Journal of Chromatography, 472 (1989) 155–161
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 21 399

INTERMOLECULAR INTERACTIONS IN THE SORBATE-MODIFIED GRAPHITIZED THERMAL CARBON BLACK SYSTEM

V. I. ZHEIVOT*, M. E. SHALAEVA, V. Yu. GAVRILOV, V. B. FENELONOV, I. A. OVSYANNIKOVA and V. V. MALAKHOV

Institute of Catalysis, Novosibirsk 630090 (U.S.S.R.)

(First received April 1st, 1988; revised manuscript received February 9th, 1989)

SUMMARY

Intermolecular interactions between sorbates and graphitized thermal carbon black modified with poly(methyl-β-cyanopropylphenyl)siloxane (OV-225) have been studied. A simple procedure is suggested for the evaluation of the monolayer capacity from the dependence of the specific retention volumes of substances that are incapable of specific intermolecular interactions with modified surfaces on the amount of modifier on the carbon black surface. X-ray spectral microprobe analysis showed that the modifier is distributed uniformly over the whole volume of the granules. Results of a comparative differential method indicated that the modified surface of carbon black remains almost constant at a modifier content of up to 0.8% (w/w) and is the same as that of the untreated material. The modified sorbent possesses specific properties and can be used for the separation of products of the catalytic oxidation of hydrocarbons.

INTRODUCTION

Adsorption modification of the surface of graphitized carbon blacks makes possible the production of various types of sorbents with different selectivities[1–6]. Of special significance is the investigation and utilization of graphitized carbon blacks that contain sufficient amounts of modifying agents to coat the surface as a monomolecular layer. Such sorbents combine the properties of the carbon black surface and those of the modifier[6,7], with their separation abilities being much better than those of capillary columns[7].

This paper reports a further investigation of modified graphitized carbon blacks aimed at producing new adsorbents. Intermolecular interactions between the sorbate and graphitized thermal carbon black (GTCB) modified by poly(methyl-β-cyanopropylphenyl)siloxane (OV-225) were studied.

For the first time the character of the distribution of a modifier over a carbon black granule has been investigated by X-ray spectral microprobe analysis, the principles of which have been published in ref. 8. Also, a comparative differential method, which allows one to eliminate the chemical effect of the surface and determine its area reliably, was applied to determine the surface area of modified GTCB[9,10]. This method is based on comparison of nitrogen (krypton) adsorption isotherms of modified and primary standard samples with a macroporous structure and known surface area, determined by an independent method (electron microscopy) in the region of polymolecular adsorption.

The sorbent obtained was applied to the gas chromatographic separation of products of catalytic reactions.

EXPERIMENTAL

Laboratory-made GTCB with a surface area of 8.5 $m^2 g^{-1}$ and a polar modifier, namely poly(methyl-β-cyanopropylphenyl)siloxane (MW $\approx$ 8000, $\rho = 1.096\,g\,cm^{-3}$)[11], were used.

A weighed carbon black sample was introduced into a solution of OV-225 in chloroform and left there for 48 h for adsorption to proceed. The solvent was then evaporated and the sorbent obtained was sieved, the 0.25–0.5 mm fraction being selected. Adsorbents containing 0.1, 0.2, 0.4, 0.8 and 1.2% (w/w) of modifying agent were prepared.

The capacity of the modifier monolayer was determined chromatographically during the study of the specific retention volumes, $V_{m,1}$, of substances of groups A, B and D (Kiselev's classification[12]) as functions of the amount of modifier on the carbon black surface[4,6,7].

The gas chromatographic and adsorption properties of the modified carbon black samples were investigated with a Khrom-5 chromatograph with a flame ionization detector and stainless-steel column (100 × 0.3 cm I.D.). The specific retention volumes of substances of various classes were measured at different temperatures. As the result, the corresponding differential molar changes in internal energy, $-\overline{\Delta U_1}$, on adsorption, and the contribution of the specific interaction energy, $-\overline{\Delta U_{1,\mathrm{spec.}}}$ of the compounds with modified surfaces to the total value of $-\overline{\Delta U_1}$ were calculated.

The distribution of OV-225 over the modified granules was investigated using a JSM-35C scanning microscope supplied with a DDS-35 microanalyser (Si $K\alpha$ line intensity, $\lambda = 7.125$ Å, thallium phthalate as a crystal analyser). The statistical error of the detection did not exceed 1%.

