CHROMSYMP. 1802

Gas chromatographic properties of modified boron nitride

T. B. GAVRILOVA* and I. V. DAIDAKOVA

Department of Chemistry, Lomonosov State University of Moscow, 119899 Moscow (U.S.S.R.)

and

N. PETSEV, I. TOPALOVA, St. IVANOV and Chr. CHANEV

Department of Chemistry, Sofia University, 1126 Sofia (Bulgaria)

ABSTRACT

Boron nitride (α-crystal modification) with significant surface non-uniformity was treated in a high-frequency, low-temperature plasma. The properties of the starting and modified samples were analysed by gas chromatography. Retention values and heats of adsorption for close-to-zero coverage of the surface for several compounds were determined. The chromatographic properties of α-boron nitride samples treated in plasma are improved. The retention time decreases and the symmetry of chromatographic peaks of oxygen-containing compounds is improved. This allows the modified boron nitride to be used for the separation of different mixtures.

INTRODUCTION

The α-crystal modification of boron nitride (BN) is a structural analogue of graphite. The isoelectronic structure of these substances and their crystallographic similarity determines the resemblance of their properties. The α-BN used in gas chromatography, like graphitized thermal carbon black (GTCB), is a non-polar adsorbent [1]. The adsorption properties of BN investigated by static [2–4] and gas chromatographic [1,5] methods show that adsorption on the surface is mainly determined by non-specific interactions [6] with the basic BN crystal module. However, it is difficult to obtain a homogeneous BN surface, formed mainly by basic modules. The existence of a contribution of high-energy crystal sides of α-BN to adsorption [4,5] has been demonstrated.

One of the methods for improving the surface properties of an adsorbent is treatment in a high-frequency, low-temperature plasma (HLP) [7,8]. This has been successfully applied to chromatographic materials such as sorbents used as carriers of a liquid phase [7] and carbonaceous adsorbents [9,10]. The effect of HLP treatment of the α-BN surface [obtained from boron(III) oxide] by gas chromatographic methods was investigated in this work.

EXPERIMENTAL

Boron nitride (99.95% purity) obtained from boron(III) oxide was used as a starting material. This sample was described in a previous paper [1]. The treatment of α-BN was carried out in HLP in an argon atmosphere [8].

For gas chromatography a Tsvet-102 gas chromatograph was used with a flame ionization detector and nitrogen as the carrier gas. Powdered α-BN was formed under pressure ($2 \cdot 10^7$–$3 \cdot 10^7$ Pa). After crushing the powder, the fraction between 0.16 and 0.25 mm was chosen for packing. The column (60 × 0.15 cm I.D.) was conditioned by a nitrogen flow at 110°C for 10 h. The retention volume, V_g (per gram of adsorbent), the relative retention volume, $V_r = V_g/V_{g(C_9H_{20})}$, and the differential heat of adsorption, $\bar{q}$, at close-to-zero coverage of the surface were determined for various substances.

RESULTS AND DISCUSSION

The adsorption of low-polarity molecules on the BN surface is determined mainly by dispersion interactions. However, for adsorbates consisting of molecules with active functional groups, the surface of such a sample is heterogeneous. This is probably due to the existence of different centres formed by the chemical impurities in the BN. Evidence for this was provided by the asymmetry of the chromatographic peaks of oxygen-containing compounds on this sorbent.

The α-BN samples treated in HLP showed significantly improved gas chromatographic properties. The peaks were more symmetrical, the asymmetry factors measured at half-heighty [11] being decreased several-fold (Table I) for polar compounds. The same values for non-polar adsorbates remained equal to unity for both samples.

When α-BN is modified in HLP, V_g for all adsorbates is decreased and the rate of decrease of V_r is significantly changed for molecules capable of specific interactions (Table II).

As the precision of V_g measurement for such compounds decreases owing to the residual asymmetry of the chromatographic peaks, the retention volumes are given for peaks of equal height for close-to-zero coverage of the surface [12]. This confirms the increase in the chemical homogeneity of α-BN after surface modification in HLP. The effect of the reduction in the rate of decrease of the relative retention volume is lower for aromatic hydrocarbons, *e.g.*, chlorobenzene, *i.e.*, for low-polarity compounds. Table II shows that for both samples the retention of *n*-alkanes is stronger than that of mono-*n*-alkylbenzenes with the same number of carbon atoms. The adsorption of these compounds is determined by the dispersion interaction, although the molecules of alkylbenzenes have a high electron density. A similar effect occurs with the modified α-BN when 2-octyne is adsorbed; the retention is weaker than that

