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Room temperature fabrication of post-modified zeolitic imidazolate framework-90 as stationary phase for open-tubular capillary electrochromatography☆

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ABSTRACT

Metal–organic frameworks (MOFs) are attractive as porous stationary phase for open-tubular capillary electrochromatography (OT-CEC) due to their fascinating structures and unusual properties. Here we report a directly covalent bonding approach to prepare uniform and dense MOF film on the inner wall of fused silica capillary at room temperature for OT-CEC. Zeolitic imidazolate framework-90 (ZIF-90) as a model MOF because it not only possesses large surface area and high stability but also provides the free aldehyde groups to bond to the inner surface of capillary via covalent bond. X-ray diffraction, scan electron microscopy, and UV–vis spectrophotometry were used to confirm the bonding of the ZIF-90 to the inner wall of the silica capillary. The ZIF-90 coating not only increased the phase ratio of open-tubular column, but also improved the interactions of tested analytes and the coating. Owing to the porous structure of ZIF-90 and hydrophobic interactions between the analytes and the organic ligands of ZIF-90, three groups of isomers, neutral and basic compounds and nonsteroidal anti-inflammatory drugs were well separated on the ZIF-90 bonded column. The precisions (relative standard deviation, RSD) of retention time, half peak width and peak area for three consecutive runs were 0.3–1.2%, 1.3–6.0% and 1.5–5.2%, respectively. The run-to-run, day-to-day, and column-to-column precisions (RSDs) for the electroosmotic flow of the ZIF-90 bonded column were 0.2%, 0.4%, and 1.9%, respectively. Moreover, the ZIF-90 bonded column could stand more than 230 runs without observable change in the separation efficiency.

1. Introduction

Metal–organic frameworks (MOFs) are novel microporous crystalline materials consisting of clusters or chains of metal ions connected by organic ligands [1–3]. Owing to their diverse structures and accessible tunnels and cages, they are increasingly in demand for application in gas storage [4], catalysis [5], separation [6], and drug delivery [7]. The unusual properties such as high surface areas, good thermal and solvent stability, adsorption affinities and the availability of in-pore functionality and outer-surface modification make MOFs attractive as separation media in analytical chemistry [8–10]. One of the most promising applications of MOFs seems to be as novel stationary phases for chromatography [11]. Various MOFs have been explored as the stationary phase in liquid chromatography (LC) or gas chromatography, the pseudostationary phase in electrokinetic chromatography [12], and the MOF-organic polymer hybrid monolithic stationary phase for microbore LC and capillary electrochromatography (CEC) [13].

Open tubular CEC (OT-CEC) has attracted increasing attention due to its advantages of ease of column preparation and no need for end frits and particles packing [14]. Although open tubular columns have been widely applied in chromatographic separations, it is still challenging to achieve high phase ratio, high sample capacity, and good stability due to the lack of fabrication techniques [15]. To date, several approaches including sol–gel-derived phases [16], etched capillary [17,18], porous silica layers [19,20], and nanoparticle phases [21–27] have been developed to address this issue. Since MOFs possess numerous structures, high surface areas, and

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adsorption affinities, the bonding of MOF to the capillary inner wall not only increases the phase ratio of open tubular column, but also improves the interactions of solute molecules and stationary phase. The combination of the unique properties of MOFs and the excellent features of open tubular column has been received attention in OT-CEC. Recently, an in situ, layer-by-layer self-assembly approach was employed to fabricate MIL-100(Fe) coated capillary column [28] and a dynamic coating method was used to prepare CAU-1-polymethyl methacrylate composite coated capillary column [29] for OT-CEC. However, previous approaches for the preparation of MOF-coated open tubular column either were off-line uncontrollable procedure or a thin MOF layer was obtained through many cycles [28,29]. Generally, direct bonding of MOF film to the inner wall of capillary should increase the phase ratio and stability due to the existence of covalent bond between the coating and the surface of capillary.