The adsorption properties of the initial and modified carbon blacks were examined using a Digisorb-2600 automatic adsorption installation by measuring the low-temperature adsorption isotherms of nitrogen and krypton.

RESULTS AND DISCUSSION

The dependences of the specific retention volumes of *n*-alkanes (substances of group A), benzene, diethyl ether, acetone (group B) and propanol (group D) on the amount of OV-225 on the surface of GTCB are presented in Fig. 1.

The values $-\overline{\Delta U_1}$ and $-\overline{\Delta U_{1,\mathrm{spec.}}}$ for adsorption on the initial GTCB and GTCB modified with 0.4% (w/w) of OV-225 are given in Table I (the choice of this concentration of the modifier is explained below).

The behaviour of the adsorbates studied (Fig. 1) is in good agreement with their energy characteristics (see Table I). For example, on introducing the modifier the

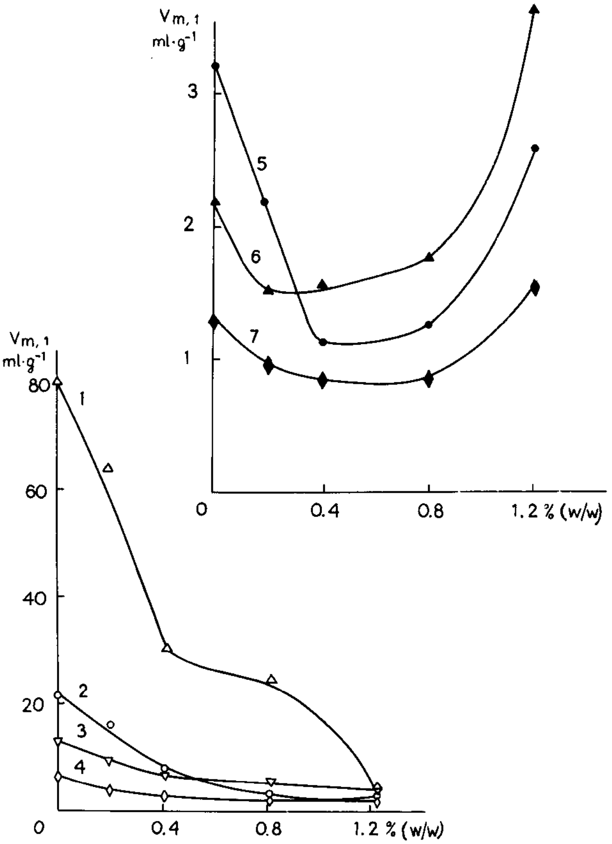


Fig. 1. Specific retention volumes of different classes of substances *vs*. modifier content on GTCB surface at 100°C. 1 = *n*-Heptane; 2 = *n*-hexane; 3 = benzene; 4 = *n*-pentane; 5 = diethyl ether; 6 = *n*-propanol; 7 = acetone.

TABLE I

SPECIFIC RETENTON VOLUMES AND VALUES OF $-\overline{\Delta U_1}$ AND $-\overline{\Delta U_{1,\text{spec.}}}$[13] FOR SUBSTANCES OF DIFFERENT CLASSES DURING THEIR INTERACTION WITH THE INITIAL GTCB AND GTCB MODIFIED WITH 0.4% (w/w) OF OV-225

Adsorbate	*Initial GTCB*			*GTCB + 0.4% OV-225*		
	$V_{m,1}$ *(ml/g)*	$-\overline{\Delta U_1}$ *(kJ/mol)*	$-\overline{\Delta U_{1,spec.}}$ *(kJ/mol)*	$V_{m,1}$ *(ml/g)*	$-\overline{\Delta U_1}$ *(kJ/mol)*	$-\overline{\Delta U_{1,spec.}}$ *(kJ/mol)*
n-Pentane	5.18	35	0	2.04	32	0
n-Hexane	20.8	41	0	7.65	39	0
n-Heptane	89.1	48	0	29.4	45	0
Benzene	14.3	38	0	6.14	37	3
Diethyl ether	3.31	32	0	1.12	31	0
n-Propanol	2.20	34	–	1.70	40	16
Acetone	1.33	31	–	0.88	31	9

specific retention volumes of most substances decreased sharply at levels down to 0.4% (w/w). This correlation is most pronounced for substances incapable of specific intermolecular interactions with modified surfaces. However, at a modifier content of up to 0.8% (w/w), the specific retention volumes remain almost constant, decreasing at 1.2% (w/w) of the modifier. Therefore, as in our previous studies[14–16], 0.4% (w/w) is taken as the monolayer capacity.

