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Hexagonal boron nitride stationary phase for gas chromatography

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ABSTRACT

This work describes the separation performance of utilizing hexagonal boron nitride (h-BN) as the stationary phase for capillary gas chromatography (GC). The statically coated h-BN column showed moderate polarity and achieved column efficiencies of 3455 plates/m and 3800 plates/m for naphthalene and *n*-dodecane, respectively. With temperature-dependent structure properties, the h-BN stationary phase exhibited stronger retention for polycyclic aromatic hydrocarbons (PAHs) over phthalic acid esters (PAEs) and showed advantageous separation performance over the g-C_3N_4 and commercial polysiloxane stationary phases. Moreover, it displayed preferential retention for halogenated analytes and high resolution performance for structural and positional isomers. In addition, the h-BN column showed good column repeatability with relative standard deviation (RSD) values of 0.03%–0.07% for run-to-run, 0.31%–0.71% for day-to-day and 2.6%–5.3% for column-to-column, respectively, and thermal stability up to 260 °C.

1. Introduction

Hexagonal boron nitride (h-BN) (Scheme 1) is a two-dimensional (2D) layered material composed of boron and nitrogen atoms [1–3], analogous to graphene and graphite carbon nitride (g-C_3N_4). Differently, the B—N bonds in h-BN show distinct ionicity stemming from the electronegativity difference between the boron and nitrogen atoms, which localizes the electronic states and leads to extremely high chemical and thermal stability [1]. Another feature of h-BN is that it has negative thermal expansion coefficient, showing wrinkle corrugations as the temperature increases [4,5]. Compared to the sp^2 covalent C—C bonds in its carbon-based analogues, h-BN shows larger corrugations in the out-of-plane because of the ionic character in the B—N bonds. Over the years, h-BN related materials have been employed as thermal conductors and electronic devices [2,3], sensors [6,7] and adsorbents for solid-phase extraction of polychlorinated biphenyls [8], selective adsorption of saccharides [9] and the removal of various pollutants from aqueous samples [10].

The aforementioned features afford h-BN a good candidate as the stationary phase for gas chromatography (GC). Its analogues, such as graphene and g-C_3N_4, showed good separation capability for a wide range of analytes as the stationary phases for GC [11–17] and liquid chromatography [17–20]. Differently, h-BN is a carbon-free 2D material and has ionic nature in the B—N bonds and larger wrinkle corrugations. These differences in the structures and properties may offer h-BN different separation performance and retention behaviours, which was highly expected and worthy to be explored.

Herein, we report the investigation of utilizing h-BN as the stationary phase for GC separations. After it was statically coated onto a fused-silica capillary column, the h-BN stationary phase was investigated regarding its column efficiency and polarity, separation performance, column repeatability and thermal stability. Its separation performance was evaluated by comparison to its analogue of g-C_3N_4 [15]. To our knowledge, this is the first report on employing a carbon-free 2D material as the stationary phase for GC separations.

2. Experimental

2.1. Materials and instruments

All the analytes were of analytical grade and dissolved in dichloromethane without further purification. Benzene, 2-pentanone, pyridine, 1-butanol and 1-nitropropane were purchased from Alfa Chemical Co. Ltd (Tianjin, China). *n*-undecane, *n*-dodecane, methyl heptanoate, methyl nonanoate, methyl decanoate, 1,2-dichlorobenzene, 1,6-dichlorohexane, 1-bromononane, 1-bromodecane, *m*-chloronitrobenzene, *m*-bromonitrobenzene, dimethylphthalate, diethylphthalate, dipropylphthalate, diamylphthalate, naphthalene, acenaph-

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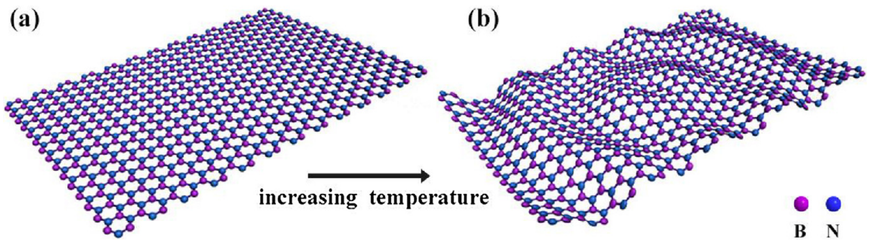

Scheme 1. Structure of h-BN.

thene, fluorene, phenanthrene, fluoranthene, 2,2-dimethylbutane, 2-methylpentane, *n*-hexane, 2,2,3-trimethylbutane, 2,3-dimethylpentane, *n*-heptane, *iso*-octane, 2,2-dimethylhexane, 3-methylheptane, *n*-octane, 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene, 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene, *o*-, *m*- and *p*-nitrotoluene, *tert*-, *sec*- and *n*-butylbenzene, *iso*- and *n*-propylbenzene, *m*- and *p*-diisopropylbenzene, and h-BN material (purity >99.9%, particle size of 1-2 μm) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). The h-BN material was composed of only B and N elements with the corresponding percentage of 48.35% and 51.65%, determined by EDS on the JMS-7500 F (JEOL, Japan). The rest of the chemicals were purchased from Beijing Chemical Reagent Company (Beijing, China).

