Journal of Chromatography, 242 (1982) 166–169
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,787

Note

Modification of sorbents and solid supports by a glow discharge plasma

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(Received January 28th, 1982)

The treatment of surfaces by a glow-discharge plasma using the vapours of various compounds has been widely used for applying polymeric coatings on to supports[1]. This technique permits polymers to be obtained from monomers that cannot be polymerized under conventional conditions, and very thin cross-linked films, insoluble in organic solvents. We have previously reported the surface modification of sorbents in gas chromatography by a glow-discharge plasma[2].

In this paper two types of chemical modification by plasmas are considered: modification of the surface of porous polymeric sorbents in order to change their polarity and treatment of solid diatomite supports in order to suppress their adsorption activity.

EXPERIMENTAL

The experiments were performed on the porous polymeric sorbent Polysorb-I (styrene–divinylbenzene a copolymer) and on the solid diatomite support Chromaton N AW. These materials were treated by a glow-discharge plasma (1 kHz a.c.) in a "vibrofluidized" state created by using a vibrator, placed in the vacuum reaction chamber[2].

The compounds used for grafting were α-vinylpyridine (I), 2[α,β-difluoro-β-chlorovinylpyridine] (II), N-methylpyrolidone (III) and *m*-fluorobenzylamine (IV). The surface of Chromaton N AW was modified in hexafluoropropylene dimer (DHFP) vapour.

The structures of the initial and modified sorbents were investigated by mercury porosimetry. The specific surface areas were determined by low-temperature adsorption of nitrogen and calculated by the BET method.

The polymeric films from the upper electrode were investigated in potassium bromide and caesium iodide tablets by IR spectroscopy with a Perkin-Elmer Model 580 spectrophotometer. In addition, the initial and modified materials were subjected to elemental analysis.

Gas chromatographic analyses were carried out with a Tsvet-4 chromatograph with a 1 cm × 4 mm I.D. column, equipped with a thermal conductivity detector. The column was conditioned in helium at 150°C. For investigating Polysorb-I the operating temperature of the column was 120°C. The effect of the plasma on chromatographic properties was determined by measuring the relative retention times of vari-

0021-9673/82/0000–0000/S02.75

ous compounds (relative to *n*-pentane) and HETP values. The properties of the solid supports were characterized by the relative retention times of the compounds that are able to undergo specific interactions, measured relative to *n*-hexane ($t_{R_{rel}}$) on 3% squalene. The $t_{R_{rel}}$ values obtained for our support (N AW DHFP) were compared with those for silanized Chromaton N AW (N AW HMDS) at 50°C with a carrier gas flow-rate of 41 ml/min and a sample volume of 0.1 μl.

RESULTS AND DISCUSSION

The structural measurements, carried out on the samples of initial and modified Polysorb-I, showed that plasma treatment leads to some reduction in the specific surface area of the adsorbent. The pore size distribution curve shows the disappearance of fine pores. Whereas untreated Polysorb-I had a specific surface area of 224 m^2/g, the specific surface area of modified I and II was 147, that of III was 145 and that of IV was 154 m^2/g. Whereas before treatment the minimum pore size of Polysorb-I was 20 Å, after treatment of I the pore size increased to 75 Å. It appears that, as a result of the disappearence of fine pores, the adsorbent surface becomes more accessible to mass transfer and the column efficiency, characterized by HETP values, increases by an average of 10%.

The deposition of a polymeric film on the sorbent surface was substantiated by elemental analysis. Whereas the analysis of the initial Polysorb-I indicated the presence of carbon and hydrogen only, the analysis of the sorbent treated in a vapour by a plasma indicated that oxygen was present in the grafted films. The presence of oxygen-containing groups was substantiated by IR spectroscopy.

