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Gas chromatographic investigation of silica supports modified in a high-frequency low-temperature plasma

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ABSTRACT

The modification of gas chromatography (GC) supports and adsorbents by glow discharge is of practical interest as it is a method of producing changes in particular surface properties. The adsorption properties of the surface of Silochrom CX-1 modified in a high-frequency low-temperature plasma with argon and benzene vapours were investigated using GC. The thermodynamic characteristics of series of aliphatic and aromatic hydrocarbons and oxygen-containing compounds were measured. The modified silica adsorbents were used for the separation of structural isomers and other mixtures of organic compounds. The modifications of silica described here improve the uniformity of the adsorbent surface and hence the separation properties, increasing the selectivity of the silica supports. This will expand the field of application of silica adsorbents.

INTRODUCTION

Silica adsorbents are often subjected to geometrical and chemical modification [1]. A very promising approach is to treat the sorbents in a high-frequency low-temperature plasma (HFLTP). This method, in an argon medium, has been used successfully to improve the gas chromatographic (GC) properties of several supports, including diatomite covered with a liquid phase [2–4], glass balls and capillary columns [5], adsorbents covered with monolayers of different compounds [6–8] and polymers [4].

The use of a HFLTP in polymer formation [9] offers the possibility of combining thermal treatment and the following co-polymerization with the formation of thin films on the sorbent surface which are resistant to aggressive media.

This paper reports a study of the application of chemical treatment in an HFLTP as a method of modifying silica adsorbents for use in GC.

EXPERIMENTAL

The silica adsorbent Silochrom CX-1 (specific surface area 32 m²/g by nitrogen and 28 m²/g by krypton absorption; pore volume 1.24 cm³/g) was studied as a column packing before and after plasma treatment. It was found that after 1 and 3 min of plasma action the specific surface area measured by the adsorption of nitrogen was 33 and 35 m²/g, respectively.

Before being modified, the Silochrom CX-1 was washed with concentrated hydrochloric acid to remove iron impurities and with distilled water to remove chloride ions.

The treatment in the HFLTP was carried out in an argon atmosphere as described previously [10,11]. The Silochrom CX-1 was impregnated with benzene as a modifying agent and then subjected to the action of the HFLTP in a benzene vapour medium.

The GC analyses were carried out on a Tswett gas chromatograph equipped with flame ionization detection and glass columns (25–100 cm × 3 mm I.D.); nitrogen was used as the carrier gas.

The retention volumes (V_g) (per gram of adsorbent) and the relative retention volume (V_{rel}) were calculated. The initial differential heats of adsorption (q_1) at low surface coverings were determined from the slope of the linear relationship $\log(V_g) = f(1/T)$, where T is the column temperature. The measurements of V_g were carried out within a temperature range in which the compounds gave symmetrical chromatographic peaks and the retention times did not depend on the amount of sample used.

RESULTS AND DISCUSSION

It is well known that adsorption on silica depends on the geometrical structure of the surface [12]. For this reason the influence of the argon plasma on the properties of the Silochrom CX-1 surface was studied.

Some chromatographic characteristics of Silochrom CX-1 treated for different periods of time in the argon HFLTP are given in Table I. These values were derived from chromatograms of compounds of different polarities, V_{rel} values (related to V_g of *n*-nonane) and coefficients of symmetry K_{as} (measured at one tenth of the height of

TABLE I
CHROMATOGRAPHIC CHARACTERISTICS OF SILOCHROM CX-1 TREATED FOR VARIOUS TIMES IN THE ARGON HFLTP

Adsorbate	T_c (°C)	Untreated		HFLTP treated			
		V_{rel}	K_{as}	1 min		3 min	
				V_{rel}	K_{as}	V_{rel}	K_{as}
<i>n</i> -Heptane	60	0.19	1.0	0.19	1.0	0.19	1.0
Benzene	60	0.89	1.0	0.89	1.0	0.93	1.0
Toluene	60	2.98	1.6	2.98	1.3	3.08	1.3
Diethyl ether	100	19.65	1.7	18.76	1.3	20.03	1.3

TABLE II

THERMODYNAMIC CHARACTERISTICS OF ADSORPTION ON TREATED SILOCHROM CX-1 IN ARGON HFLTP

Column temperature $T_c = 100^\circ\text{C}$.

