY.

II.* SOLID STRUCTURE INVESTIGATIONS BY HYDROGEN CHLORIDE GAS PURIFICATION

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SUMMARY

The changes in geometric and crystallographic structures of Polish diatomaceous supports and Chromosorb P after washing with hydrogen chloride gas at elevated temperatures in connection with chemical composition changes were examined. The results of X-ray diffraction spectroscopy and microanalysis together with scanning electron microscopic and transmission electron microscopic investigations are presented.

INTRODUCTION

The most important properties of gas chromatographic supports are adsorptivity and catalytic properties as well as chemical purity and homogeneity of the surface, all of which determine the ability of the support to achieve uniform coverage with liquid stationary phase with low mass transfer and good selectivity.

In practice, ideal diatomaceous supports do not exist and much research has been carried out to improve their chromatographic performance. The presence on the surface of supports of metals such as aluminium, iron and titanium as well as their oxides causes adsorptive and catalytic activity. In an earlier paper[1] we concluded that the percentage of the metals removed from the supports is highly dependent on the chemical form of the metal, *e.g.* oxide, silicate or halide. This depends on the origin of the deposits from which the raw material for the supports comes, as well as on the mineralogical form of that material. Therefore, it was interesting to determine how the mineralogical form of a support influences its cleaning-up ability using the gas-phase method described by Aue *et al.*[2] and how this procedure influences the geometric and crystallographic structure of the supports. Both these effects are clearly visible after bonding of Carbowax 20M and checking of the chromatographic properties of the support-bonded phase, described in the previous paper[1].

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* For Part I, see ref. 1.

EXPERIMENTAL

Supports

Polish diatomite supports of the type Polsorb B and C[7] (Permedia, Lublin, Poland) and Chromosorb P (Johns-Manville, Denver, CO, U.S.A.) were employed.

Methods

To evaluate the surface properties of the supports the following methods were used: X-ray diffraction spectroscopy, microanalysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Apparatus

A Dron-2 diffractometer, a JEOL JXA-5-CMD microprobe, a Cambridge S4-10 scanning electron microscope and a JEM 100 B transmission electron microscope were employed.

Preparation of samples

Samples for X-ray microanalysis were prepared using the following procedure. The support grains, submerged in epoxy resin, were polished with diamond powder and covered with a gold layer in a vacuum. Single grains were examined for their homogeneous surface parts as well as parts with various intrusions. Linear and facial distributions of elements such as aluminium, titanium, iron and silicon were recorded using a photographic method.

Changes in the shape of the support grains were studied using SEM (200 × magnification); the primary and secondary structure was observed using 1000 × magnification[3]. A relatively small magnification for surface research was used owing to the fact that sponge-like diatoms are particulary difficult subjects for SEM studies.

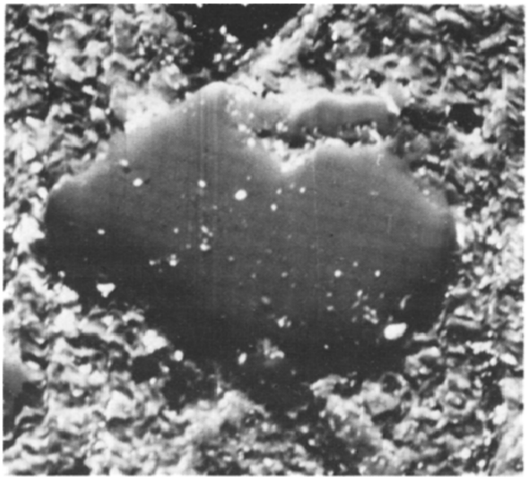
These difficulties are connected with electrification of the electron beam even after covering the specimens with an insulating layer. To diminish this effect saturation of the surface with osmium tetraoxide and covering with carbon and gold layers was used. The Pt–C direct replica method using TEM was employed while studying the secondary and tertiary structure of the diatom at magnification 70.000 × . After a five-fold photographic blow-up, the final magnification was 350.000 × .

