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Exploitation of a microporous organic polymer as a stationary phase for capillary gas chromatography

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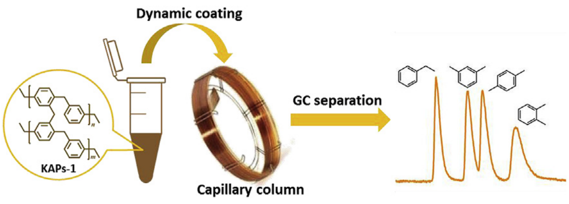
HIGHLIGHTS

- A microporous organic polymer was explored as a novel stationary phase for capillary GC.
- The column showed high separation performance for VOCs including the challenging ethylbenzene and xylene isomers.
- Thermodynamic and kinetic parameters for BTEXs were determined to study the analyte-stationary phase interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Microporous organic polymers (MOPs) have emerged as a new class of functional porous materials with unique characteristics and potential uses in diverse areas. However, the field of MOPs for gas chromatographic (GC) separations has not been well explored. Herein, a MOP namely KAPs-1 was dynamic coated onto a capillary column for the first time. The fabricated column exhibited a nonpolar nature and the column efficiency for *n*-dodecane was up to 7769 plates m^{-1}. The KAPs-1 coated column showed high GC separation performance for a series of volatile organic compounds (VOCs) including the challenging ethylbenzene and xylene isomers, which could not be resolved at baseline on the commercial 5% phenyl polysiloxane stationary phase. Moreover, the relative standard deviations for five replicate determinations of the studied analytes were 0.0–0.6%, 0.9–3.2%, 1.1–5.9%, 0.8–3.7% for retention time, peak area, peak height and peak width, respectively. To investigate the interaction between some analytes and the stationary phase, thermodynamic and kinetic parameters were also evaluated. The results of this study show it is very promising to utilize MOPs as stationary phases for capillary GC.

1. Introduction

Over the past few decades, great efforts have been devoted to the development of microporous materials featured with average pore sizes less than 2 nm and the well-known examples include zeolites, activated carbons, silicas, metal organic frameworks (MOFs) and MOPs [1–3]. In particular, MOPs which are composed of light, non-metallic elements (e.g. C, H, O, N, B) [2] have recently become the focus of significant attention owning to their outstanding characteristics and enormous potential in diverse applications.

In general, MOPs could be constructed by linkage of polymerizable monomers as organic building blocks or post-crosslinking of performed polymer chains through kinds of chemical reactions [4,5], exhibiting very broad synthetic diversity in comparison with

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other microporous solids. Accordingly, the past few years have witnessed the rapid growth of a wide variety of MOPs with different structures and specific properties involving covalent organic frameworks (COFs) [6], conjugated microporous polymers (CMPs) [7], polymers of intrinsic microporosity (PIMs) [8], porous polymer networks (PPNs) [9] and hypercrosslinked polymers (HCPs) [10], etc. However, most of the exploitations of these emerging MOPs have been concentrated on gas separation and storage [11,12], catalysis [13] and sensing [14], fewer data have been presented on their potential serving as stationary phases for GC although there have been two reports on the applications of chiral MOPs (a PPN and a porous organic cage, respectively) in GC separations very recently [15,16]. In sharp contrast, MOFs as the inorganic-organic hybrid counterparts of MOPs have been studied extensively in the utilizations as new stationary phases for GC [17]. It should be noted that with robust covalent bonds interlinked by organic building blocks instead of weak coordinative interaction [18], MOPs tend to be more stable than MOFs. Therefore, the excellent physicochemical stability coupled with other remarkable properties such as permanent porosity, feasible functionalization and large specific surface area [18–20] renders MOPs to be appealing and possibly superior candidates for separation media in high-resolution GC. The field of MOPs for GC separation remains to be well investigated.

Herein, we report the first example of HCPs based on organic building blocks for fabrication of porous layer open tubular (PLOT) column for GC. The selected novel HCP namely KAPs-1 was prepared by a cost-effective strategy of “knitting” rigid aromatic building blocks with an external cross-linker [21]. This strategy eliminated the need of polymerizable monomers and the use of expensive metal coupling catalysts [4]. In addition, since the sole byproduct was methanol, this strategy was environmentally friendly. KAPs-1 was explored as a potential stationary phase for GC because it possesses the advantages of high surface area, good thermal and chemical stability, predominantly microporosity as well as easy preparation. A series of VOCs were used as targets for separations, including ethylbenzene and xylene isomers of which the separation is significant for both environmental research and chemical industry but challenging because of their close matching boiling points and molecular sizes [22–24]. Furthermore, thermodynamic and kinetic parameters were determined to get insight into the interaction between the stationary phase and some analytes in this work.