Using the carbon black surface area of 8.5 m^2 g^{-1}, the monolayer capacity obtained corresponds to specific adsorption of 0.47 mg m^{-2}, which is in good agreement with data for a statistic monolayer of some high-molecular-weight modifiers on the surface of graphitized carbon blacks[4,6,14–18]. Close values of the specific adsorption in monolayers of substances of different chemical compositions are likely to indicate the dominant parallel orientation of fragments of the modifier molecule with respect to the plane of the surface with an average layer thickness of 0.5 nm for OV-225, for example.

Note that a decrease in the specific retention volumes of substances that are incapable of specific intermolecular interaction with the modified surface may depend, in the long run, on a decrease in the surface area of the graphitized carbon black during its adsorption modification[4,7,17]. However, the surface areas of modified GTCB, which were determined by the comparative differential adsorption method[19], remain almost constant up to 0.8% (w/w) of the modifier and equal to that of unmodified GTCB.

The surface areas of untreated and modified GTCBs determined by the comparative method are given in Table II. The values of the C_{BET} constant in the BET equation are also listed.

According to Table II C_{BET}, which characterizes the sorbate–sorbent interactions, decreases significantly on modification of the carbon black surface. A decrease in the specific retention volumes of *n*-alkanes, for example, on the modified GTCB might be explained by the fact that the adsorption field of the surface of graphitized carbon black is due mainly to molecular forces rather than to atomic interactions of surface carbon atoms[4]. Thus, the $-\overline{\Delta U_1}$ values of *n*-alkanes decreased in comparison with the untreated GTCB (see Table I).

However, in contrast to an Apiezon L monolayer supported on GTCB, for which the specific retention volumes of *n*-alkanes decrease by one order of magnitude

TABLE II

SURFACE AREAS (S) DETERMINED BY THE COMPARATIVE METHOD AND C_{BET} CALCULATED FROM NITROGEN ADSORPTION ISOTHERMS[19] FOR THE INITIAL AND MODIFIED GTCB

No.	*OV-225 (%, w/w)*	C_{BET}	*S (m^2 g^{-1})*
1	0	2200	8.3
2	0.1	410	8.4
3	0.2	54	8.6
4	0.4	44	8.6
5	0.8	28	8.0
6	1.2	27	7.6

in comparison with the untreated GTCB[17], the values for an OV-225 monolayer decrease only 2–3-fold.

Such behaviour of *n*-alkanes can be explained, as for salts of sulphonic acids of phthalocyanines of different metals[18], by a much stronger dispersion interaction in the adsorbate–OV-225 monolayer system on the GTCB due to the presence of highly electron-polarized ($\overline{N}$) atoms in the modifier molecules. As a result, $-\Delta U_1$ for *n*-alkanes decreased insignificantly compared with the untreated GTCB (see Table I).

For *n*-hexane, a decrease in the specific retention volume of non-specifically interacting molecules with 1.2% (w/w) OV-225 on GTCB may be attributed to a decrease in the sample surface area (see Fig. 1 and Table II).

For the given modifier (Table I), acetone and *n*-propanol are capable of specific intermolecular interaction even before the surface has been coated by a monolayer. As a result, the observed inflection point on the plot of $V_{m,1}$ *vs.* modifier content of GTCB is shifted towards lower values of the modifier content.

For diethyl ether, this specificity is revealed when the surface coverage exceeds a monolayer. For GTCB with a monolayer of OV-225, $-\Delta U_{1,\mathrm{spec.}}$ remains zero (see Table I) and the curve bending is clearest at a modifier content of 0.4% (w/w).

From the results obtained, it follows that the capacity of the modifier monolayer may be evaluated from the $V_{m,1}$ dependences of substances that are incapable of specific intermolecular interaction on the amount of modifier on the GTCB surface. However, the investigation of such dependences for compounds of different classes is especially useful for the purpose of finding the regions where additional specific intermolecular interactions of compounds with modified surfaces take place and, consequently, new sorbent selectivities can be obtained.

It is seen in Table II that on introducing a modifier C_{BET} decreases to 0.4% (w/w). On further additions, C_{BET} remains practically constant. Hence the results of the chromatographic determination of the monolayer capacity are confirmed by the adsorption method.

