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Note

Surface characterization of acid- and base-treated Chromosorb W by electron spectroscopy for chemical analysis

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The selection of a chromatographic support depends on its structure, size and surface characteristics. These features are important since the efficiency of the separation is dictated by the uniformity and total surface area of the particles. Surface characteristics also dictate the extent to which the support itself can enter into the separation process. For many applications, such as trace analysis, the preparation of bonded chromatographic supports, and the separation of certain polar materials, the support must be as inert as possible.

Since the early period of gas chromatography, various methods of support deactivation have been attempted. A review of the pre-1963 deactivation procedures is given by Ottenstein¹. Recently, Aue *et al.*² showed the effect of exhaustive acid washings on the bulk support material. In this report, various types of Chromosorb NAW were treated sequentially by (1) extracting in a Soxhlet apparatus with a 6 *N* HCl solution for one day, (2) heating to 850-900° with nitrogen flow with small additions of hydrogen chloride, (3) extracting in a Soxhlet apparatus with 6 *N* HCl for one day and (4) washing to neutrality. This procedure removed more than 95% of the bulk iron. The authors believed iron was probably removed from the surface of the particles rather than the bulk of the diatom skeleton.

Electron spectroscopy for chemical analysis (ESCA) has been used for a wide variety of surface analyses³ and provides a simple method of evaluation of the relative number of atoms in the surface region from 10 to 50 Å depth. Since several approximations are needed to quantitate data in surface segregated samples, the accuracy of ESCA as an absolute analytical method is not very high. However, the method can give valuable information not available from other methods, especially when comparing similar samples. Thus, we believed that ESCA might be used to determine elemental changes in the surface of Chromosorb W after various treatments to ascertain which treatment eliminated most of the surface-active elements.

EXPERIMENTAL

Apparatus

The ESCA investigations were carried out with a Varian IEE-15 spectrometer.

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using $MgK\alpha$ radiation with a vacuum of 10^{-6} – 10^{-7} Torr (10^{-8} – 10^{-9} Pa). The powdered samples were fixed onto a double-sided adhesive tape.

A Perkin-Elmer Model 900 gas chromatograph with a glass column (1 m \times 2 mm) was used for heating the sample with helium flow.

Chemicals

Chromosorb W NAW, 60–80 mesh (Johns-Manville, Denver, Colo., U.S.A.) was obtained from Applied Science Labs. (State College, Pa., U.S.A.). Chromosorb W and other white supports are prepared from filter aids which are manufactured by adding *ca.* 2% sodium carbonate to diatomaceous earth and heating to temperatures greater than 900° in a rotary kiln. Reagent-grade hydrochloric acid, sodium hydroxide and acetic acid were obtained from Fisher Scientific (Fairlawn, N.J., U.S.A.). All samples were washed with water that had been distilled in aluminum to minimize sodium contamination.

Procedure

The untreated support was analyzed directly from its container with no additional treatment (support 1). The acid-washed (AW) support (2) was soaked in 3 *N* HCl for 2 h with periodic stirring, then collected by filtration on a medium-porosity glass-fritted funnel, and washed to neutrality with distilled water. The support was then dried at 110° in a vacuum oven for 16 h. The acid-washed base-washed support (3) was treated as the AW support (above), but before drying was soaked in 1 *N* NaOH, then washed to neutrality.

Support 4 was treated as the AW support, but, before drying, was refluxed for 1 h with glacial acetic acid and then washed to neutrality.

Some of the AW support was packed into a glass chromatographic column (1 m \times 2 mm) and heated for 27 h at 300° with 50 cm³/min helium flow (support 5) to simulate chromatographic conditions.

To investigate the effect of base washing, some of support 1 was soaked in 6 *N* HCl solution, then washed with 1 *N* NaOH solution (support 6). Another sample of support 1 was washed with 1 *N* NaOH solution (support 7). All supports were washed to neutrality with distilled water.

RESULTS

Photoionization cross-sections calculated by the Scofield method were used to determine atomic ratios from measured peak areas since a fixed analyzer transmission instrument was used⁴.

$$\text{Normalized counts} = \frac{\text{Counts}}{\text{Cross section}} \quad (1)$$

$$\text{Atomic ratio} = \frac{\text{Normalized counts element 1}}{\text{Normalized counts element 2}} \quad (2)$$

Data were collected by computer-controlled signal averaging to enhance weak signals. The count rates and atomic ratios for each sample are shown in Table I.

TABLE I

NORMALIZED COUNTS AND (IN PARENTHESES) ATOMIC RATIOS OF ELEMENTS STUDIED

The atomic ratios are relative to silicon, *i.e.*, normalized counts element/normalized counts silicon.

Support	O	Fe*	Al	Na	Si	C
1	46,800** (1.81)	163 (0.006)	1650 (0.064)	6560 (0.255)	27,800 (1.00)	10,600 (0.411)
2	48,400 (1.68)	5 (—)	1030 (0.036)	1490 (0.052)	25,800 (1.00)	10,300 (0.358)
3	48,700 (1.74)	65 (0.002)	1400 (0.050)	2230 (0.069)	28,200 (1.00)	13,000 (0.480)
4	56,800 (1.57)	9 (—)	1100 (0.032)	642 (0.024)	35,100 (1.00)	35,000 (1.00)
5	55,600 (1.57)	12 (—)	1140 (0.032)	2660 (0.074)	36,000 (1.00)	7680 (0.4574)
6	25,100 (1.90)	8 (0.0006)	440 (0.0335)	976 (0.0741)	13,200 (1.00)	6030 (0.4574)
7	22,500 (1.95)	17 (0.0015)	650 (0.0560)	698 (0.0605)	11,500 (1.00)	3980 (0.3456)

* Noise level *ca.* 5 normalized counts/sec.

** Normalized intensity.

DISCUSSION

Simple treatment with distilled water to neutrality appeared to be sufficient to remove most of the iron and much of the sodium from the surface. This treatment also caused a significant dealumination to take place, which is consistent with results for HCl washing of mordenite⁵. Acid washing followed by base washing, or acid washing followed by refluxing with acetic acid, did not appear to improve the purity of the support surface. In fact, base washing appeared to deposit iron selectively on the surface of the support. The analysis of the base used showed 0.0007% iron which would be more than sufficient to account for the iron found in this study if it were largely deposited on the surface.

The support material, which was acid washed then heated to 300° with helium flow to simulate chromatographic conditions, showed no discernable changes in levels of iron or aluminum. Thus, no significant migration of these elements appears to occur under these conditions.

Carbon is an ubiquitous contaminant of all exposed surfaces and is significantly present in each one examined here. In the acetic acid treatment (sample 4), this level increased, perhaps because of acetate products formed. In sample 5, which was heated to 300°, this level has decreased substantially, because of volatilization or oxidation to volatile compounds.

Since it is commonly agreed that treatment of supports is necessary for many chromatographic applications, the simplest treatment, interestingly, removed the bulk of the impurities of interest on Chromosorb W. For some critical situations, additional treatment to the support may be necessary to remove aluminum and sodium.

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