Untreated fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Ruifeng Chromatogram Apparatus Co. Ltd. (Hebei, China). A commercial DB-35 capillary column (5 m × 0.25 mm, i.d., 0.25 μm film thickness) coated with 35% phenylmethylpolysiloxane was purchased from Agilent Technologies (California, USA). An Agilent 7890 A gas chromatograph equipped with a split/splitless injector, a flame ionization detector (FID) and an autosampler was used for GC separations. All the separations were performed under the following GC conditions: nitrogen of high purity (99.999%) as carrier gas, flow rate at 1 mL/min, injection port at 300 °C, split ratio at 50:1, FID detector at 300 °C. Oven temperature programs for the GC separations were individually provided in their figure captions.

2.2. Fabrication of the h-BN capillary column

The h-BN capillary column was fabricated by a static coating method. First, a bare fused-silica capillary column (5 m × 0.25 mm, i.d.) was pretreated with a saturated solution of sodium chloride in methanol for its inner surface roughing. Afterwards, the column was conditioned up to 200 °C and held for 3 h under nitrogen atmosphere. Then, the pretreated capillary column was statically coated with a dispersion of the h-BN stationary phase in dichloromethane (0.25%, w/v) at 40 °C. After the column was filled with the coating solution and sealed at one end, the solvent was evaporated at a steady speed from the other end under vacuum (600 mmHg). Afterwards, the coated column was conditioned with the temperature program: 40 °C for 30 min, ramp from 40 °C to 200 °C at a rate of 1 °C/min, and 200 °C for 7 h. Nitrogen of high purity was employed as carrier gas. The g-C$_3$N$_4$ was obtained according to the reference [15] and its column was fabricated by the same procedure. Finally, the as-fabricated columns were used for the following work.

3. Results and discussion

3.1. Column efficiency and polarity

To overall appraise the efficiency of the h-BN column, its Golay curves were determined by measuring the height equivalent to a theoretical plate (HETP) of naphthalene and *n*-dodecane at different flow rates at 120 °C and the results are illustrated in Fig. 1. On the basis of the Golay curves, the Van Deemeter equations ($H = B/u + Cu$, H and u represent HETP and flow rate, respectively) were obtained as $H = 0.058/u + 0.363u$ for naphthalene and $H = 0.046/u + 0.368u$ for *n*-dodecane. Notably, the HETP attained the minimum of 0.29 mm at 0.40 mL/min for naphthalene and 0.26 mm at 0.35 mL/min for *n*-dodecane, corresponding to the column efficiency of 3455 plates/m and 3800 plates/m, respectively. These results suggest the good efficiency of the h-BN capillary column. Comparatively, the h-BN column exhibited similar column efficiency to the g-C$_3$N$_4$ column (3760 plates/m for *n*-dodecane) in our previous report [16].

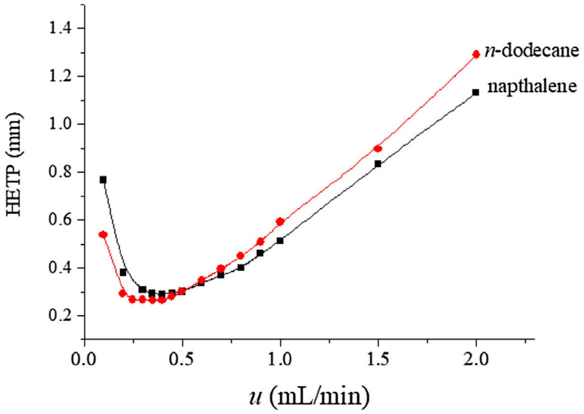

Fig. 1. The Golay curves of the h-BN capillary column determined by *n*-dodecane and napthalene at 120 °C, respectively.

Moreover, the polarity of the h-BN stationary phase was evaluated by McReynolds constants of the five probe compounds, *i.e.*, benzene (X'), 1-butanol (Y'), 2-pentanone (Z'), 1-nitropropane (U') and pyridine (S'), and the results are provided in Table 1. As can be seen, the h-BN stationary phase has the average value of 136, suggesting its moderate polarity slightly higher than that of the g-C$_3$N$_4$ stationary phase. Comparatively, the h-BN stationary phase exhibits distinctly larger Y', U' and S' values, indicating its possibly stronger H-bonding/halogen-bonding and dipole-dipole interactions with specific analytes, which may produce different retention behaviour and resolving capability for their separations. In addition, Table 1 provides the McReynolds constants of a commercial stationary phase of 35% phenylmethylpolysiloxane with close polarity for reference.

3.2. Separation performance and retention behaviors

The separation performance and retention behaviors of the h-BN stationary phase were investigated by employing ten mixtures of a wide variety, including the mixture of polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs), the mixture of analytes of different types and eight isomer mixtures of aliphatics and aromatics. Meanwhile, the g-C$_3$N$_4$ column was utilized as the reference for the evaluation.

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