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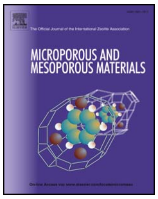

MOF@SiO_2 core-shell composites as stationary phase in high performance liquid chromatography

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ABSTRACT

Mesoporous silica spheres were functionalized with microporous metal-organic frameworks (MOFs), namely MIL-101(Fe)_NH_2 ($Fe_3(O)(BDC\_NH_2)_3(OH)(H_2O)_2$, BDC = benzene-1,4–dicarboxylate) and UiO-67 ($Zr_6O_4(OH)_4(BPDC)_6$, BPDC = 4,4′-biphenyldicarboxylate) to produce core-shell particles for application as stationary phase in high performance liquid chromatography (HPLC) columns using a layer-by-layer method. The composites were studied for application as stationary phase in normal phase HPLC for separation of C_8-isomers, dichlorobenzene isomers, styrene and ethylbenzene. Both silica/MOF composites show the highest affinity towards the *ortho* substituted analytes, indicating that the selectivity is dominated by the polarity of the analytes. Moreover, the UiO-67@SiO_2 composite shows high separation efficiency in the separation of dimethyl phthalate and diethyl phthalate, since the number of theoretical plates per meter is very high (37570 m^{-1}).

1. Introduction

Metal-organic frameworks are modular porous materials with high potential in applications such as gas storage or catalysis, but in recent years, they have also attracted interest as stationary phase in separation technologies. Nowadays there are several examples for the successful implementation of various MOFs as stationary phase in gas chromatography (GC) or thin-layer chromatography (TLC) [1–5]. However, in addition to analytical separation problems which are often solved by using GC a lot of industrial relevant separation problems have a preparative character. A common example is the separation of substituted aromatic isomers. High performance liquid chromatography (HPLC) is the most commonly used technique to counter these challenges. Although, there are numerous different materials usually applied as stationary phase in HPLC columns, in recent years a great effort has been made to find new, more efficient adsorbents [6,7]. The potential of the MOFs for HPLC applications was recognized quite early, but in the most initial studies the MOFs were used as crystalline powder resulting in high column backpressure, low column efficiency, and undesirable peak shape [8]. One possibility to overcome these challenges is to use silica spheres as template material [9]. Such MOF@silica composites could combine both the outstanding packing characteristics of the silica spheres and the specific influence of the used MOF material.

One possibility to produce MOF-silica particles is the liquid phase epitaxy method widely used by Wöll and co-workers [10–12]. In this contribution a dip coating approach was used which could be easily automatized. Two chemically different MOF materials with varying porosity MIL-101(Fe)_NH_2 (MIL – Matérial Institute Lavoisier) and UiO-67 (UiO - Universitetet i Oslo) were used to obtain silica/MOF composites and to get a deeper insight into the separation behavior of a polar MOF (MIL) and a non-polar MOF (UiO-67) in the NP-HPLC. The resulting materials were studied for application in normal phase HPLC (NP-HPLC).

The MIL-101(Fe) has a cubic structure with pores of different size (29–34 Å) and large pore volume. The trimeric clusters are bridged by terephthalate anions (BDC^{2-}) to build a super tetrahedron (ST). Each metal ion is located in an octahedral environment with four oxygen atoms of the bidentate linker, a μ_3-oxygen atom, and, depending on the synthesis route, with an oxygen coming from the solvent, water or fluoride [13]. A post synthetic removal of these can lead to coordinatively unsaturated sites (CUS) [14] which act as soft Lewis acid [15] and therefore introduce a certain polarity into the framework [16]. The UiO-67 consists of 4,4′-biphenyldicarboxylate ($BPDC^{2-}$) as linker and $Zr_6O_4OH_4$ as cluster [17]. Due to the high coordination number of the cluster (12) and strong Zr-O bonds, UiO-67 has outstanding thermal and chemical stability. It has two different pore types: octahedral one (d = 16 Å) surrounded by 8 tetrahedral (d = 12 Å) pores. Ideally, the UiO-67 does not have any open metal sites, however, if a modulator is

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used in the synthesis some defects are generated which results in both a higher surface area and pore volume, and open metal sites [18].

To adopt these MOFs as a stationary phase of a HPLC column, commercially available silica spheres, optimized for HPLC applications, were coated with a MOF of interest to obtain core-shell particles. For coating, a layer-by-layer (lbl) method was chosen to ensure a homogenous surface modification whilst the monodispersity of the silica particles is maintained.

To investigate the separation efficiency of the obtained MOFs@SiO_2 composites several separation experiments were carried out. One of the most challenging separation problem investigated, was the separation of C8-isomers (*ortho*-, *meta*-, *para*-xylene and ethyl benzene) since all compounds have very similar boiling points [19]. On an industry level this separation is performed on cation-exchanged zeolites, however adsorbents with higher separation efficiency are still needed [20,21].

2. Experimental details

2.1. Materials and chemicals

The silica spheres (NUCLEOSIL® 100-3) were purchased from MACHERREY-Nagel (Germany). The spheres have a diameter of 3 µm and the pores of 10 nm. According to the supplier's information, the surface of the particles should be non-modified, but FTIR measurements (see ESI) have proven the presence of carboxylate groups on the surface.

All chemicals were used as purchased without further purification. Solvents used for synthesis (p.a.) and for HPLC measurements (HPLC grade) were used as purchased.