RESULTS AND DISCUSSION

The X-ray microanalyser (electron microporobe) gives information about each chosen area of the specimen, while X-ray diffraction makes confirmation of the presence of particular crystallographic phases possible, and X-ray spectroscopy describes how these crystallographic phases are located in the single grain. It is also possible to determine the composition and size of the crystals.

Both methods yield useful information and supplement each other. We have found that in Polsorb C, silica is present in the form of α-quartz, after gas washing more than half of which is converted into α-crystobalite. In the case of Polsorb B and Chromosorb P we have found two forms of silica, α-crystobalite and α-quartz. Washing with hydrogen chloride gas did not give any changes in this case.

Amorphous silica, present in the diatom, changes partially into α-crystobalite



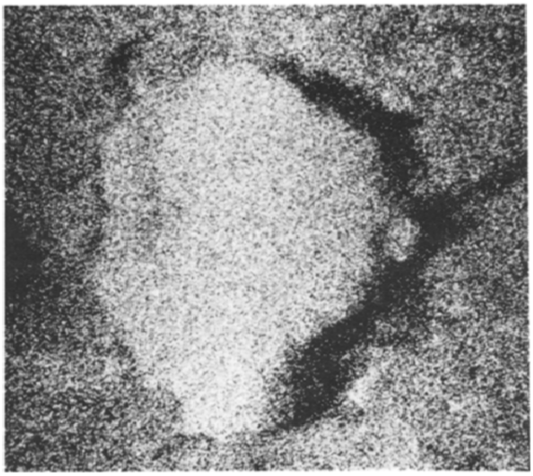
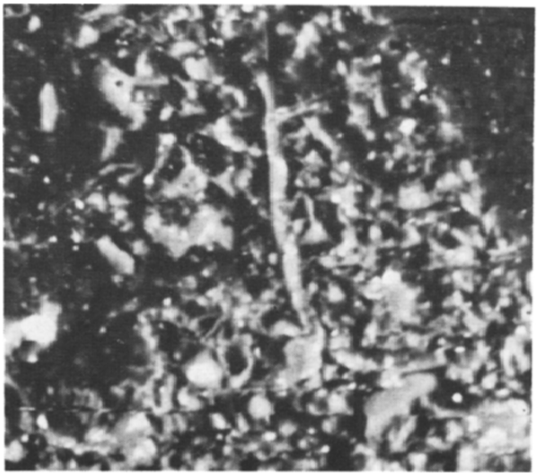


Fig. 1. Surface of commercial Polsorb C, large crystalline form of silica: topological picture (415 ×).

Fig. 2. As Fig. 1: facial distribution of silica.

(low-temperature form, 180–270°C) or into α-quartz (573–870°C) in the production process of commercial supports. As a result of our investigations it may be concluded that commercial as well as gas-washed supports consist of silica in both amorphous and crystalline forms. These two forms show different surface properties. The critical surface tension of the two forms traditionally coated by a liquid stationary phase may be different and may also influence the support bonding process due to a different distribution of OH groups on the surface. Pink supports such as Chromosorb P and Polsorb C, compared with white supports, contain more crystalline forms of silica, aluminosilicates, iron and titanium compounds as well as having larger crystals. The



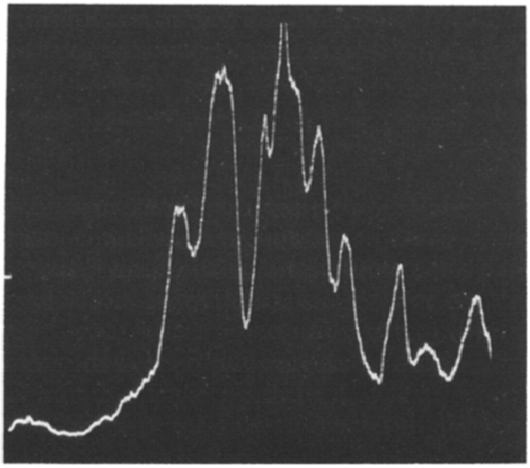
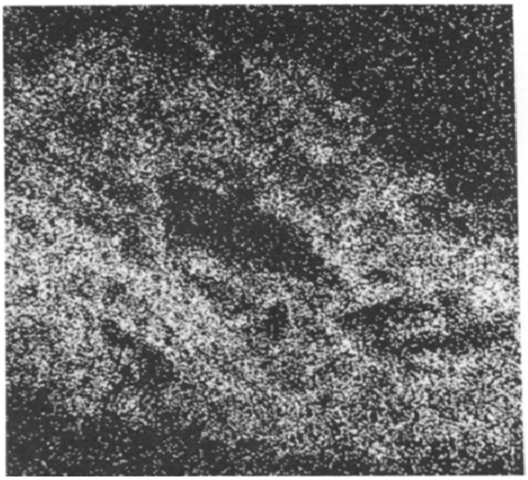


