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Note

Bis(octadecyl phosphate)zirconium(IV)

Novel support for reversed-phase chromatography

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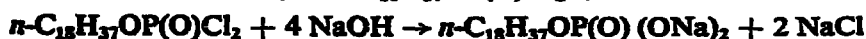
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In a recent study¹ the structure and chromatographic application of crystalline compounds $Zr(O_3POR)_2$, where R = butyl, lauryl and octylphenyl, were explored. Preliminary results, obtained with the lauryl derivative in the separation of aromatic hydrocarbons by reversed-phase chromatography (RPC), showed that this type of compound could offer an alternative to the well established silica based RPC supports. Clearly, the advantage in using the zirconium phosphate-based supports resides in the control of the carbon loadings that can be obtained since these compounds are the products of a homogeneous reaction with a well defined stoichiometry.

This communication describes the preparation of the octadecyl derivative and the evaluation of its performance as a RPC support.

EXPERIMENTAL

Monooctadecyl phosphoric acid was prepared according to the following scheme:



To a solution composed of 12.7 ml (0.14 mole) $POCl_3$ in 60 ml CCl_4 held in a three-neck flask at 25°, solid octadecanol (22 g, 0.081 mole) was added stepwise from a side-arm over a 2-h period. The HCl formed in the reaction was eliminated by maintaining the system at 200 mmHg pressure while sweeping with a stream of dry argon. Solvent losses were prevented by a reflux condenser maintained at 0°. After completion of the reaction the condenser was turned to a slanted position in order to distill the solvent and unreacted $POCl_3$. The residue was dissolved in ether and treated with 1 M NaOH. The sodium salt is insoluble in either phase and formed a layer at the interface. This material was isolated and briefly boiled with excess dilute hydrochloric acid. The crude acid was extracted into ether, washed with water and the extract evaporated to dryness. The final product was obtained in a pure form, $\geq 99\%$, after recrystallization from glacial acetic acid.

Bis(octadecyl phosphate)zirconium(IV) (ODPZ) was obtained by the addition of 4.1 g octadecyl phosphoric acid dissolved in 130 ml ethanol to a solution prepared by dilution of 15.0 ml stock zirconium solution, 0.4 M Zr in 10 M HNO₃, to 150 ml with distilled water. The reaction mixture was stirred overnight, filtered and the solid washed with water and acetone. The product was dried under vacuum and analyzed: found (wt. %): C, 54.08; H, 9.45; O, 17.0; P, 7.44; N, 1.11; Zr, 12.0. Calculated: C, 54.89; H, 9.40; O, 16.26; P, 7.86; Zr, 11.6. The relatively high nitrogen content is due to occluded nitric acid. Removal of excess acid takes place during loading and column conditioning with solvent as shown by a leveling off of the base line after a few bed volumes have passed through the column.

Chromatographic separations were performed using Laboratory Data Control accessories in a glass column (6.3 mm I.D.). The eluate was monitored at 254 nm with a HS 870 Schoeffel spectrophotometer.

RESULTS AND DISCUSSION

Structural considerations

The X-ray powder diffraction pattern of ODPZ, shows maxima at 44.14, 22.07, 14.71, 10.91 and 8.84 Å. The regularity of the spacings is evident; and, by analogy with the zirconium phosphate derivatives reported in ref. 1 and those studied by Alberti *et al.*², it appears that ODPZ also has a layered structure of the α -zirconium phosphate type. The α -zirconium phosphate structure³ consists of zirconium layers capped on both ends by the acid phosphate group; thus, the repeat unit is HOPO₃ZrO₃POH. In the case of the alkyl derivatives, the hydrogen atom is substituted by the alkyl group which causes an expansion of the interlayer distance. Particularly significant in the pattern of ODPZ is the first *d* spacing which corresponds to the interlayer distance. A value of 45.3 Å was calculated for this distance, as described in ref. 1, from the contribution of all the bond distances and angles. Agreement with the observed value is good. This indicates that there is little bending or interpenetration of the alkyl chains within the layers.