TABLE I

ASYMMETRY FACTORS [11] OF PEAKS OBTAINED ON UNMODIFIED BN AND BN MODIFIED IN HLP AT 373 K

Adsorbate	Unmodified BN	HLP-treated BN
Di-*n*-butyl ether	2.7	1.5
Acetone	5.5	1.7
Ethyl acetate	9.4	3.8
Acetonitrile	3.8	1.6

TABLE II

RELATIVE RETENTION VOLUMES, V_r, (WITH RESPECT TO n-NONANE), AT 373 K ON UN-MODIFIED AND MODIFIED BN

Adsorbate	Unmodified BN	HLP-treated BN
n-Heptane	0.10	0.10
n-Octane	0.32	0.32
2,5-Dimethylhexane	0.16	0.15
n-Nonane	1.00	1.00
Isooctane	0.10	0.08
Ethylbenzene	0.26	0.23
2-Octyne	0.34	0.29
n-Propylbenzene	0.70	0.65
Cumene	0.41	0.34
Chlorobenzene	0.19	0.17
Di-n-butyl ether	0.99	0.75
Acetone	0.12	0.06
Acetonitrile	0.06	0.03

for n-octane. The adsorption behaviour of these compounds on GTCB is the same [13]. However, for the starting BN, the order of elution of these compounds is reversed. Because the surface is not very uniform, an additive specific interaction between 2-octyne molecules, with a highly concentrated electron density at the triple bond, and the adsorbent surface is demonstrated.

For non-polar adsorbates (alkanes), V_r is almost constant, because these molecules are not very sensitive to the surface uniformity. Nevertheless, in both instances the order of elution for hydrocarbons with eight carbon atoms in the molecule is isooctane, 2,5-dimethylhexane, n-octane, corresponding to an increase in the number of molecular contacts with the flat regions of the basal α-BN crystals planes.

Using the ln V_g vs. $1/T$ dependence, the differential heats of adsorption of hydrocarbons in the range 50–100°C were calculated (Table III).

The heat of adsorption of n-alkanes is higher than that of mono-n-alkylbenzenes with the same number of carbon atoms. The same dependence is observed for other non-polar adsorbents such as GTCB [6]. However, the $\bar{q}_1$ values are fairly high on GTCB. For all the compounds investigated, $\bar{q}_1$ decreases when α-BN is treated in

TABLE III

VALUES OF $\bar{q}_1$ (kJ/mol)

Adsorbate	α-BN			GTCB [13,14]
	Untreated	HLP-treated	BN [1]	
n-Octane	47	43	43	49
Ethylbenzene	42	40	39	47
n-Hexane	34	33	33	38
Benzene	31	30	31	37

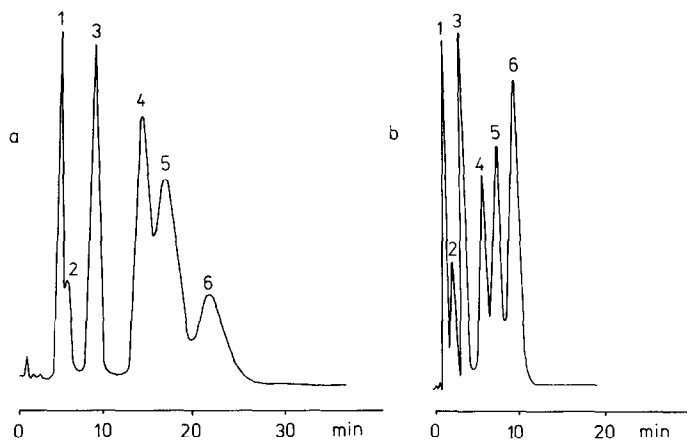Fig. 1. Gas chromatograms of a mixture of hydrocarbons adsorbed on (a) unmodified α-BN and (b) HLP-treated α-BN. Peaks: 1 = *n*-heptane; 2 = 2,5-dimethylhexane; 3 = isooctane; 4 = *cis*-2-octene; 5 = *trans*-2-octene; 6 = *n*-octane. Column, 60 × 0.2 cm I.D., particle size 0.16–0.25 mm; carrier gas flow-rate, 20 cm³/min; column temperature, 329 K.

HLP. Moreover, they are similar to those for the less polar α-BN sample investigated previously [1].

The sample treated in HLP was used for the separation of an alkane mixture including structural and stereoisomers with close boiling temperatures, which appear to be the main components of petroleum fractions (Fig. 1). The analysis was almost twice as fast when α-BN treated in HLP was used. At the same time the resolution of the peaks of *cis*- and *trans*-2-octene (Fig. 1, peaks 4 and 5), measured under the same experimental conditions, was considerably higher with the modified adsorbent.