The distribution of the modifier with CN groups over the support granules was studied by X-ray spectral microprobe analysis using the Si *Kα* line intensity. The beam diameter was approximately 2 μm.

Curves of Si *Kα* intensity variations for modified samples (spectra 1, 2 and 3) along the diameter of the carbon black granule are shown in Fig. 2. As can be seen the modifier is distributed over the whole volume of the granules with some slight

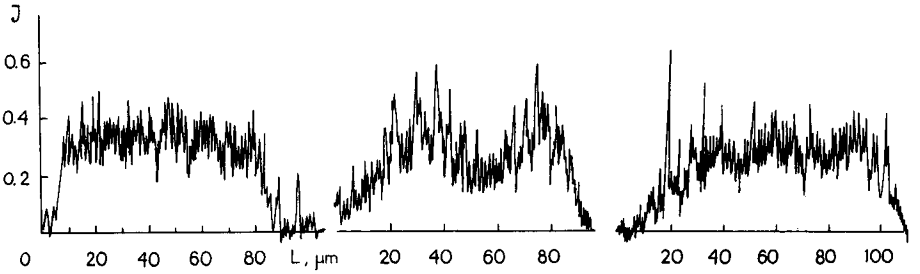


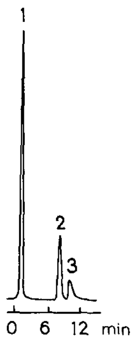
Fig. 2. Intensity of Si *Kα* on scanning three adsorbent granules [0.8% (w/w) OV-225 on graphitized carbon black].

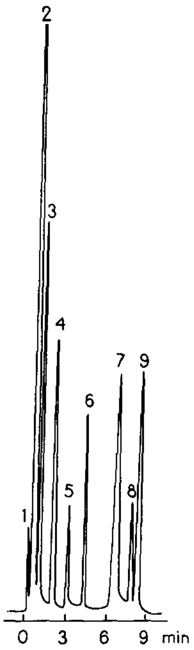
differences in distribution, probably caused by structural differences in the carbon black particles. In Fig. 2 the Si *Kα* line intensity (*ca.* 0.3%) relative to pure silica is indicated without corrections.

Using the ability of the OV-225 monolayer on GTCB to undergo additional specific intermolecular interactions with alcohols, it is possible to separate the products of cyclohexane oxidation. These products include cyclohexane, cyclohexanone and cyclohexanol, which cannot be separated on unmodified GTCB[12]. The results of the separation of products are given in Fig. 3.

Fig. 4 shows a chromatogram of the separation of the catalytic oxidation products of *o*-xylene on a 1 m × 2 mm I.D. column with GTCB modified with 0.8% (w/w) of OV-225. Phthalide, obtained in small amounts, elutes, as on untreated GTCB, before phthalic anhydride and can therefore be determined with sufficient accuracy. In addition, *o*-toluic acid, which is commonly adsorbed on unmodified GTCB, can also be determined with the given adsorbent.

The chromatogram of the catalytic oxidation products of toluene is presented in Fig. 5. Benzoic acid, which is the main product of this process, can also be determined.





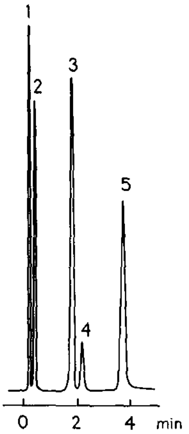


Fig. 3. Chromatogram of cyclohexane catalytic oxidation products obtained in a column with GTCB modified with 0.4% (w/w) of OV-225 at 100°C. 1 = Cyclohexane; 2 = cyclohexanone; 3 = cyclohexanol.

Fig. 4. Chromatogram of products of catalytic oxidation of *o*-xylene to phthalic anhydride obtained in a column of GTCB modified with 0.8% (w/w) of OV-225 with programmed heating of the column from 60 to 180°C at 20°C/min and flame ionization detection. 1 = Air; 2 = acetone; 3 = toluene; 4 = *o*-xylene; 5 = maleic anhydride; 6 = *o*-tolualdehyde; 7 = *o*-toluic acid;8 = phthalide; 9 = phthalic anhydride.

Fig. 5. Chromatogram of products of catalytic oxidation of toluene to benzoic acid obtained in a 1 m × 3 mm I.D. column of GTCB modified with 0.8% (w/w) OV-225 with programmed heating of the column from 65 to 180°C at 32°C/min and flame ionization detection. 1 = Acetone; 2 = toluene; 3 = benzaldehyde; 4 = benzyl alcohol; 5 = benzoic acid.