A micrograph obtained by transmission electron microscopy is shown in Fig. 1. The particles shown consist of agglomerates of smaller crystallites which are evident at the edges of the large particles. The size of these features is consistent with an estimate of about 100 Å for the size of the crystallites derived from the line broadening of the diffraction lines. Given an interlayer distance of 44 Å, this indicates that the crystallites are just a few layers thick.

Chromatographic separations

Initial tests were conducted with a column bed, 90 × 6.3 mm, filled with ODPZ of a coarse particle size (\approx 180 μ m). This column gave good separations of a naphthalene, anthracene and pyrene mixture using acetonitrile-water (95:5) as eluent. Elution with 30% water in methanol resulted in excessive retention. The flow-rate was 36 ml/h and the pressure was 10 p.s.i. The efficiency of this column was about 2200 plates per meter. No chemical changes of the support were detected, other than a lowering of the nitrogen content, after passage of a few liters of solvent. The analysis of this material shows in wt. %: C, 54.5; H, 9.81; N, 0.3; Zr 11.60.

Use of a finer particle size, \approx 60 μ m, to improve efficiency led to bed compac-

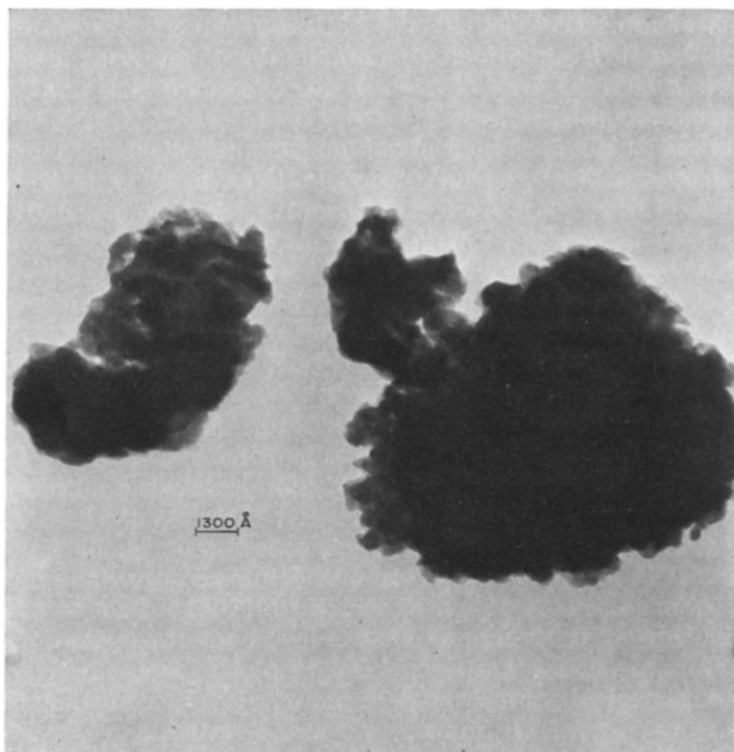


Fig. 1. ODPZ particles.

tion and excessive pressures. Finally, a column was loaded, 112×6.3 mm, with a 75:25 mixture of ODPZ and Celite 535 (diatomaceous earth; Johns-Manville, Denver, Colo., U.S.A.) which had been previously sieved between 230 and 325 mesh ($\approx 60 \mu\text{m}$). Solvent, 5% water in acetonitrile, was flowed through the column at 18 ml/h resulting in a 250-p.s.i. pressure. Efficiency of this column was about 4000 plates per meter. A previous test showed no interaction of the Celite with aromatic hydrocarbons using the same solvent mixture.