Adsorbate	Untreated			Treated in HFLTP for 1 min		
	V_g (cm^3/g)	V_{rel}	q (kJ/mol)	V_g (cm^3/g)	V_{rel}	q (kJ/mol)
<i>n</i> Heptane	2.2	0.29	38	3.8	0.29	—
<i>n</i> -Octane	4.0	0.54	42	7.2	0.54	43
<i>n</i> -Nonane	7.4	1.00	46	13.2	1.00	45
Ethylbenzene	28.8	3.90	53	44.2	3.35	55
1,3,5-Trimethylbenzene	84.7	11.40	64	127.4	9.65	65
Toluene ^a	—	7.30	—	—	6.20	—
Ethylbenzene ^b	—	7.20	—	—	6.10	—

^a Relative retention with respect to *n*-heptane.^b Relative retention with respect to *n*-octane.

the chromatographic peak) [13]. As seen from Table I, the results were optimal when the samples were treated in the HFLTP for 1 min. The lowest values of V_{rel} and K_{AS} for polar toluene and diethyl ether show that in these instances the modified surface is less specific and more uniform. It is suggested that after a 3-min plasma treatment an erosion effect increases the silichrom surface and its geometrical ununiformity and V_{rel} increase too.

The differential heats of adsorption of *n*-aliphatic and aromatic hydrocarbons

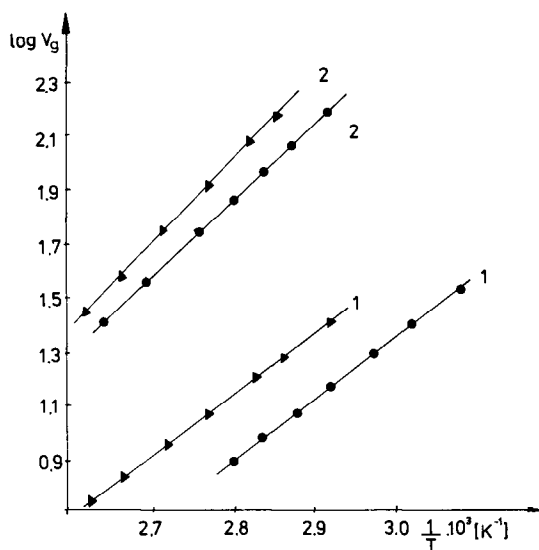


Fig. 1. Plot of $\log V_g$ versus $1/T$. 1 = *n*-Octane; 2 = ethylbenzene; (●) = untreated Silochrom CX-1; (▲) = Silochrom CX-1 treated in argon HFLTP. Column, 70×0.25 cm; particle size, 0.160–0.250 mm.

TABLE III

RETENTION VOLUMES V_g ON UNMODIFIED AND ON BENZENE-MODIFIED SILOCHROM CX-1 TREATED IN THE HFLTP

Adsorbate	T_c (°C)	Untreated		Treated in HFLTP with benzene	
		V_g (cm ³ /g)	K_{as}	V_g (cm ³ /g)	K_{as}
<i>n</i> -Hexane	60	6.4	1.0	7.9	1.0
<i>n</i> -Heptane	60	15.0	1.0	18.3	1.0
Benzene	60	69.4	1.0	48.9	1.0
Toluene	60	231.0	1.6	98.0	1.0
Diethyl ether	80	381.3	1.7	109.4	1.0
Acetone	80	746.4	1.8	211.5	1.1

(Fig. 1 and Table II) were determined from the retention volumes Silochrom CX-1. Treatment in the argon HFLTP leads to an increased specific retention of the hydrocarbons compared to retention on untreated Silochrom CX-1. The decrease in the relative retention volumes of the aromatic hydrocarbons on treated adsorbents shows decrease in the amount of adsorption due to specific interactions (according to the classification of Kiselev [14]). This could also be explained by the removal of hydroxy groups from the adsorbent surface as a result of the action of plasma (Table II). The values of the heats of adsorption of the hydrocarbons on untreated and treated Silochrom CX-1 do not significantly change.

The modification in the HFLTP was carried out in various organic vapours to achieve changes in the chemistry of the silica adsorbent surface. In this investigation benzene was chosen as a modifying agent as it polymerizes under the action of the plasma and covers the surface with a hydrocarbon film [9]. Using a gravimetric method it was found that after impregnation with benzene and treatment in the HFLTP with benzene vapour, the Silochrom CX-1 sample contains 1.2% of a carbon product.

A comparison of the values of K_{as} and V_g (Table III) of compounds with various polarities shows that the modification leads to changes in the surface properties. There is a significant improvement in the symmetry of the chromatographic peaks and a decrease in the values of V_g of the compounds under investigation. This indicates that the surface homogeneity was also improved.

The surface of an adsorbent is sensitive to the structural differences of isomeric aromatic hydrocarbons (Fig. 2). Polymethylbenzenes are always retained to a greater degree on modified Silochrom CX-1 than the corresponding isomeric alkylbenzenes. Similar differences in the retention of alkylbenzenes have been observed on adsorbents of different polarities and on Silochrom C-120 [15].

