Journal of Chromatography A, 1406 (2015) 299–306

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Fabrication of zeolitic imidazolate framework-8-methacrylate monolith composite capillary columns for fast gas chromatographic separation of small molecules

Kareem Yusuf*, Ahmed Yacine Badjah-Hadj-Ahmed, Ahmad Aqel, Zeid Abdullah ALOthman

Advanced Materials Research Chair, Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form 10 June 2015
Accepted 11 June 2015
Available online 19 June 2015

Keywords:
Metal organic framework
Zeolitic imidazolate framework
Organic polymer monolith
Gas chromatography
Fast separation

ABSTRACT

A composite zeolitic imidazolate framework-8 (ZIF-8) with a butyl methacrylate-*co*-ethylene dimethacrylate (BuMA-*co*-EDMA) monolithic capillary column (33.5 cm long × 250 μm i.d.) was fabricated to enhance the separation efficiency of methacrylate monoliths toward small molecules using conventional low-pressure gas chromatography in comparison with a neat butyl methacrylate-*co*-ethylene dimethacrylate (BuMA-*co*-EDMA) monolithic capillary column (33.5 cm long × 250 μm i.d.). The addition of 10 mg mL^{-1} ZIF-8 micro-particles increased the BET surface area of BuMA-*co*-EDMA by 3.4-fold. A fast separation of five linear alkanes in 36 s with high resolution ($R_s \geq 1.3$) was performed using temperature program. Isothermal separation of the same sample also showed a high efficiency (3315 plates m^{-1} for octane) at 0.89 min. Moreover, the column was able to separate skeletal isomers, such as iso-octane/octane and 2-methyl octane/nonane. In addition, an iso-butane/iso-butylene gas mixture was separated at ambient temperature. Comparison with an open tubular TR-5MS column (30 m long × 250 μm i.d.) revealed the superiority of the composite column in separating the five-membered linear alkane mixture with 4–5 times increase in efficiency and a total separation time of 0.89 min instead of 4.67 min. A paint thinner sample was fully separated using the composite column in 2.43 min with a good resolution ($R_s \geq 0.89$). The perfect combination between the polymeric monolith, with its high permeability, and ZIF-8, with its high surface area and flexible 0.34 nm pore openings, led to the fast separation of small molecules with high efficiency and opened a new horizon in GC applications.

1. Introduction

For more than a century, chromatography has been one of the most important analytical techniques, particularly column chromatography, which is considered the most public chromatographic technique. The stationary phase within the columns in column chromatography has experienced continuous development since the first *Tswett* calcium carbonate column in 1901. The aim of the development is to achieve faster separation with high efficiency. Monolithic capillary columns are one of the newest types of chromatographic columns. The high permeability of capillary monolithic columns allows for faster separations; moreover, they are characterized by easy fabrication and modification, low backpressure and the ability to work at the miniaturization scale due to a capillary size that reduces the consumption of carrier gas [1]. The two most popular types of monolithic columns are: inorganic silica and organic polymeric monoliths. Silica based inorganic monoliths have the ability of fast separation of small molecules, whereas polymeric monoliths are more efficient in separating macro-molecules. One of the most convenient methods used to enhance the separation of small molecules using polymeric monoliths is the incorporation of various nano- and micro-particles into the monolithic matrix. Several attempts have successfully been made using this technique, including carbon nanotube (CNT) [2–5], graphene oxide (GO) [6], C_{60}-fullerene [7], sporopollenin [8], and metal-organic frameworks [9–11].

Metal-organic frameworks (MOFs) were first introduced in 1995 by Yaghi et al. to describe the youngest group of porous materials [12]. In parallel, the main concepts were proposed by Kitagawa [13] and Férey et al. [14]. MOFs are highly ordered and precisely controlled crystalline systems that are composed of an inorganic

* Corresponding author. Tel.: +966 596245977.
E-mail addresses: dr_kareemyusuf@yahoo.com, kmahmoud@ksu.edu.sa (K. Yusuf).

http://dx.doi.org/10.1016/j.chroma.2015.06.026
0021-9673/

metal-containing unit that is self-assembled with an organic ligand. MOFs crystalline structures can be selected through the precise selection of its components (metal cation and ligand) and rely on the wide choice of metal cations and organic linkers available. The main advantages of MOFs compared with the conventional inorganic porous frameworks are their almost unlimited diversity, very high surface area, ability for post-synthetic modifications and designable structures. The outstanding properties of MOFs have made them a successful candidate for many applications, such as gas storage for energy purposes, supercapacitors, catalysis, sensing, drug delivery, and chromatography [15].

Over the last decade, chromatography has become an application of interest for metal-organic frameworks. Chromatographic separations generally depend on the adsorption nature and strength of the stationary phase and its surface area. Hence, the high absorbability and high surface area of MOFs make them attractive targets as stationary phases for chromatographic applications. Our research group recently published a review entitled "Metal organic frameworks in chromatography" which summarized the applications of MOFs in chromatography among other excellent reviews [16–18].

Although using MOFs in chromatography has already given promising and surprising results, the use of MOFs incorporated with polymers (MOF–polymer) to form a composite stationary phase is still very limited [9–11]. The composite material combines the advantages of the MOF stationary phase and the monolithic organic stationary phase and avoids their disadvantages. The advantages gained from MOFs are the controlled pore size and shape, the high pore volume, higher surface area, the desired functionality and control of the apolar character, whereas the advantages of monolithic polymers are represented in the high permeability obtained while eliminating the low surface area problem of organic monoliths.