A typical chromatogram of a hydrocarbon mixture is shown in Fig. 2. Peak identity and concentrations in molarity are: 1, naphthalene (1.0×10^{-6}); 2, fluorene (2×10^{-6}); 3, phenanthrene (1.4×10^{-6}); 4, anthracene (1.6×10^{-6}); 5, fluoranthrene (1.5×10^{-5}); and 6, 9,10-dimethylanthracene (2.8×10^{-6}). The sample size was 0.1 ml. Full scale on the ordinate corresponds to 0.02 absorbance units.

The effect of loading and flow-rate on the performance of the column was examined. The concentration of the hydrocarbon mixture was increased by two orders of magnitude with no serious loss in efficiency. The results of these tests, along with those for the dependence of the HETP on flow-rate at 9.3 ml/h (160 p.s.i.), 18 ml/h (250 p.s.i.) and 23 ml/h (500 p.s.i.) are given in Table I. The higher pressure caused a total 3-mm compaction of the bed.

It is seen that ODPZ can be used for the separation of complex mixtures of hydrocarbons; however, further work is required to develop fully the potential of

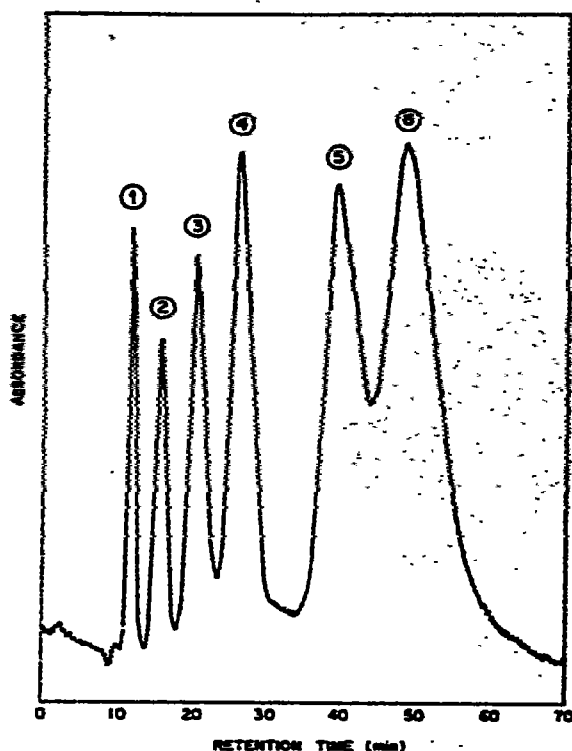


Fig. 2. Hydrocarbon separation. Peaks: 1 = naphthalene; 2 = fluorene; 3 = phenanthrene; 4 = anthracene; 5 = fluoranthrene; 6 = 9,10-dimethylantracene. For details, see text.

this type of support. Incentives for this are manifold; the simplicity of the preparation, the relatively high carbon loadings that can be achieved (54.5% in the case of ODPZ), and the complete absence of polar sites (such as unreacted hydroxyl groups in silica). Potential uses clearly are in the area of preparative chromatography, although analytical applications are also feasible. Areas for development include a better

TABLE I

EFFECT OF CONCENTRATION AND FLOW-RATE ON HETP (mm)

Compound	Concentration*			Flow-rate (ml/h)**	
	X	10X	100X	9.3	23
Naphthalene	0.26	0.25	0.26	0.16	0.30
Fluorene	0.30	0.26	0.21	0.21	0.29
Phenanthrene	0.34	0.27	0.28	0.19	0.30
Anthracene	0.35	0.36	0.60	0.24	0.32
Fluoranthracene	0.50	0.46	0.61	0.34	—
9,10-Dimethylantracene	0.66	0.65	1.1	0.53	—

* X is the concentration represented in the chromatogram in Fig. 2. Flow-rate for this set was 18 ml/h.

** Concentration for this set is X.

control of the particle size and mechanical strength of the support. Adsorption of zirconium onto silica microspheres followed by reaction with an alkyl phosphoric acid might produce a useful support.

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