Fig. 3. Surface of commercial Polsorb B, small crystalline form of silica: topological picture (415 ×).

Fig. 4. As Fig. 3: linear distribution.



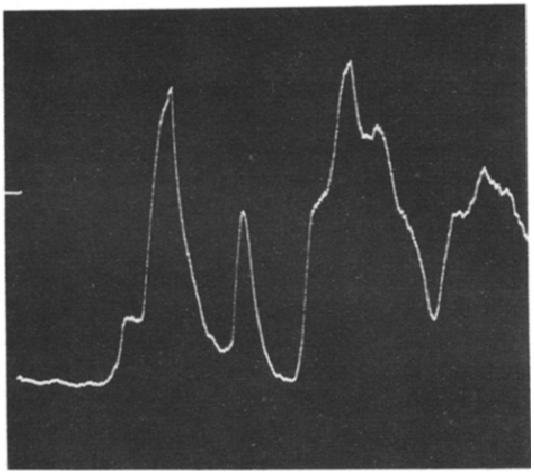


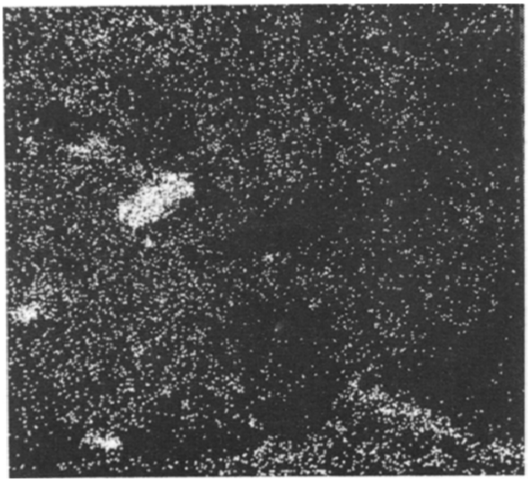
Fig. 5. Distribution of alumina in commercial supports: facial distribution.

Fig. 6. As Fig. 5: linear distribution.

differrence in size is due to the different composition of the raw material: the mean size of the crystals in the pink material is 50 μm (Figs. 1 and 2) while that for the white ones is smaller (10 μm) (Figs. 3 and 4).

All the commercial supports, according to our X-ray diffraction examination, contain illite, an aluminosilicate, as a separate crystalline form. The gas-washing procedure has no influence on the form in Polsorb B and Chromosorb P while in Polsorb C, illite is converted into sillimanite.

Sillimanite, a polymorphous variety of $AlSiO_5$, represents the highest energy of the crystal network. The above-mentioned property is probably responsible for the



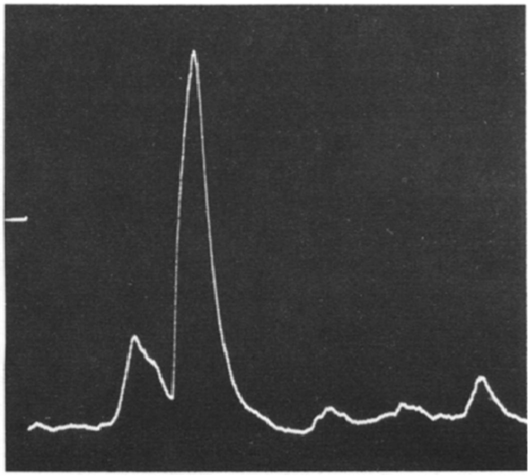


Fig. 7. Distribution of alumina in supports after gas washing: facial distribution.

