ADSORPTION PROPERTIES OF THE FLUORINATED CARBON

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Introduction

Fluorine containing compounds of carbon attract attention of scientists from different fields of study. In particular this is connected with the perspectives of their usage as cathode materials of powerful sources of current and solid oiling, being effective under aggressive environments and in deep vacuum [1]. Besides that, these hydrophobic heat-resistant materials with the developed porosity can be used as effective adsorbents, however adsorptional characteristics of the fluorinated carbon are studied not well [2]. In the work being presented now the adsorptional, structural and gas chromatographic characteristics of the fluorinated carbon obtained by fluorination of carbon fibre were studied.

Experimental part

The adsorption-structural study of the original carbon fibre (CF) and fluorinated carbon (FC) being synthesized on its basis was carried out by static method with McBain scales. The following structural parameters were defined by BET and Dubinin-Radushkevich formulas from the full isotherms of adsorption-desorption of benzene steam: total volume of pores, V_Σ cm^3/g; specific surface area, $S_{C_6H_6}$ m^2/g; micropore volume, W_{mi} cm^3/g; half-width of the slit, X nm. Simultaneously there were determined S by adsorption of N_2. The chromatograph Chrom-5 (Czechia) with flaming-ionization detector and He as the carrier gas were used for the gas chromatographic study. There were determined the absolute retained volumes, V_A (cm^3/m^2); relative retained volumes, V_{rel} to n-hexane within the wide range of temperatures and differential heats of adsorption, q_1 more than 30 organic compounds at chromatographic columns, filled with CF, FC and the standard adsorbent graphitic thermal carbon-black (GCB).

Results and discussion

The results of the adsorption-structural investigation are presented in table 1 and in Fig. 1.

Table 1. Structural characteristics of the fluorinated carbon fibre.

S_{N_2}	$S_{C_6H_6}$	V_Σ	Wmi	Wme	X
317	219	0.38	0.076	0.10	1.86

Fig. 1 indicates that original CF adsorbs benzene extremely negligibly according to the very low value of S_{N_2} = 1.7 m^2/g of this macroporous material.

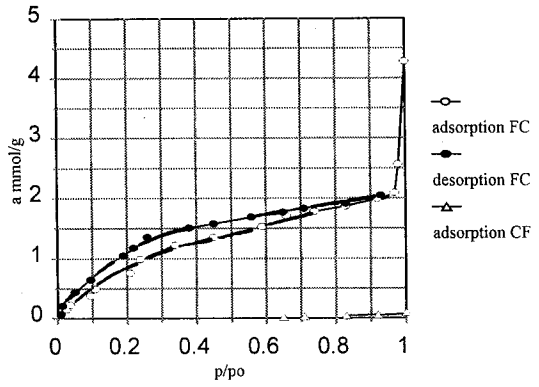

Fig 1. Isotherms of adsorption of C_6H_6 under 25°C at the fluorinated carbon fibre.

To the contrary, fluorizing of CF leads to a considerable growth of S due to formation of developed porous structure. $S_{C_6H_6}$ for the sample FC is noticeably lower than S_{N_2}. This indicates the presence of pores in the porous structure of FC, inaccessible for the adsorption of benzene under low p/p_o. The appearance of the isotherm of adsorption-desorption for FC shows, that in the structure of this sample there predominate micro- and mezo-pores of the slit form. The specificity of the isotherm of adsorption of C_6H_6 at FC is its full irreversibility. Histerethis under low p/p_o is connected with the swelling of the adsorbent particles, which to all appearances distructs irreversibly its structure. The observed events correlates well with the literature data on the stratified crystallic structure and strength characteristics of the fluorinated carbon materials, described for instance in [1,3]. It is interesting that S determined by the desorption branch of the isotherm. for C_6H_6, coincides practically with S_{N_2}. This confirms the supposition on the irreversible deformation of the micro-porous structure of FC.