2. Experimental

2.1. Materials and instruments

All chemicals are of high purity (analytical grade or higher) and used as supplied without further treatment. *p*-, *m*-, *o*-Xylene and toluene were purchased from Alfa Aesar (Beijing, China). Benzene was purchased from Guanghua Chemical Factory Co. Ltd. (Guangdong, China). Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were from Guangzhou Chemical Reagent Company (Guangzhou, China). Methanol was from Sigma–Aldrich (Shanghai, China). The rest chemicals were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Untreated fused silica capillary (30 m long × 0.32 mm i.d.) was purchased from Yongnian Optic Fiber Plant (Hebei, China). A HP-5MS capillary column (30 m long × 0.25 mm i.d. × 0.25 μm film thickness) was purchased from Agilent Technologies (USA).

Infrared (IR) spectra were recorded on an EQUINOX Fourier Transform Infrared spectrometer (FTIR) (Bruker, Germany) in the 400–4000 cm^{-1} region. The ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectra were acquired on a Bruker Avance 400 spectrometer at resonance frequencies of 400 MHz. Scanning electron microscope (SEM) images were obtained by a Quanta 400F SEM instrument (FEI/Oxford/HKL, Netherlands) at 20 kV. Thermogravimetric analyses (TGA) data were collected on a thermal gravimetric analyzer (NETZSCH, Germany) from 30 to 800 °C at a ramp rate of 10 °C min^{-1} under N_2. Transmission electron microscope (TEM) micrographs were acquired on a Tecnai G2 Spirit microscope (FEI, Netherlands) operating at a 120 kV accelerating voltage. N_2 adsorption–desorption isotherms were measured at 77.3 K on Micromeritics ASAP 2020 V3.04H surface area and porosity analyzer based on the Brunauer, Emmet, and Teller (BET) method. GC measurements were performed on an Agilent 6850 GC system equipped with a flame ionization detector (FID). Nitrogen (99.999%) and Hydrogen (99.999%) were used as the carrier gas and the fuel gas, respectively. The inlet temperature was set at 250 °C and the detector temperature was 280 °C.

2.2. Synthesis of KAPs-1

KAPs-1 was obtained by a simple one-step Friedel–Crafts reaction according to Li et al. [21]. Typically, benzene (0.02 mol) as the monomers and formaldehyde dimethyl acetal (0.06 mol) as cross linkers were dissolved in 1,2-dichloroethane (20 mL), and then the catalyst (anhydrous $FeCl_3$, 0.06 mol) was introduced into the mixture solution and mixed well at room temperature. The reaction system was stirred at 45 °C for 5 h to achieve initial networks and subsequently heated at 80 °C for 19 h to complete the condensation reaction. After filtrated and washed with methanol thoroughly, the product was collected by Soxhlet extraction in methanol for 24 h. Finally, the brown powders were obtained by drying in vacuo at 60 °C for 24 h.

2.3. Preparation of KAPs-1 coated capillary column

The pretreatment of the capillary column prior to coating was as follows: untreated fused silica capillary was washed sequentially with 1 M NaOH for 2 h, ultrapure water for 0.5 h, 0.1 M HCl for 2 h and again with ultrapure water until the washings were neutral. The capillary was then purged with nitrogen at 150 °C overnight.

The KAPs-1 coated capillary column was prepared by a dynamic coating method [25]: 2.5 mg KAPs-1 was dispersed in 2.0 mL toluene and sonicated for 10 min. After set aside for 15 min, the supernatant of the suspension was collected, filled into the capillary as a plug and then pushed through the capillary with nitrogen at a rate of 30 cm min^{-1}. A 1 m long buffer tube (0.32 mm i.d.) as a restrictor was attached to the end of the capillary to avoid the acceleration of the solution plug near the end of the capillary. The resulting wet coating layer on the inner wall of the capillary was dried under nitrogen overnight. Finally, the KAPs-1 coated capillary column was conditioned by increasing its temperature at a rate of 1 °C min^{-1} from 30 to 270 °C (held for 30 min) and then decreasing to 30 °C at the same rate. The procedure was repeated for three times.

2.4. Thermodynamic analysis

Thermodynamic parameters involving enthalpy change ΔH, entropy change ΔS and Gibbs free energy change ΔG, which could elucidate the energy effect on the interaction between targets and the studied stationary phase, were calculated on the basis of the van't Hoff model [26] (Eq. (1) and (2)).

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