Fig. 8. As Fig. 7: linear distribution.

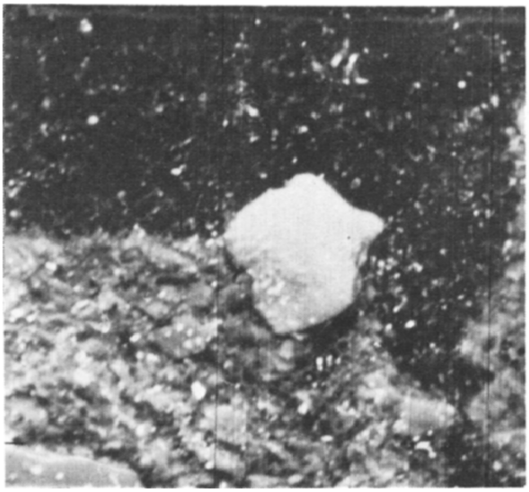


Fig. 9. Distribution of iron and titanium: topological picture (415 ×).

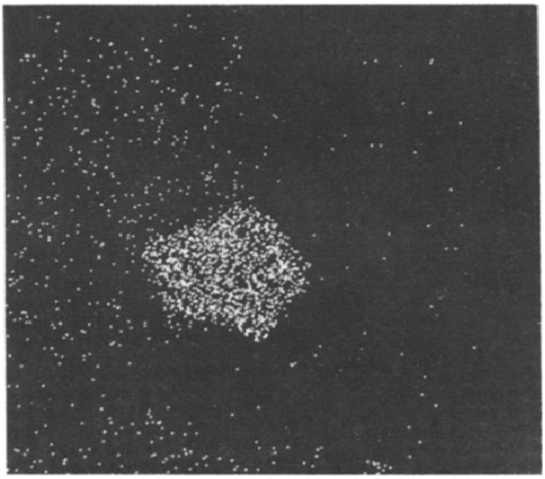


Fig. 10. As Fig. 9: facial distribution of Ti.

difficulties in removing the Polsorb C alumina compared with Chromosorb P and Polsorb B.

Elemental analyses are listed in Table I from ref. 1, from which it can be seen that gas-washed Polsorb C contains 6.61 % Al, even more than commercial Polsorb B (5.5 % Al). This relatively high content in the gas-washed supports did not affect the bonding procedure of Carbowax 20M, unlike for commercial products such as Chromosorb P and Polsorb B and C. Commercial supports show a higher contents of alumina in crystalline intrusions (Figs. 5 and 6).

Gas-washed supports generally show a lower alumina content (Fig. 7). Linear analysis of the concentration of this element showed a sharp peak only in places

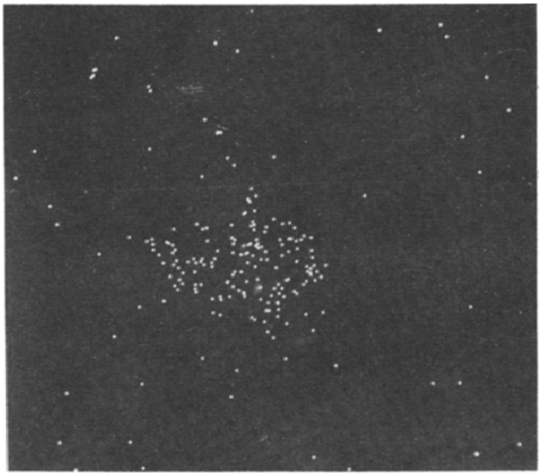


Fig. 11. As Fig. 9: facial distribution of Fe.

