

Preparation and Properties of a Chromatographic Adsorbent Based on γ -Alumina Modified with Octylphosphonic Acid Diethyl Ester

M. V. Buchnev, P. G. Mingalev, A. A. Serdan,
A. N. Morozov, and G. V. Lisichkin

Department of Chemistry, Moscow State University,
Leninskie gory, Moscow, 119899 Russia

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Abstract—Aluminum oxide modified with octylphosphonic acid diethyl ether with the concentration of bound groups equal to 3.4 nm^{-2} (6.6% C) was synthesized. The retention times and Kovats indices were determined for pentane, hexane, heptane, benzene, methyl ethyl ketone, nitromethane, pyridine, and ethanol.

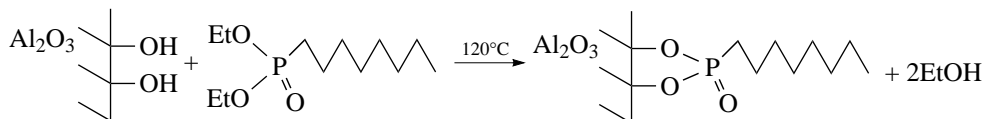
Recently, organophosphorus modifiers (phosphoric, phosphonic, and phosphinic acid derivatives) have been increasingly used to modify oxide supports. These modifiers are more frequently used for the surface modification of TiO_2 , ZrO_2 , etc., compared to traditional organosilicon compounds. These modifiers also play an important role in the preparation of modified alumina. Modifiers of this kind may be promising, because the chemistry of phosphonic acids is dramatically different from that of organosilicon compounds. This provides an opportunity for synthesizing bound layers with functional groups, such as alcohol groups, on oxide surfaces in a single step. An additional special feature of such modifiers is the strong specific interaction of an anchoring group with the oxide surface [1], which results in the considerable weakening of the acidity of the surface acid sites in these oxides. In our opinion, this can extend the area of application of the above oxides as supports for gas chromatography.

This work was devoted to a study of the properties of alumina modified with octylphosphonic acid diethyl ester.

EXPERIMENTAL

Preparation of alumina with a supported squalane layer. Puralox SB A-150 alumina with a specific surface area of $150 \text{ m}^2/\text{g}$ and an average pore diameter of 13.5 nm was used as a support. A fraction with an average pore diameter of $80 \mu\text{m}$ was separated by sedimentation in water. Squalane (20% of the weight of alumina) was dissolved in hexane so that the mixing of alumina with the solution gave a not very stiff mass. After the mixing, hexane was removed on a rotary evaporator. Silochrome S-120 with supported squalane was prepared in a similar manner.

Modification of alumina with octylphosphonic acid diethyl ester. The octylphosphonic acid diethyl ester was applied to 10 g of the sedimented dry alumina (1 mL per gram of the support). The resulting mass was sealed in an ampoule and heated at 120°C for 10 h. Thereafter, the product was washed on a filter initially twice with toluene and then successively with isopropanol, a water–isopropanol mixture, isopropanol, and hexane and dried on the filter. According to the data of elemental analysis, the surface concentration of the bound groups was 3.4 nm^{-2} (6.6% C). The reaction scheme is given below.



Surface modification of alumina

Chromatography. Stainless-steel columns 3 mm in internal diameter and 1.5 m in length were used. The

measurements were performed on a Chrom-5 chromatograph with a flame ionization detector at injector,

Retention indices of substances

Substance	Al ₂ O ₃ with C ₈ H ₁₇ PO(OEt) ₂		Al ₂ O ₃ with squalane		SiO ₂ with squalane	
	<i>t_R</i> , s	<i>I_R</i>	<i>t_R</i> , s	<i>I_R</i>	<i>t_R</i> , s	<i>I_R</i>
Dead time	24		20		14	
Pentane	78	500	100	500	63	500
Hexane	132	600	193	600	100	600
Heptane	226	700	377	700	165	700
Benzene	167	645	475	733	163	697
MEK	228	702	1080	850	350	850
Nitromethane	360	781	Not eluted	–	195	745
Pyridine	Not eluted	–	The same	–	Not studied	–
Ethanol	The same	–	"	–	The same	–

oven, and detector temperatures of 150, 120, and 180°C, respectively. Nitrogen was used as a carrier gas (flow rate, 50 mL/min).

RESULTS AND DISCUSSION

We determined the retention times of substances (table). The Kovats retention indices were calculated from these results using the equation

$$I_x = 100z + 100 \frac{\log(t'_{R_x}/t'_{R_z})}{\log(t'_{R_{z+1}}/t'_{R_z})}$$

It can be seen that the substances were more weakly retained on the alumina modified with the octylphosphonic acid ester than on the alumina coated with squalane. Moreover, the retention time of benzene on the column with squalane was longer than the retention time of heptane under the same conditions. Therefore, specific interactions occur between benzene and the adsorbent surface, and these interactions increased the retention time. It is believed that these are donor–acceptor interactions between the π -electron system of benzene and surface Lewis acid sites. At the same time, it is well known [1] that the phosphoryl groups of the bound phosphonic acids effectively interact with these acid sites. Therefore, it would be expected that the adsorbate (benzene in the case under consideration) does not interact with these sites; correspondingly, it emerged from the column earlier (because the boiling temperature of benzene is lower than that of heptane). In the case of methyl ethyl ketone (MEK), interactions

of this kind were also observed; however, they were incomparably weaker than those in the case of Al₂O₃ with squalane. It is also of interest that nitromethane did not emerge from the column packed with squalane on alumina even after 30 min, whereas its retention time on the column with the alumina modified with the phosphonic acid ester was 6 min. Evidently, this is due to the same reasons. The Kovats indices obtained with the test adsorbent are much closer to the indices obtained with squalane supported on Silochrome; at the same time, it is well known that Lewis acid sites are practically absent on Silochrome.

An undoubted advantage of the proposed adsorbent is a much higher thermal stability of the resulting phase. Thus, with the use of squalane as a stationary phase, the maximum allowable column temperature is 120–140°C, whereas alumina with the bound octylphosphonate groups is stable up to 200–250°C.

Thus, it would be expected that alkylphosphonic acid derivatives could be applied to the preparation of alumina-based adsorbents for gas chromatography. Note that, with the formation of a covalent bond between the surface of alumina and the phosphorus atom incorporated into the anchoring group, not only hydrocarbon radicals but also compounds with various functional groups can be bound to the surface.

REFERENCES

1. Ramsier, R.D., Henriksen, P.N., and Gent, A.N., *Surf. Sci.*, 1988, vol. 203, p. 72.