Recently, UiO-66 incorporated in a polymethylarylic acid-*co*-ethylene dimethacrylate (MAA-*co*-EDMA) monolithic stainless steel conventional column (7 cm long × 4.6 mm i.d.) was fabricated by Fu et al. for HPLC applications [9]. The (UIO-66)–(MAA-*co*-EDMA) composite successfully enhanced the separation of polycyclic aromatic hydrocarbons with efficiency (28,000 plates m^{-1} for 2,6-dimethylphenol). Huang et al. presented the first capillary monolithic column incorporated with MOF material [10]. They prepared an MIL-101(Cr)–(BuMA-*co*-EDMA) composite capillary column for electrochromatography (CEC) and nano-liquid chromatography (nano-LC). The prepared columns exhibit a satisfactory performance (52,000 in CEC and 24,000 plates m^{-1} in nano-LC) in comparison to previous reports on MOF packed columns. HKUST-1 nanoparticles were also examined to enhance the performance of glycidyl methacrylate-*co*-ethylene dimethacrylate capillary monolithic columns in liquid chromatography [11]. The efficiency of the separation increased for all comparable analytes separated in the conventional column of Fu et al.

To the best of our knowledge, MOF–polymer composites have not been used as a monolithic stationary phase in gas chromatography to date. The extraordinary properties of MOFs may bring more attention to the utilization of monolithic columns in GC, which is one of the less common applications, particularly for methacrylate monoliths [1,19–21]. The present research presents a novel composite stationary phase by incorporating a capillary methacrylate monolithic column with ZIF-8 [Zn (2-methylimidazole)$_2$] microparticles for GC applications using a conventional low-pressure GC instrument. ZIF-8 was explored for GC applications as a packed column [22] and as an open tubular column [23,24]. The most significant features reported for the ZIF-8 chromatographic separation are its unique molecular sieving nature of branched alkanes from linear alkanes through flexible pore openings and its apolar character, which enhanced the high resolution GC separation of linear alkanes series. Zeolitic imidazolate framework-8 (ZIF-8) is characterized by its stable structure, high surface area (1500–1600 m^2 g^{-1}), uniform flexible narrow six-membered ring pore windows (0.34 nm) and large pores (1.14 nm) and very high chemical and thermal stability (380–550 °C) [25]. Thus, ZIF-8 was used in a different percentage with butyl methacrylate-*co*-ethylene dimethacrylate to investigate its effect on the separation efficiency of nonpolar alkanes, polar organic solvents, isomers, gases and a thinner sample from the local market via conventional low pressure gas chromatography. The selected analytes are small enough to fit into the flexible ZIF-8 pores. A comparison with a conventional open tubular capillary column and with a ZIF-8 coated capillary column from a previous study revealed the superiority of the prepared columns for separating small molecules.

2. Experimental

2.1. Reagents and materials

2-Methylimidazole zinc salt (ZIF-8) was purchased from Sigma–Aldrich (St. Louis, MO, USA) and produced by BASF under the commercial name of Basolite®Z1200. Polyimide-coated 250 μm i.d. fused silica capillaries were purchased from Restek (Bellefonte, USA). 3-(trimethoxysilyl) propyl methacrylate (TMSM) and azobisisobutyronitrile (AIBN) were purchased from Fluka (Buchs, Switzerland). Butyl methacrylate (BuMA) and ethylene dimethacrylate (EDMA) were obtained from Sigma–Aldrich (St. Louis, MO, USA). The gases (methane, helium, hydrogen, nitrogen and air), all of high-purity grade (99.9999%), were purchased from SIGAS (Riyadh, Saudi Arabia). For the comparative study, the TR-5 MS column, 30 m length and 250 μm inner diameter was purchased from Thermo Scientific (Waltham, MA, USA).

2.2. Instrumentation

All experiments were performed using a conventional Thermo Scientific gas chromatograph (Trace GC Ultra, USA). The system used a split/splitless injector, an oven with a temperature range of 50–400 °C, a heating rate of up to 14.5 °C s^{-1} (870 °C min^{-1}), programmability of 3 ramps/4, a flame ionization detector (FID) with a 1:10 hydrogen/air mixture as the flame fuel and an acquisition rate of 300 Hz. The sample was injected manually into the instrument. Both the injector and the detector were adjusted to 190 °C. Data analysis was performed using the Chrom-Card data handling software package. The carrier gas was dried, high-purity helium.

Thermal stability of the prepared materials was measured using a Mettler-Toledo TGA/DSC Stare system (Schwerzenbach, Switzerland). The sample was heated from 25 to 400 °C at a heating rate of 10 °C min^{-1}.

2.3. Preparation of ZIF-8-butyl methacrylate monoliths

The monolithic capillaries were prepared according to a previously described method [21] with some changes. The polymerization mixture consisted of 30% monomers (70% BuMA, 30% EDMA) and 70% porogen (50% 1-propanol, 50% 1,4-butandiol). ZIF-8 was dispersed and homogenized in the polymerization mixture under sonication for 10 min and was then purged with helium for 5 min. Four batches columns were prepared to examine the effect of adding ZIF-8 in different percentages ZIF-8–(BuMA-*co*-EDMA)-0, ZIF-8–(BuMA-*co*-EDMA)-1, ZIF-8–(BuMA-*co*-EDMA)-2, ZIF-8–(BuMA-*co*-EDMA)-3 with 0, 5, 10 and 15 mg mL^{-1} ZIF-8, respectively. The empty fused silica capillary tubing (250 μm i.d) has been activated with 1.0 mol L^{-1} NaOH solution for 5 min and soaked for 10 min, then it rinsed with water and dried. The column was then flushed with 1.0 mol L^{-1} HCl for 2 min and dried with