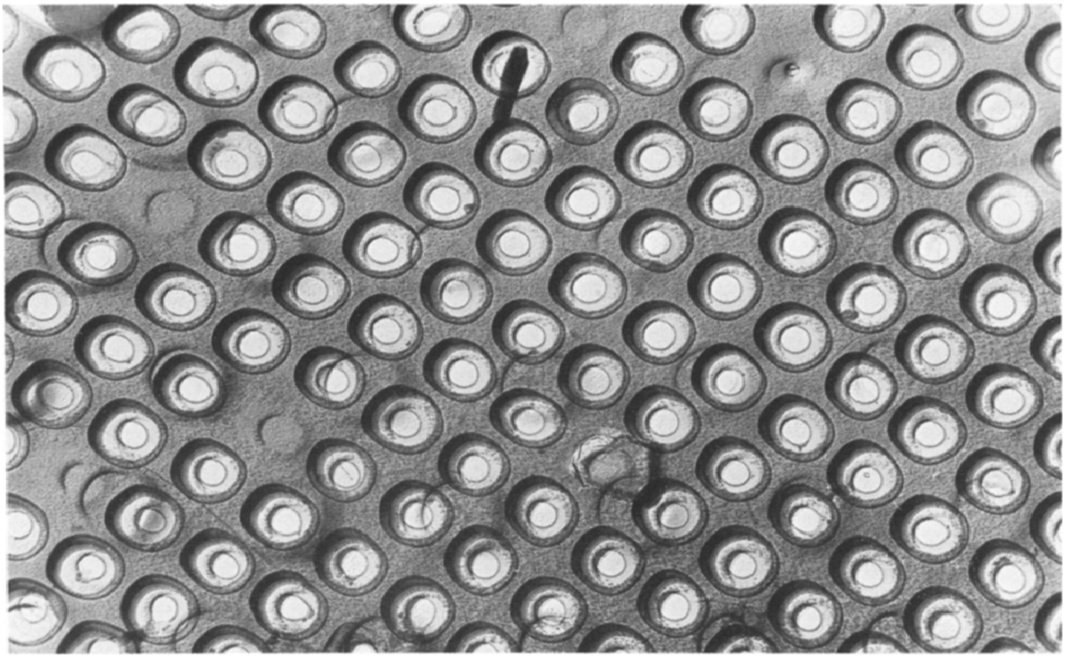
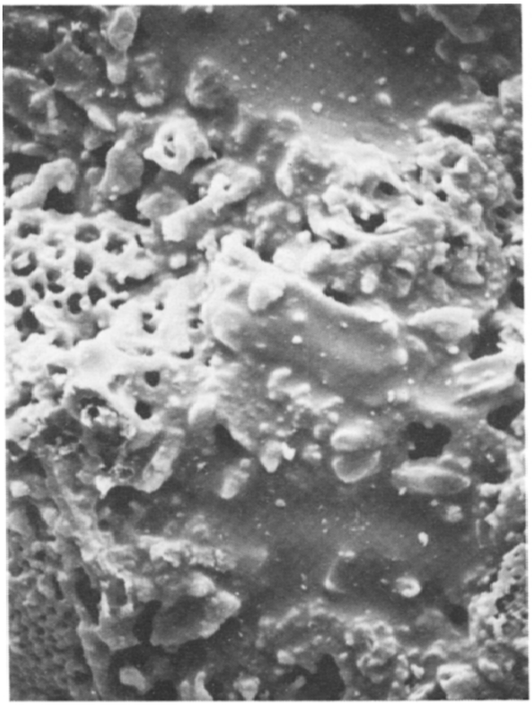


Fig. 12. External topology of commercial supports: macropores of selections of diatom (TEM, 8100 ×).



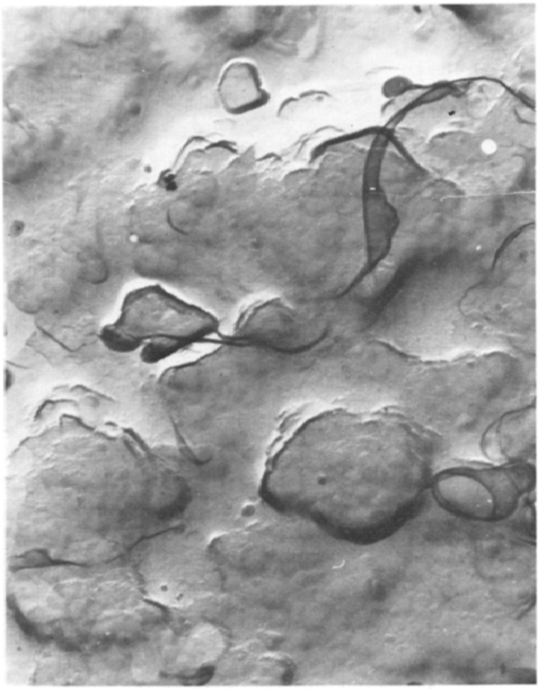


Fig. 13. As Fig. 12: macropores created by production process (SEM, 5940 ×).