Here, we report a directly covalent bonding approach to prepare firm MOF film on the inner wall of capillary at room temperature for OT-CEC. Zeolitic imidazolate framework-90 (ZIF-90) was employed as a model MOF because it possesses not only large surface area and high stability [30], but also ease of preparation at room temperature [31]. ZIF-90 shows a new sodalite topology with permanent porosity containing a narrow size of the six-membered ring pores (3.5 Å) and especially possesses the free aldehyde group in the framework that allows the covalent functionalization with amine groups through an imine condensation reaction [32,33]. In this work, ZIF-90 was prepared at room temperature [31], and modified with 3-aminopropyltriethoxysilane (APTES). The APTES modified ZIF-90 was then directly immobilized onto the capillary wall via covalently bonding at room temperature. The performance of the ZIF-90 bonded capillary column was evaluated as a new stationary phase for OT-CEC separation of nonsteroidal anti-inflammatory drugs, anilines, and the isomers of xylene, chlorotoluene, and dichlorobenzene.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were at least of analytical grade unless otherwise stated. Ultrapure water was purchased from Tianjin Wahaha Foods Co. Ltd. Sodium formate (99%, $NaCO_2H$) and zinc nitrate hexahydrate (99%, $Zn(NO_3)_2{\cdot}6H_2O$) were purchased from Tianjin Standard Science and Technology Co. (Tianjin, China). Imidazolate-2-carboxyaldehyde (99%), methanol (MeOH), 3-aminopropyltriethoxysilane (APTES) (98%), and isomers (xylene, dichlorobenzene, chlorotoluene) were purchased from Aladdin Reagent Co. (Shanghai, China). Acetanilide, aniline, 2-nitroaniline, and 1-naphthylamine were purchased from Tianjin No. 1 Chemical Reagent Plant (Tianjin, China), Tianjin Huayue Chemical Reagent Plant (Tianjin, China), Shanghai No. 3 Chemical Reagent Plant (Shanghai, China), and Beijing Chemical Plant (Beijing, China), respectively. Thiourea, naphthalene, anthracene, sodium dihydrogen phosphate, and disodium hydrogen phosphate were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). Ibuprofen, naproxen and ketoprofen were purchased from Zhejiang Xianju Pharmaceutical Corporation (Xianju, China). Fused silica capillary (375 μm o.d. × 75 μm i.d.) was obtained from Yongnian Optic Fiber Plant (Handan, China).

2.2. Synthesis and APTES-modification of ZIF-90

ZIF-90 was synthesized as reported previously [31]. Typically, a solution of 20 mmol of $NaCO_2H$ and 20 mmol of imidazolate-2-carboxyaldehyde in 50 mL of MeOH was heated to 50 °C until it became clear, then cooled to room temperature. Another solution of 5 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ and 50 mL of ultrapure water was poured into the above solution and allowed to stir at room temperature for 1 h. The resulting milky mixture was centrifuged at 11,200 × *g* for 5 min, and the precipitate was washed with 45 mL of MeOH for three times. The ZIF-90 crystals were dried in an oven at 85 °C.

For the APTES-modification, the as-prepared ZIF-90 crystals were immersed in the solution of MeOH and APTES, and refluxed at 110 °C for 30 min. The prepared APTES modified ZIF-90 crystals were washed with MeOH several times and then dried in air at room temperature over night.

2.3. Fabrication of ZIF-90 bonded capillary columns

The as-bought capillary was washed with 1 M NaOH for 2 h, ultrapure water for 1 h and 0.1 M HCl for 2 h, then washed with ultrapure water again until the outflow reached pH 7.0. The capillary was dried with nitrogen purging at 150 °C in a gas chromatographic oven overnight. To produce a thin layer of ZIF-90, the APTES modified ZIF-90 was dispersed in MeOH under ultrasonication to give a homogeneous suspension. The suspension was then introduced into the preconditioned fused silica capillary via syringe injection, after which the capillary was sealed at both ends for 12 h at room temperature.

2.4. Characterization

The X-ray diffraction (XRD) experiments were performed on a D/max-2500 diffractometer (Rigaku, Japan) using Cu*K*α radiation (λ=1.5418 Å). Scan electron microscopy (SEM) images of the bare capillary and the ZIF-90 bonded capillary were recorded on a SS-550 scanning electron microscope at 15.0 kV (Shimadzu, Japan). Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr plate were obtained on Magna-560 spectrometer (Nicolet, Madison, WI, USA). Solid UV–vis absorption spectra (200–800 nm) were collected on a V-550 spectrometer (JASCO, Japan).

2.5. CEC separation

CEC experiments were carried out on a P/ACE MDQ capillary electrophoresis system (Beckman, Fullerton, CA, USA) equipped with a diode array detector (DAD) at 25 °C. Data acquisition and processing was controlled by the Beckman ChemStation software. The mobile phase was obtained by mixing the phosphate buffer solution (PBS) with the appropriate amount of water and MeOH. Prior to separation, all solutions were filtered through a 0.45 μm filter and degassed under ultrasonication and injected electrokinetically at 3.45 kPa for 5 s. The ZIF-90 bonded capillary column (total length, 31.2 cm; effective length, 20.0 cm) was rinsed with MeOH (15 min), ultrapure water (4 min), and PBS (10 mM, pH 7.4) (2 min) before the first use, and with running buffer containing 10 mM PBS (2 min) between consecutive runs. The column was then installed in the CEC instrument and equilibrated at 15 kV until a stable current and baseline was achieved.

3. Results and discussion

3.1. Fabrication and characterization of the ZIF-90 bonded capillary

Fig. 1 shows the schematic illustration for the fabrication of the ZIF-90 bonded capillary. ZIF-90 crystals were prepared from imidazolate-2-carboxyaldehyde and $Zn(NO_3)_2{\cdot}6H_2O$ at room temperature according to Thompson et al. [31]. The good agreement between the experimental and the simulated XRD patterns shows