The modification of the surface leads to an increase in the retention of *n*-alkanes, the adsorption of which is based on dispersion forces. Aromatic hydrocarbons are retained on the surface of the HFLTP-modified Silochrom CX-1 less than on the unmodified surface. In this instance it can be assumed that most of the silanol groups are removed by the plasma action or are covered by a modifying layer. The

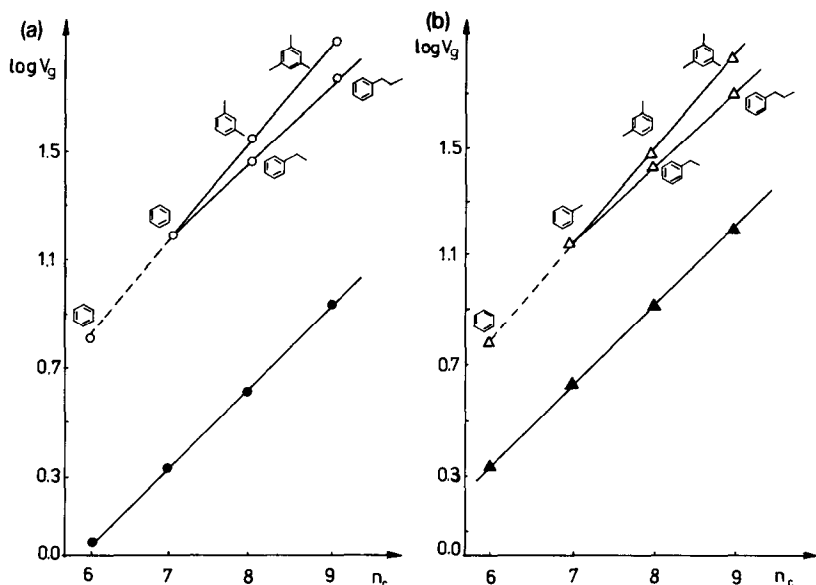


Fig. 2. Relationship between $\log V_g$ and the number of carbon atoms at 100°C. (a) Unmodified Silochrom CX-1; (b) modified Silochrom CX-1. (●, ▲) = *n*-alkanes; (○, △) = alkylbenzenes. Column as in Fig. 1.

specific interaction between silanols and the π -electrons of the aromatic ring will decrease as well as the retention volumes.

The relative retentions and heats of adsorption of *n*-alkanes (C_5 – C_{10}), aromatic

TABLE IV

RETENTION VOLUMES V_g AT 120°C AND INITIAL DIFFERENTIAL ADSORPTION HEATS q ON SILOCHROM CX-1

Adsorbate	V_g (cm^3/g)	Untreated			Modified in HFLTP with benzene			
		V_{rel}^a	q (kJ/mol)	q_{sp}	V_g (cm^3/g)	V_{rel}	q (kJ/mol)	q_{sp}
<i>n</i> -Octane	2.1	0.58	42	—	4.0	0.56	41	—
<i>n</i> -Nonane	3.6	1.00	46	—	7.1	1.00	45	—
<i>n</i> -Decane	6.8	1.90	51	—	12.6	1.80	50	—
Ethylbenzene	13.5	3.70	53	11	10.5	1.50	49	8
<i>n</i> -Propylbenzene	21.4	5.90	59	13	20.2	2.80	51	6
<i>n</i> -Butylbenzene	39.4	10.90	64	13	37.6	5.30	54	4
Diethyl ether	39.4	10.90	61	33	15.8	2.20	57	29
Di- <i>n</i> -propyl ether	81.2	22.50	66	28	38.9	5.50	62	25
Di- <i>n</i> -butyl ether	226.0	62.8	71	24	117.5	16.50	67	22
Ethyl acetate	107.0	29.70	62	29	42.0	5.90	59	26
<i>n</i> -Propyl acetate	186.0	51.7	65	27	79.9	11.10	62	25
<i>n</i> -Butyl acetate	489.0	135.8	67	25	149.0	21.00	65	24

^a Relative retention time with respect to *n*-nonane.

hydrocarbons (C_8 – C_{10}), some ethers and esters on benzene-modified and unmodified Silochrom CX-1 were determined (Table IV).

The retention of those adsorbate molecules which interact specifically with the surface, is decreased on the modified Silochrom CX-1 whereas the retention of *n*-alkanes increases as they are not adsorbed specifically on the surface. A similar effect was observed when a pyrocarbon film covered the Silochrom CX-1 surface [16]. A comparison of the values of V_{rel} of modified and unmodified Silochrom CX-1 confirms this statement.