2.2. Modification of silica with MIL-101(Fe)_ NH_2 (1): synthesis of 1@SiO_2

The silica particles (500 mg) were modified using a layer-by-layer (lbl) method comprising different numbers of cycles. First, the particles were dried under reduced pressure at 373 K over night to remove water traces on the surface. After that, Fe^{3+} ions were immobilized on the surface. Therefore, the particles were stirred in 10 mL of a 5 mM solution of $FeCl_3$ in EtOH for 15 min at room temperature. The supernatant solution was removed by suction and the resulting powder was washed with EtOH and *N,N*-dimethylformamide (DMF). To finish a cycle, the spheres were suspended in 10 mL of a 5 mM solution of 2-aminoterephthalic acid in DMF for 30 min at 120 °C. The supernatant was removed by suction and the particles were washed with DMF and EtOH consecutively. The procedure was repeated several times. After reaching the desired amount of cycles the modified particles were washed several times with EtOH (abs.) and dried overnight under reduced pressure.

2.3. Modification of silica with UiO-67 (2): synthesis of 2@SiO_2

The functionalization of the silica particles with UiO-67 was carried out according to the procedure described for MIL-101. As Zr^{4+} source $ZrCl_4$ (2.5 mmol) dissolved in 500 mL EtOH was used. The organic linker biphenyl-4,4′-dicarboxylic acid (2.5 mmol, H_2BPDC) and the modulator benzoic acid (50 mmol) were dissolved in 500 mL DMF.

2.4. MOF synthesis

2.4.1. MIL-101(Fe)_NH_2

Typically, 2-aminoterephthalic acid (135 mg, 1.08 mmol) was dissolved in 13 mL DMF in a 25 mL Schott bottle and $FeCl_3 \cdot 6H_2O$ (582 mg, 2.16 mmol, 2 eq.) was added. After 72 h heating at 120 °C, the red-brownish solution was filtered over a G4 frit and precipitate was washed with EtOH and DMF. The resulting solid was stirred in EtOH at 80 °C overnight. The solid was again separated by suction and washed with EtOH before the resulting powder was dried at reduced pressure over night.

2.4.2. UiO-67

Typically, $ZrCl_4$ (30 mg, 0.13 mmol) and benzoic acid (0.289 g, 2.6 mmol, 20 eq.) were dissolved in 5 mL DMF. To the resulting clear solution H_2BPDC (31 mg, 0.13 mmol, 1 eq.) was added. The milky solution was tempered at 120 °C for 48 h. Subsequently the colorless crystals were washed with DMF and EtOH and dried under reduced pressure over night.

2.5. Material characterization

The degree of surface modification of the silica spheres was examined by scanning electron microscopy (SEM) using the measurement systems SU 8020 from HITACHI. For nitrogen physisorption measurements at 77 K a Belsorp Max from MicrotracBEL Corp. (Japan) was used. Prior the measurements, the materials were activated at room temperature for at least 12 h. Fourier transformed infrared (FTIR) spectra were measured using a Vertex 70 from BRUKER in the range of 600–4000 cm^{-1} with a resolution of 2 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were collected on a Stoe StadiP diffractometer in transmission geometry. The flat sample was irradiated with CuK_α radiation ($\lambda = 1.5405$ Å). HPLC measurements were performed on an ELITE LACHROM System from VWR/HITACHI using a UV L2400 detector. For data evaluation EZCHROM ELITE software from AGILENT TECHNOLOGIES was applied.

2.6. Packing of HPLC columns and HPLC experiments

The columns were packed by the GOEHLER HPLC-ANALYSENTECHNIK located in Chemnitz, Germany. Before sending the core-shell particles, the material was sedimented in ethanol to remove smaller particles and activated under reduced pressure over night. The dried hybrid material was suspended in isooctane and packed in a down flow into a stainless-steel column (250 mm × 3 mm i.d.) under 600 bar for 60 min. Column evaluation was carried out by using the integrated software. All HPLC measurements were carried out at room temperature using a flow of 0.5 mL/min and UV/Vis detection at 265 nm.

3. Results and discussion

3.1. Characterization of core-shell particles

To achieve homogenous MOF coverage of the spheres, the layer-by-layer method was applied. First of all, the dependence of the MOF layer thickness (MOF loading) on the number of performed synthetic cycles was studied. Therefore, the obtained composite was investigated with PXRD, N_2 physisorption and SEM after every 5 cycles. Corresponding to the PXRD data, (see Figs. S1 and S5 ESI), the reflections of the MOFs could be observed only after 20 coating cycles for MIL-101 and after 15 cycles for UiO-67, corresponding to a loading higher than ca. 5 wt%. The filling of silica mesopores with microporous MOF could be followed by nitrogen physisorption, since the shape of the isotherm characteristic for the pure mesoporous silica changes (Figs. S2, S3, S6 ESI). SEM images (Figs. 1 and S4, S7 ESI) show that the surface is homogenously coated with MOF crystals when the number of cycles is increased, so the surface becomes smooth and homogenous after 20 cycles for both silica/MOF composites.

For further investigation, the composites obtained after 20 cycles for MIL-101(Fe)_NH_2@SiO_2 (**1**@SiO_2) and 18 cycles for UiO-67@SiO_2 (**2**@SiO_2), respectively, were used, since these materials show on the one hand the best surface functionalization degree according to the SEM and PXRD (Fig. 2c) and at the same time micro- and mesoporosity. SEM pictures show that after 18 (for **2**) and 20 (for 1) synthetic cycles the surface of the particles is homogenously coated without any MOF