Fig. 14. As Fig. 12: "flat" surface of support, namely quartz (TEM, 5940 ×).

where alumina–silicate intrusions were present (Fig. 8). This phenomenon clearly indicates that removal of the aluminium present in the supports as aluminosilicates is impossible while the other elements may be easily removed. Iron and titanium are present in commercial supports in crystalline forms (Fig. 9), *e.g.* rutile as a crystalline form of TiO_2 in Polsorb C.

Figs. 10 and 11 show an unequal distribution of iron and titanium. Such plases, as well as aluminosilicate intrusions, may disturb not only the bonding of Carbowax 20M but also, owing to their crystallographic activity, generally diminish the chromatographic performance of the support. After the gas-washing procedure the iron and titanium content is low, being undetectable even using X-ray spectrometry. The gas-washed supports are thus silica with small aluminosilicate intrusions.

Aue and co-workers[1–4] have stated that the chemical composition and the method of preparation of the supports play crucial roles in the bonding of the Carbowax 20M layer. However it seems to be important to take into consideration the external topology of the support grains. The topology of the commerical supports is shown in Figs. 12–14. It may be characterized by the presence in the diatom skeleton of micropores (Fig. 12) and macropores created by the production process (Fig. 13), and "flat" surfaces, namely quartz (Fig. 14).

After gas-washing the surface appears different. There is no diatom skeleton and the macropores and the surface have become fused and sponge-like (Figs. 15 and 16). Aluminosilicates present on the surface are in macro-crystal forms (Fig. 17).

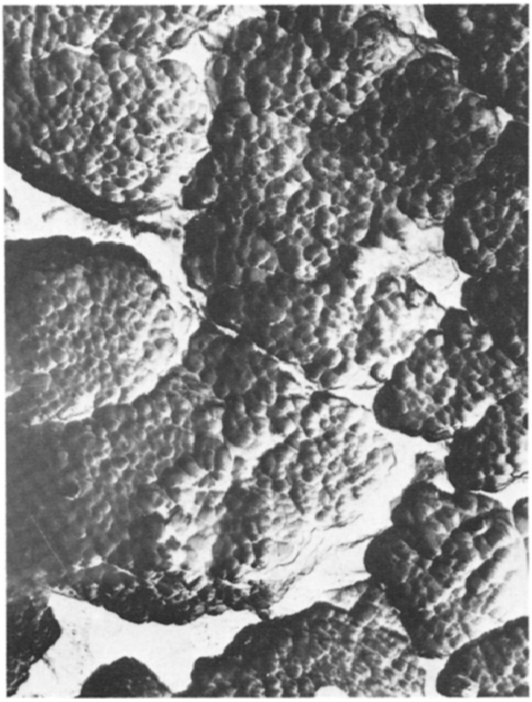


Fig. 15. Sponge-like surface of support after gas washing (TEM, 5940 ×).

Fig. 16. As Fig. 15.

Fig. 17. Macro-crystal forms of aluminosilicate on the surface of support after gas washing (SEM, 5940 ×).

Even after gas-washing, the supports are chemically pure although their external topology is far from the ideal macroporous structure. Thus it can be concluded that the surface, after coating with a liquid stationary phase, represents a mean value for the structures of different geometry and topology, with the additional influence of the spots with different chemical composition. It thus seems that the model assumptions of Giddings[5] and Sepinet[6] regarding distribution of the liquid stationary phase are of limited value, being applicable only to gas-washed and not commercial supports. The phenomenon of statistically uneven coatings of the liquid stationary phase on the support grains, especially in the case of non-polar phases, may be of great importance, particularly with only low percentages of the stationary phase.

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