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Incorporation of metal-organic framework HKUST-1 into porous polymer monolithic capillary columns to enhance the chromatographic separation of small molecules

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ABSTRACT

Metal-organic framework (MOF) HKUST-1 nanoparticles have been incorporated into poly(glycidyl methacrylate-co-ethylene dimethacrylate) (HKUST-1-poly(GMA-co-EDMA)) monoliths to afford stationary phases with enhanced chromatographic performance of small molecules in the reversed phase capillary liquid chromatography. The effect of HKUST-1 nanoparticles in the polymerization mixture on the performance of the monolithic column was explored in detail. While the bare poly(GMA-co-EDMA) monolith exhibited poor resolution ($R_s < 1.0$) and low efficiency (800–16,300 plates/m), addition of a small amount of HKUST-1 nanoparticles to the polymerization mixture provide high increased resolution ($R_s \geq 1.3$) and high efficiency ranged from 16,300 to 44,300 plates/m. Chromatographic performance of HKUST-1-poly(GMA-co-EDMA) monolith was demonstrated by separation of various analytes including polycyclic aromatic hydrocarbons, ethylbenzene and styrene, phenols and aromatic acids using a binary polar mobile phase (CH_3CN/H_2O). The HKUST-1-poly(GMA-co-EDMA) monolith displayed enhanced hydrophobic and π–π interaction characteristics in the reversed phase separation of test analytes compared to the bare poly(GMA-co-EDMA) monolith. The experiment results showed that HKUST-1-poly(GMA-co-EDMA) monoliths are an alternative to enhance the chromatographic separation of small molecules.

1. Introduction

Metal-organic frameworks (MOFs) are an emerging class of highly porous materials made of inorganic ions or clusters coordinated to organic ligands. MOFs have received great attention as novel candidate materials for use as stationary phases in chromatography due to their fascinating structures and unusual properties such as exceptionally large surface areas, highly uniform pores and tunable pore geometry, versatile structures [1,2]. Recently, the vapour phase separation using MOFs as stationary phases for either packed columns or coated capillary columns in gas chromatography have been extensively investigated and results demonstrated remarkable success in small molecule separation [3–12].

It was found that microsized MOFs with good solvent stability are quite applicable as stationary phases for high performance liquid chromatography (HPLC) [13]. Since the application of a glass tube column packed with a homochiral Zn–organic framework in HPLC by Fedin and coworkers [14], to date, most of the reported MOFs (MIL-101, MIL-53, MIL-100, HKUST-1, MOF-5, MIL-47) as stationary phases for HPLC have been concentrated on the MOFs particles or powders that have been ground or directly packed into columns [15–20]. Although impressive progress on the MOFs-based HPLC columns has been made, there still remain some problems. Because the sizes of MOFs particles are often widely distributed and the shapes of the particles are generally irregular, the direct packing of MOFs particles often resulted in low column efficiency, high column backpressure, and undesirable peak shapes.

To overcome the above-mentioned problems, one of effective strategies is preparation of uniform spherical MOFs composites. In an attempt to combine of good column packing properties of a spherical substrate and the unique separation ability of MOFs, MOFs/silica composites were further explored as stationary phases in HPLC. Tanaka et al. [21] reported a homochiral MOF-silica composite as a new chiral stationary phase for selective separation of chiral sulfoxides. Ameloot et al. [22] fabricated silica-HKUST-1

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composite spheres by loading the nanosized HKUST-1 inside silica pores for HPLC. Ahmed et al. [23] described the preparation of HKUST-1 nanocrystals on spheres-on-sphere composite microspheres (silica SOS@HKUST-1) composite as packing materials for fast and efficient HPLC. Fu et al. [24] reported the fabrication of monodisperse ZIF-8@SiO_2 core-shell microspheres by the controllable growth of a ZIF-8 shell on spherical carboxylate terminated SiO_2 cores for HPLC application. Another effective solution could be making use of hybrid MOFs/organic polymers, which combine the unique properties of MOFs and the excellent features of polymer monoliths. However, only a few attempts using MOFs/organic polymers as stationary phases for HPLC have been reported. Huang et al. [25] reported a novel MIL-101(Cr)-organic polymer monolith as stationary phase for capillary liquid chromatography (cLC) and capillary electrochromatography (CEC). The inclusion of MIL-101(Cr) provided high surface areas and high permeability in the produced MOF-polymer monolith. Fu et al. [26] have fabricated UiO-66 incorporated polymer monoliths for HPLC separation of small molecules with enhanced resolution and high column efficiency. Li et al. [27] reported the fabrication of CAU-1@polymethyl methacrylate coated capillary for open tubular CEC. The incorporation of CAU-1 into polymethyl methacrylate not only increases surface area, but also electroosmotic flow. MOFs also can be used as a porogenic template to prepare macroporous affinity polymer monoliths [28].