Along the gas chromatographic investigation there were determined the thermodynamic characteristics of adsorption of the test organic compounds of different electronic and geometric structure under the slight filling of the surface. The comparison of the molecules' retention, capable to interactions of the electrostatic origin and n-alkans with the similar polarization capacity allows to characterize the nature of the adsorbent's surface. The simultaneous study of retention of the same compounds at the standard adsorbent — non-porous, homogenous and non-polar GCB gives additional information about the surface of FC. The thermodynamic characteristics of adsorption are given in tables 2 and 3 for some of the studied adsorbats at all studied adsorbents.

Table 2. Relative retention volumes V_{rel} (with respect to n-hexane) at 100°C on adsorbents studied.

Adsorbate	FC	CF	GCB
Ethanol	0.029	0.54	0.026
Butanol-1	0.33	2.36	0.26
Acetone	0.094	-	0.053
Acetonitrile	0.038	0.37	0.028
Nitromethane	0.065	0.47	0.034
n-Butane	0.088	-	-
Cyclohexane	0.53	0.54	0.26
Dioxane	0.39	1.24	0.20
Toluene	3.14	5.69	3.85

These data shows that the surface of CF differs considerably as from FC, so as from GCB. Vrel of the molecules capable to electrostatic interactions - exceed the similar values for other adsorbents. The surface of CF is chemically heterogeneous. Probably it includes some amount of the oxygen-containing groups. This is confirmed by the asymmetry of chromatographic peaks of the molecules, capable to formation of hydrogen bonds. It is necessary to account the geometric heterogenity of CF, because it includes as textured carbon with turbostratus elements, so as amorphous carbon of different hybrid forms [3]. This considerable shortages disappear after fluorine modification of CF. The chromatographic peaks of all studied substances became symmetric. V_A and q of n-alkans, capable only to dispersion interactions with the surface of adsorbent fall down. After fluorination especially more great is decrease of Vrel of polar molecules such as nitrogen and oxygen-containing compounds. FC comes near to GCB by its characteristics (table 2,3). The same as on the non-polar surface of GCB, benzene adsorbs on FC more weakly than n-hexane, diethyl either weakly than n-pentane, dioxane weakly than cyclo-hexane and retention in the raw CH_3CN, CH_3NO_2, n-butane is in the reverse relationship to its dipolar moments. Presence of π-bonds in molecules doesn't bring noticeable contribution into the adsorption at FC in the row: n-hexane, hexene-1 and hexine-1, the retention comes down.

The crystallic structure of FC is similar to the structure of graphite and particals of GCB are formed mainly with the basic sides of graphite. Despite the difference in the chemical origin of these materials, the retention of the compounds of different classes by their surfaces are identical. The dispersion interaction is the main in the adsorption at both adsorbents. The fluorization of carbon fibre makes the fluorine atoms of small sizes and high electric negative value to form the chemical bond of a very small length and low polarity [1] with the atoms of carbon. Considerably lower values of V_A for FC are connected with the lower free energy of adsorption comparing to GCB.

Table 3. Retention volumes V_A (cm^3/m^2) at 100°C and heats of adsorption q (kJ/mol) on adsorbents studied.

Adsorbate	FC		CF		GCB	
	V_A	q	V_A	q	V_A	q
n-Pentane	0.24	36	0.49	40	0.79	34
Diethyl either	0.16	34	0.58	38	0.50	32
n-Hexane	0.84	45	1.71	48	3.15	39
Benzene	0.70	43	2.96	41	2.05	35

At the same time the heats of adsorption of all substances at FC are a little bit higher, than at GCB. Probably they reflect the differences in the porous structure of adsorbents: GCB - the non-porous adsorbent, FC - has the well developed porous structure.

In this way, the fluorization of carbon fibre changing the chemistry of the surface, changes also greatly the energetic characteristics of the surface and geometric structure of the adsorbent. Fluorinated carbon is a material with non-polar and chemically homogenous surface. On its background it is possible the creation of adsorbents for chromatography and other adsorption tasks.

References

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