The increase in surface uniformity due to the treatment in HLP and the decisive role of the number of molecular contacts with the crystal plane surface allow the use
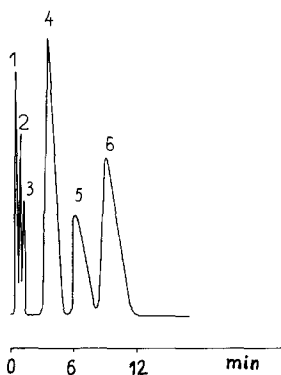

Fig. 2. Separation of halogen-containing compounds on HLP-treated α-BN. Peaks: 1 = dichloromethane; 2 = chloroform; 3 = tetrachloromethane; 4 = chlorocyclohexane; 5 = chlorobenzene; 6 = 1-chlorohexane. Column, 60 × 0.2 cm I.D., particle size 0.16–0.25 mm; carrier gas flow-rate, 20 cm³/min; column temperature, 383 K.
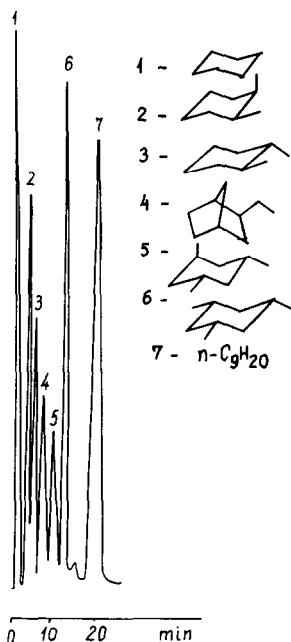
Fig. 3. Separation of cyclic hydrocarbons on HLP-treated α-BN with temperature programming from 333 to 373 K. Column, 100×0.1 cm I.D., particle size 0.16–0.25 mm; carrier gas flow-rate, 15 cm³/min.

of this adsorbent for the determination of halogen compounds in mixtures. The retention of chloro derivatives of hydrocarbons (Fig. 2) depends on the molecular structure of the adsorbates. Chlorocyclohexane has a lower retention than chlorobenzene or 1-chlorohexane, although it has a higher boiling temperature.

Fig. 3 shows the chromatographic separation of a mixture including isomers of cyclic hydrocarbons. For both 1,3,5-trimethylcyclohexane and 1,2-dimethylcyclohexane the adsorption increases when the number of substituents in equatorial positions on the ring increases. The same results are also observed on GTCB [15], as in this instance there is a maximum number of molecular contacts with the flat surface of the adsorbent.

In conclusion, treating BN in HLP significantly improves its gas chromatographic properties and its applicability in analytical chemistry.

REFERENCES

1 T. B. Gavrilova, A. V. Kiselev, I. V. Parshina and T. M. Roshchina, Kolloidn. Zh., 48 (1986) 421.
2 L. D. Belyakova and A. V. Kiselev, Izv. Akad. Nauk SSSR, OCHN, 4 (1966) 638.
3 J. Reginer, A. Thomy and X. Duval, J. Colloid Interface Sci., 70 (1979) 105.
4 H. E. Thomas, R. N. Ramsey and R. A. Pierotti, J. Chem. Phys., 59 (1973) 6163.
5 J. Curthoys and P. Elkington, J. Phys. Chem., 71 (1967) 477.
6 A. V. Kiselev, Intermolecular Interactions in Adsorption and Chromatography, Vysshaya Shkola, Moscow, 1986.
7 S. Oka, J. Jamamoto and K. Hagashi, Bull. Chem. Soc. Jpn., 55 (1982) 3496.
8 N. Petsev, I. Topalova, St. Ivanov, Chr. Dimitrov, T. B. Gavrilova and E. V. Vlasenko, J. Chromatogr., 286 (1984) 57.

 9 N. Petsev, T. B. Gavrilova, I. Topalova, Chr. Dimitrov, G. B. Pavlova-Verevkina and St. Ivanov, *Izv. Khim. Inst. Bulg. Akad. Nauk*, 15 (1982) 123.

10 T. B. Gavrilova, I. V. Parshina, Chr. Dimitrov, St. Ivanov, N. Petsev and I. Topalova, *J. Chromatogr.*, 402 (1987) 97.

11 L. A. Kogan, *Quantitative Gas Chromatography*, Khimiya, Moscow, 1975, p. 22.

12 *Fiziko-Khimicheskoye Primeneniye Gazovoy Khromatografii*, Khimiya, Moscow, 1973, p. 8.

13 A. V. Kiselev and Ya. I. Yashin, *Gas- und Flüssigkeits-Adsorptions Chromatographie*, Berlin, 1985, pp. 48 and 55.

14 E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova, K. D. Shcherbakova and D. P. Poshkus, *Chromatographia*, 12 (1979) 799.

15 W. Engewald, E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova, K. D. Shcherbakova and A. L. Shilov, *J. Chromatogr.*, 152 (1978) 453.