The combination of the unique structure of porous polymer monoliths and the specific features of MOFs might provide a promising improvement of the performance of monoliths for HPLC. This work focused on the development of novel HKUST-1 incorporated capillary monoliths as stationary phase for reversed phase capillary liquid chromatography (RP-cLC). HKUST-1 is a well known MOF material constructed from dimmer Cu paddle wheels linked by 1,3,5-benzenetricarboxylates with a three dimensional square-shaped channel system (9 × 9 Å) [29]. Although the selective separation of aromatics on HKUST-1 [15], silica-HKUST-1 [22] and silica SOS@HKUST-1 [23] composites packed columns have been reported, these previous studies were performed in normal phase mode using nonpolar organic solvent as the mobile phase. As we know, RP-HPLC is the most widely used separation technique in life and environmental sciences and biomedical research. However, no studies to date focused on the preparation of HKUST-1 incorporated polymer monoliths as stationary phase for RP-HPLC. This article demonstrates the use of HKUST-1 nanoparticles entrapped within poly(glycidyl methacrylate-co-ethylene dimethacrylate) (HKUST-1-poly(GMA-co-EDMA)) monoliths for improving the performance of the monolithic capillary columns in the separation of small molecules.

2. Experimental

2.1. Reagents and materials

Glycidyl methacrylate (GMA), ethylene dimethacrylate (EDMA), cyclohexanol, dodecanol and 3-(trimethoxysilyl)propyl methacrylate were purchased from Alfa Aesar (Ward Hill, MA, USA). Azobisisobutyronitrile (AIBN), polycyclic aromatic hydrocarbons (PAHs), ethylbenzene (EB) and styrene (St), aromatic acids, phenols, 1,3,5-benzenetricarboxylic acid (H_3BTC), *N*,*N*-dimethylformamide(DMF), $Cu(Ac)_2$ and HPLC-grade CH_3CN were obtained from Shanghai Chemical Reagents Corporation (Shanghai, China). All other reagents were of analytical grade. Ultrapure water used for the preparation of solutions was produced by a Milli-Q water system (Millipore, Bedford, MA, USA). Fused-silica capillary of 100 μm i.d. and 375 μm o.d. was obtained from Hebei Yongnian Optical Fiber Factory (Hebei, China).

2.2. Instrumentation

All chromatographic experiments were performed on a TriSep-2100 pressurized CEC system (this instrument can also be utilized as cLC system, Unimicro Technologies, Pleasanton, CA, USA). The FT-IR (Fourier transform infrared) spectra (4000–400 cm^{-1}) in KBr were recorded using a PE Spectrum One FT-IR spectrometer (PE, USA). Powder X-ray diffraction (XRD) patterns were recorded on a D/max 2550 VB/PC diffractometer (Rigaku, Japan) with Cu Kα radiation ($\lambda = 0.15418$ nm). Scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDS) were carried out on FEI Quanta 200 FEG SEM (Philips, The Netherlands).

2.3. Synthesis of HKUST-1 nanoparticles

HKUST-1 nanoparticles were synthesized according to Na et al. [30]. Typically, 0.9 g of $Cu(Ac)_2$ and 12 g of benzoic acid were dissolved in 60 mL of n-butanol (referred as Solution A) and 2.0 g of H_3BTC was dissolved in 60 mL of DMF (referred as Solution B). At room temperature, Solution B was added dropwise to Solution A with vigorous stirring over 30 min. The resulting solution was stirred for an additional 1 h. The blue precipitate was collected by centrifugation, rinsed with ethanol for three times *via* successive centrifugation–redispersion cycles. The product was dried at 150 °C in vacuum over night. Finally, the blue solid was characterized by FT-IR, XRD spectrometry and SEM.

2.4. Preparation of HKUST-1-poly(GMA-co-EDMA) monoliths

The monoliths were prepared according to a previously described procedure [31] with some modifications. In brief, a specific amount of HKUST-1 nanoparticles were dispersed in the polymerization mixture comprised of GMA, EDMA, dodecanol, cyclohexanol and AIBN according to the proportions specified in Table 1. This solution was homogenized in an ultrasonic bath for 10 min, and then purged with nitrogen for 5 min before being introduced into the vinylized capillaries. Both ends of the capillary were sealed and the capillary was placed in a thermostated water bath for polymerization at 60 °C for 20 h. A few centimeters were cut from both ends of the capillary. The monoliths were flushed with methanol to remove the residual monomers and porogens. The bare poly(GMA-co-EDMA) monolith, as a negative control, was also prepared in the absence of HKUST-1 nanoparticles by using the same preparation procedure as described above. Synthesis processes of HKUST-1-poly(GMA-co-EDMA) monolith were depicted in Fig. 1. A detection window was created at 1–2 mm after the end of the polymer bed using thermal wire stripper. A 2-cm length of the capillary containing the monolith was cut for SEM and EDS analysis. The poly(GMA-co-EDMA) and HKUST-1-poly(GMA-co-EDMA) materials were also prepared in 5 mL centrifuge tube and were dried at 150 °C over night after Soxhlet extraction with methanol for FT-IR, SEM and XRD.

2.5. Calculations

The permeability (*K*) is calculated by the following formula: [32]

$$K = \frac{F \times \eta \times L}{\Delta P \times \pi \times r^2}$$

where F is the volume flow rate of the eluent, η is the dynamic viscosity of the mobile phase, L is the column length, and ΔP is the pressure drop across the column. In this work, methanol was used as mobile phase and corresponding value of dynamic viscosity was 0.580×10^{-3} kg/(m s) at 25 °C [33].