The IR spectra of the grafted films exhibit absorption bands corresponding to the vibrations in aromatic rings with nitrogen atoms (1060–1080, 1600, 1640 cm^{-1}) and C = O bonds (1720 cm^{-1}) for both compounds and to C–F bond (1430 cm^{-1}) and C–Cl (760 cm^{-1}) for films of II. With metafluorobenzylamine, together with bands attributed to a benzene ring with disubstitution there were additional intense absorption bands due to amino groups (1350, 1610 cm^{-1}), C–F bonds (1410–1430 cm^{-1}) and C = O bonds (1720 cm^{-1}). The additional band in the IR spectrum of the films grafted with N-methylpyrolidone was a band at 1680 cm^{-1} corresponding to the stretching vibrations of carbonyl in such compounds. According to IR and elemental analysis data the main structural fragments common to the initial monomers were retained in the investigated films.

Table I lists the relative retention times for compounds of various classes on columns packed with initial and modified Polysorb-I. Grafting of various functional groups resulted in an increase in the retention times of polar compounds and compounds able to undergo specific interactions. Although this increase was not strongly affected by the nature of the grafted compound, it was more pronounced with Polysorb-I treated by a plasma. The retention times increased to the greatest extent with acetonitrile, acetone and diethyl ether. The modified sorbent permitted the separation of the mixture diethyl ether–acetone, which was virtually impossible on the initial sorbent (α = 1.02). The sequence of elution of compounds was changed with acetone–pentane and acetone–diethyl ether mixtures: acetone was first to elute on the initial Polysorb-I, and the less polar diethyl ether was first on the modified sorbent. With alcohols the variation of retention times was lower.

TABLE I

RELATIVE RETENTION TIMES FOR INITIAL AND MODIFIED POLYSORB-I (RELATIVE TO PENTANE)

Compound	*Initial Polysorb-I*	*Modified Polysorb-I*			
		I	*II*	*III*	*IV*
Water	0.17	0.20	0.21	0.21	0.19
Methanol	0.24	0.33	0.31	0.34	0.33
Ethanol	0.58	0.64	0.64	0.64	0.62
Acetonitrile	1.06	1.32	1.30	1.34	1.30
Acetone	0.90	1.27	1.23	1.27	1.25
Diethyl ether	1.02	1.20	1.17	1.21	1.18
Benzene	3.66	3.76	3.70	3.84	3.69
Chloroform	2.42	2.58	2.50	2.58	2.52
Carbon tetrachloride	3.33	3.54	3.35	3.71	3.35

Another problem, solved by using chemical modification with a plasma, was to suppress the absorption activity of a diatomite solid support. The fluorine-containing polymer obtained from hexafluoropropylene dimer (DHFP) and deposited as a film on the support was sufficiently stable to thermo-oxidative degradation (a loss of weight *ca.* 50% corresponded to a temperature of *ca.* 370°C).

Table II indicates that modification of the support permitted the retention times of the listed compounds examined to be reduced by a factor of 1.5, thus providing more accurate separation. For nearly all of the compounds the surface of modified support was found to be more inert than that of silanized Chromaton N AW. Apparantly the silanized Chromaton N AW was more inert than the initial Chromaton N AW. As the mechanical properties of the modified support were similar to those of the initial support, there were no difficulties in packing and repacking the columns, which usually occur with solid fluoroplastic supports, such as Polychrom-I.

The results show that there is a possibility of using chemical modification by plasmas for solving important problems in chromatography such as the modification of sorbents and solid supports. Another interesting trend in this field, the modifi-

TABLE II

RELATIVE RETENTION TIMES OF PLASMA-TREATED AND SILANIZED CHROMATON N AW (RELATIVE TO PENTANE)

Compound	$t_{R_{rel}}$	
	N AW DHFP	*N AW HMDS*
Benzene	1.73	2.50
Methyl ethyl ketone	0.71	0.75
Nitromethane	0.44	0.60
Carbon tetrachloride	1.77	2.13
Ethanol	0.29	0.25
Cyclohexane	1.55	2.18

cation of solid supports with deposited fixed phases, was recently reported[3]. It should be noted, however, that the current procedure of plasma treatment seems not to provide a modified polymer film on the whole surface of the support, as the surface of fine pores appears to remain partly untreated. This follows in particular from the comparatively small variation of the relative retention times on Polysorb-I after treatment, in spite of the presence of the functional groups able to undergo specific interactions (C = O, C–F, pyridine rings) on its surface. The plasma method of chemically modifying the surfaces of sorbents and supports, however, should be developed further.

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