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Metal-organic framework MIL-100(Fe) as the stationary phase for both normal-phase and reverse-phase high performance liquid chromatography

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ABSTRACT

Metal-organic framework MIL-100(Fe) was explored as a novel stationary phase for both normal-phase and reverse-phase high performance liquid chromatography. Two groups of analytes (benzene, toluene, ethylbenzene, naphthalene and 1-chloronaphthalene; aniline, acetanilide, 2-nitroaniline and 1-naphthylamine) were used to test the separation performance of MIL-100(Fe) in the reverse-phase mode, while the isomers of chloroaniline or toluidine were employed to evaluate its performance in the normal-phase mode. The MIL-100(Fe) packed column gave a baseline separation of all the tested analytes with good precision. The separation was controlled by negative enthalpy change and entropy change in the reverse-phase mode, but positive enthalpy change and entropy change in the normal-phase mode. The relative standard deviations of retention time, peak area, peak height, and half peak width for eleven replicate separations of the tested analytes were 0.2–0.7%, 0.5–3.6%, 0.6–2.3% and 0.8–1.7%, respectively. The mesoporous cages, accessible windows, excellent chemical and solvent stability, metal active sites and aromatic pore walls make MIL-100(Fe) a good candidate as a novel stationary phase for both normal-phase and reverse-phase high performance liquid chromatography.

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1. Introduction

The chromatographic column is the heart of a high performance liquid chromatography (HPLC) system. The availability of a stationary phase characteristic of high surface area, narrow size distribution, thermal and chemical stability and chemical modification is essential to prepare the column with good reproducibility and high column efficiency [1]. Although there are great varieties of traditional chromatographic stationary phases, novel stationary phases are still required for diverse applications of normal-phase (NP) and reverse-phase (RP)-HPLC. In NP-HPLC, the stationary phase is more polar than the mobile phase, while the opposite for RP-HPLC. Therefore, the surface of the stationary phase for NP-HPLC should possess polar active groups, such as silica-based NP packings with –CH(OH)–CH_2OH or –NO_2 polar groups. For RP-HPLC, the stationary phases are made usually by covalently bonding an organosilane (for example, n-octadecysilane, trichloro(n-octyl)siliane) on the support surface to create hydrophobic packings. The polar active sites of NP stationary phase would irreversibly adsorb polar solvent used in RP-HPLC, while the hydrophobic groups of the RP stationary phase is unstable in the nonpolar or low polar mobile phase used in NP-HPLC. Therefore, it is usually difficult to use one stationary phase in both NP and RP modes.

Metal-organic frameworks (MOFs) are an emerging class of porous materials constructed from metal ion or cluster nodes and organic linkers [2]. The diverse structures and pore topologies, accessible cages and tunnels make MOFs attractive as potential stationary phases in capillary gas chromatography and HPLC [3–25]. The presence of polar groups (active metal sites) and hydrophobic groups (pore walls) consisting of aromatic rings stimulates the dual applications of MOFs as stationary phases in both NP-HPLC and RP-HPLC. However, not all the MOFs are applicable to both NP and RP chromatographic modes due to the stability problems with many MOFs in mobile phases used in RP-HPLC. Thus, previous studies on the utilization of MOFs for HPLC mainly focussed on NP mode [12–23]. Up to now, only two papers dealing with the application of MOFs for RP-HPLC have been published [24,25]. MIL-53(Al) with an appropriate particle size distribution and good solvent stability is the only MOF used as the stationary phase for both NP-HPLC and RP-HPLC separation [3,12,24]. In NP mode, MIL-53(Al) was explored as the stationary phase for HPLC separation of position isomers using hexane/dichloromethane (DCM) or DCM/methanol (MeOH) as the mobile phase [12]. In RP mode, the chromatographic column packed with MIL-53(Al) was assessed for HPLC separation of a wide range of analytes from non-polar to polar, and acidic to basic solutes [24].

Here we report MIL-100(Fe) as a novel stationary phase for HPLC in both NP and RP mode. MIL-100(Fe), based on μ_3-oxo-centered

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trimers of Fe^{III} octahedra, is a crystalline three-dimensional iron(III) trimesate, and possesses two-types of mesoporous cages (25 and 29 Å), accessible windows (5 and 9 Å) (Fig. S1 in Supplementary Data), excellent chemical and solvent stability, metal active sites and aromatic pore walls [26], making it a good candidate as the stationary phase for HPLC separation both in NP and RP modes.

In this work, the slurry-packed MIL-100(Fe) column was first investigated for RP-HPLC separation using MeOH/H_2O as the mobile phase. As the staple targets for evaluating the separation mechanism of RP-HPLC, two groups of analytes (benzene, toluene, ethylbenzene, naphthalene and 1-chloronaphthalene; aniline, acetanilide, 2-nitroaniline and 1-naphthylamine) were tested [27]. As the markers of false positive or negative detection, chloroaniline and toluidine isomers were used to investigate the performance of MIL-100(Fe) packed column for NP-HPLC. The isomers of chloroaniline and toluidine are also widely used as important intermediates in the production of insecticides or other pesticides [28–30]. Selective separation of these isomers is of great significance and high value. The MIL-100(Fe) column offered a baseline separation of all the tested analytes with good precision, underlining the potential of MIL-100(Fe) for dual applications in both NP and RP-HPLC.