In general, the adsorbent obtained seems to belong to type III sorbents according to the Kiseler classification[12].

It was shown that for the determination of the monolayer capacity it is sufficient to study the dependence of the specific retention volumes of group A substances on the modifier content on the carbon black surface. For substances in other groups, a study is necessary to establish the regions of additional specific intermolecular interactions and, consequently, to find new possibilities for the separation of different types of substances.

It was found that on adsorption modification of GTCB with these modifiers (up to 0.8%, w/w), the modified surface of carbon black remains almost the same as that of the initial material. This fact is especially important for the determination of the absolute retention volumes of adsorbates, which characterize exclusively the sorbate–sorbent interactions and serve as physico-chemical constants for the identification of components of mixtures. By modifying the surface of GTCB with a monolayer of OV-225, an adsorbent of type III was obtained.

. X-ray microprobe analysis was applied for the first time to study the distribution of a modifier over carbon black granules. It was found that the modifier is distributed uniformly over the whole volume of the granules.

The separation ability of the adsorbent obtained differs from that of unmodified GTCB. The modified sorbent has been used for th gas chromatographic analysis of products of the catalytic oxidation of hydrocarbons.

REFERENCES

1 C. Vidal-Madjar and G. Guiochon, *Bull. Soc. Chim. Fr.*, (1966) 1096.
2 C. Vidal-Madjar and G. Guiochon, *Sep. Sci.*, 2 (1967) 155.
3 C. Vidal-Madjar and G. Guiocon, *C.R. Acad. Sci.*, 265 (1967)26.
4 A. V. Kiselev, *J. Chromatogr.*, 49 (1970) 84.
5 A. Di Corcia, D. Fritz and F. Bruner,.*Anal. Chem.*, 42 (1970) 1500.
6 A. V. Kiselev, N. V. Kovaleva and Yu. S. Nikitin, *J. Chromatogr.*, 58 (1971) 19.
7 L. Ya. Gavrilina, A. V. Kiselev, N. V. Kovaleva, V. I. Zheivot and Ya. I. Yashin, *Chromatographia*, 10 (1977) 744.
8 V. A. Batyrov, *Rentgenospektral'nyi Elektronnozondovyi Mikroanalys*, Metallurgia, Moscow, 1982.
9 V. Yu. Gavrilov, R. V. Zagrafskaya, A. P. Karnaukhov and V. B. Fenelonov, *Kinet. Katal.*, 22 (1981) 452.
10 V. I. Zheivot, M. E. Shalaeva, V. Yu. Gavrilov, V. B. Fenelonov, I. A. Ovsyannikova and V. V. Malakhov, paper presented at the *9th All-Union Gas chromatographic Conference, Kuibyshev, May 25–29, 1987.*
11 A. N. Korol, *Nepodvizhnye Fazy v Gazozhidkostnoi Khromatografii*, Khimiya, Moscow, 1985, p. 85.
12 A. V. Kiselev and Ya. I. Yashin, *Gazo-Adsorptsyonnaya Khromatografiya*, Nauka, Moscow, 1967.
13 R. M. Barrer, *J. Colloid Interface Sci.*, 21 (1966) 415.
14 V. V. Vorontsov, N. V. Kovaleva and V. I. Rudas', paper presented at the *5th All-Union Gas Chromatographic Conference, Tallin, July 3–5, 1969.*
15 V. V. Vorontsov, N. V. Kovaleva, V. I. Rudas' and Yu. A. El'tekov, *Kolloidn. Zh.*, 35 (1973) 741.
16 A. V. Kiselev, V. I. Rudas' and N. V. Kolaleva, paper presented at the *6th All-Union Scientific-Technical Conference, Baku, October 16–18, 1973.*
17 L. Ya. Gavrilina, O. A. Yemelyanova, V. I. Zheivot, A. V. Kiselev and N. V. Kovaleva, *Kolloidn. Zh.*, 40 (1978) 636.
18 A. Bertkol'd, N. V. Kovaleva, V. I. Zheivot, L. Ya. Gavrilina and V. M. Bubenshchikova, *Kolloidn. Zh.*, 44 (1982) 3.
19 V. Yu. Gavrilov, V. B. Fenelonov, V. I. Zheivot and M. E. Shalaeva, *Kinet. Katal.*, 28 (1987) 959.