In contrast to the retention data the heats of adsorption of the *n*-alkanes do not change significantly when Silochrom CX-1 is modified with benzene in the HFLTP. However, the modification leads to a decrease in the heats of adsorption of hydrocarbons and oxygen-containing compounds and to a decrease in the percentage contribution of specific interactions (Table IV) in the total adsorption energy [14]. This effect is more predominant when alkylbenzenes are adsorbed onto the modified Silochrom CX-1.

The adsorption energy of alkylbenzenes increases with the carbon chain length of the molecule. This is due to an increase in dispersion interactions, which means that the share of q_{sp} (calculated as the difference between an alkane and an alkylbenzene with an equal number of carbon atoms) on unmodified Silochrom CX-1 is insignificant for alkylbenzenes (11–13 kJ/mol). Their adsorption on the modified

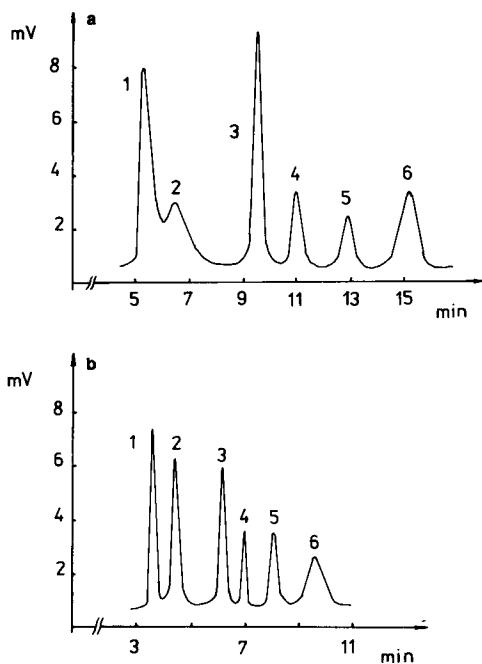


Fig. 3. Separation of dialkyl ethers. Peaks: (1) = diisopropyl ether; (2) = dipropyl ether; (3) = diisobutyl ether; (4) = dibutyl ether; (5) = diisopropyl ether; (6) = dipentyl ether. (a) Unmodified Silochrom CX-1; (b) modified Silochrom CX-1. Column as in Fig. 1; column temperature, 120–150°C.

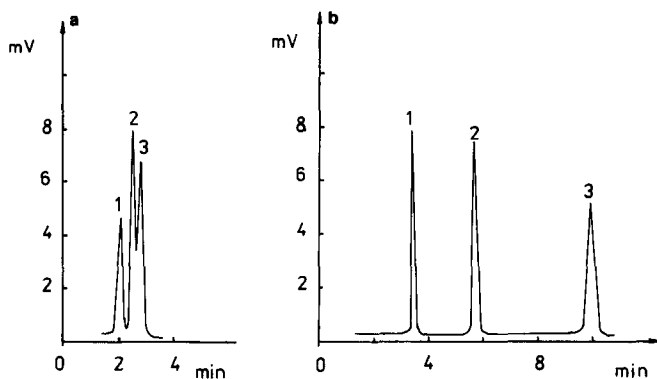


Fig. 4. Chromatogram of a mixture of: (1) 2,2,4-trimethylpentane, (2) *trans*-1,2-dimethylcyclohexane and (3) *cis*-1,2-dimethylcyclohexane. (a) Unmodified Silochrom CX-1; (b) Silochrom CX-1 modified with benzene vapour in HFLTP. Column as in Fig. 1; column temperature 50°C.

Silochrom CX-1 surface is characterized by a decrease of q_{sp} with an increase in the number of methylene groups (from 4 to 8 kJ/mol).

It is likely that during the modification of the Silochrom CX-1 with benzene in the HFLTP a hydrocarbon film is formed which has a shielding effect on the active adsorption centres on the surface.

CONCLUSIONS

It can be concluded that this modification leads to an increase in the surface uniformity of Silochrom CX-1 and significantly changes the energy of specific interactions between the adsorbent and adsorbate (compared to the adsorption of unmodified Silochrom CX-1). As a result of this, the selectivity of the Silochrom CX-1 surface towards isomeric compounds increases. Chromatograms of the two different test mixtures on unmodified and modified Silochrom CX-1 are shown in Figs. 3 and 4.

The results of the experiments show the possibility of changing the surface properties of Silochrom CX-1 by treatment with an HFLTP in the presence of benzene. This will expand the field of applications of silica adsorbents.

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