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents used were at least of analytical grade. Ultrapure water (18.2 MΩ cm) was obtained from a Water-Pro Water Purification System (Labconco Corp., Kansas City, MO, USA). Iron powder, trimesic acid (1,3,5-BTC), hydrofluoric acid (40.0%), naphthalene, 1-chloronaphthalene, aniline, acetanilide, 2-nitroaniline and 1-naphthylamine, chloroaniline and toluidine isomers were purchased from Shanghai Aladdin Chemistry Co., Ltd., (Shanghai, China). Nitric acid (65–68%) was purchased from Tianjin Chemical Reagent No. 5 Plant (Tianjin, China). Benzene, toluene and ethylbenzene were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China). DCM and MeOH were purchased from Concord Fine Chemical Research Institute (Tianjin, China).

2.2. Instrumentation

D/max-2500 diffractometer (Rigaku, Japan) using $Cu_{K\alpha}$ radiation (λ = 1.5418 Å) was used to obtain the X-ray diffraction (XRD) patterns. The thermal gravimetric analysis (TGA) was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 800 °C at a ramp rate of 8 °C min^{-1}. The scanning electron microscopy (SEM) images were collected on a Shimadzu SS-550 scanning electron microscope at 15.0 kV. A NOVA 2000e surface area and pore size analyzer (Quantachrome, Florida, FL, USA) was used to measure the Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size distribution of the synthesized MIL-100(Fe) at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$. The Barrett–Joyner–Halenda (BJH) method was used to calculate the mesopore distribution. Particle size distribution was measured on the Mastersizer 2000 particle size analyzer (Malvern, UK) with water as dispersant.

All HPLC separations were performed on a chromatographic system consisting of a Waters 510 HPLC pump and a 486 tunable absorbance detector. Data acquisition and processing were carried out on a N2000 chromatography data system. The Ameritech CO-5060 column heater was used to control the column temperature during HPLC separation.

2.3. Synthesis and activation of MIL-100(Fe)

MIL-100(Fe) was synthesized under hydrothermal conditions according to Férey et al. [31]. Typically, 687.5 mg 1,3,5-BTC, 277.5 mg iron powder, 200 μL hydrofluoric acid and 190 μL concentrated nitric acid were mixed with 25 mL ultrapure water in a Teflon-lined bomb (1.0 Fe:0.67 1,3,5-BTC:2.0 HF:0.6 HNO_3:277 H_2O). The bomb was then sealed, placed in an oven and heated at 150 °C for 12 h. The light orange solid product was obtained by filtration and washing with ultrapure water. The as-synthesized MIL-100(Fe) was further purified by a two-step procedure using hot water and ethanol. To remove the residual unreacted substances, the solid was immersed into water at 80 °C for 5 h and subsequently hot ethanol at 60 °C for 3 h until no colored impurities in the mother liquor solution were detected. The highly purified MIL-100(Fe) was evacuated in vacuum at 150 °C for 12 h to form activated MIL-100(Fe).

2.4. Preparation of MIL-100(Fe) packed column for RP and NP-HPLC

1.30 g of MIL-100(Fe) was dispersed in 50 mL DCM under ultrasonication for 5 min. The suspension was then downward packed into a stainless steel column (5 cm long × 4.6 mm i.d.) under 6000 psi for 10 min. The stationary phase was kept intact by the stainless steel frits with a pore size of 1 μm. The packed column was conditioned with MeOH at a flow of 0.5 mL min^{-1} for 1 h for RP-HPLC experiments or with DCM at a flow of 0.5 mL min^{-1} for 1 h for NP-HPLC experiments.

2.5. Calculation of the thermodynamic parameters

The Gibbs free energy change (ΔG, kJ mol^{-1}), enthalpy change (ΔH, kJ mol^{-1}) and entropy change (ΔS, J mol^{-1} K^{-1}) [32] for the transfer of the analytes from the mobile phase to the stationary phase MIL-100(Fe) were measured at six different temperatures in the range of 25–75 °C under RP mode and 20–35 °C under NP mode. During the HPLC separation, the mobile phase was preheated to the same temperature as the column in a water bath. ΔG, ΔH, and ΔS were calculated according to the van't Hoff equation (Eqs. (1) and (2)).

$$\ln k' = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} + \ln \Phi \quad (1)$$

$$\Delta G = \Delta H - T\,\Delta S \quad (2)$$

where k' is the retention factor, R is the gas constant, T is the absolute temperature and Φ is the phase ratio. k' was calculated according to Eq. (3):

$$k' = \frac{t - t_0}{t_0} \quad (3)$$

where t is the retention time and the t_0 is the column void time which was determined by injecting a small plug of hexane in NP mode or thiourea in RP mode and recording the perturbation signals. Φ was calculated according to Eq. (4):

$$\Phi = \frac{V_S}{V_0} \quad (4)$$

where V_S, the volume of the stationary phase in the column, was calculated based on Eq. (5), while V_0, the void volume of the column, was evaluated according to Eq. (6).

$$V_S = V_{Col} - V_0 \quad (5)$$

$$V_0 = t_0 \times F \quad (6)$$

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