Chromatographic separation through confinement in nanocages

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ABSTRACT

Porous materials such as metal-organic frameworks offer great potential for separation technologies. Over the past decade the synthesis of a large number of new structures has been reported but relatively little attention has been given to the application of these novel adsorbents as stationary phases in gas or liquid chromatography. In this work, we report on the potential of the metal-organic framework UiO-66 for the separation of cyclic isomers. The extremely high preferential retention of cyclic hydrocarbons of the aromatic's and functionalized cycloalkane's type is exploited to achieve difficult separations. Confinement effects play a crucial role in fine-tuning the adsorbent's properties.

1. Introduction

Metal-organic frameworks (MOFs) have received interest in modern analytical chemistry for the use of this novel advanced class of microporous crystalline materials as stationary phase in chromatography. Because of their unique properties, such as a uniform pore size distribution, an ordered pore structure and more variable pore functionality in comparison with the conventional (functionalized) silica or alumina stationary phases, they look promising as a chromatographic separation medium in analytical applications. Due to their hybrid inorganic–organic character, MOF-based stationary phases show different interactions with the analytes, opening more possibilities to separate different mixtures. Several MOFs, such as MOF-5 (or IRMOF-1) [1–3], IRMOF-3 [2], ZIF-8 [3,4], MOF-508 [5], CUK-1 [6], MIL-100(Cr/Fe) [7], MIL-101(Cr) [3,8], MOF-CJ3 [9], UiO-66 [10], JUC-110 [11], a charge-polarized MOF [12], HKUST-1 (or [Cu₃(BTC)₂]) [13] and homochiral MOFs ([Cu(sala)]n[14] and D-camphoric acid based MOFs [15,16]), were successful tested as a stationary phase in gas chromatography (GC). Mostly, MOF crystals were deposited on the inner layer wall of a capillary column to fabricate the so-called PLOT columns (porous layer open tubular) [1–4,7–10,13–16] with the intention to obtain high-resolution GC separation(s) of target analytes in complex samples. These MOF-coated capillaries overcome the poor resolution on MOF packed GC columns due to significant diffusion

resistance of the bulky packing [2,4,8]. Important targets in industry and environmental sciences (alkane and aromatic positional isomers) were chosen as analytes. For example the separation of linear alkanes from branched isomers is a very important process in the petroleum refining industry, including the improvement of the gasoline octane number [17–22]. ZIF-8 showed strong power to sieve linear alkanes from branched alkanes owing to the narrow pore windows (∼3.4 Å) [3,4], while MOF-5 [3], MOF-508 [5] and MIL-100(Cr/Fe) [7] follow the order of the boiling points. The MIL-100(Fe) coated capillary column yields even better results for the separation of C6–C7 alkane isomers than the commercial GC-Gaspro and HP-5MS capillary columns, while the MIL-100(Cr) coated capillary gave a poor separation performance. Stronger energetic interactions between the alkanes and MIL-100(Cr) and loss of more freedom during separation lead to longer retention times, tailing chromatographic peaks and lower resolution on the Cr(III) variant [7]. Although MOF-CJ3 [9] does not display a molecular sieving effect, isooctane (bp: 372.2 K) elutes earlier than n-heptane (bp: 371.4 K) which is not in agreement with their boiling point. Probably supramolecular interactions (mainly CH–π interactions) with alkanes are involved, where the benzene rings are almost parallel to the pore direction, which favors these supramolecular interactions. Unlike MOF-5, MOF-508 and MIL-100(Cr/Fe), branched C6 isomers are more strongly retained in UiO-66 than their linear ones [10]. Its specific structure displays reverse shape selectivity, which means that the adsorption of these alkane molecules is dictated by their rotational freedom inside the small cavities [23]. The selectivity for the GC separation of lin-

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ear alkanes on MOF-5 [1], ZIF-8 [4], MOF-508 [5], MOF-CJ3 [9] and UiO-66 [10] mainly arises from the van der Waals interactions between the linear alkanes and the hydrophobic inner surfaces of their micropores. For the separation of more bulky molecules, such as substituted aromatics, the need for frameworks with appropriate pore windows is required. Therefore, MOF-5 (11.2 Å) [2], IRMOF-3 (9.6 Å) [2], MIL-101 (14 Å and 16 Å) [8], MOF-CJ3 (11.6 Å × 11.6 Å) [9] and UiO-66 (5–7 Å) [10] were used as stationary phase for these separations. Only MIL-101(Cr) [8], UiO-66 [10] and HKUST-1 [13] offered baseline separation for the separation of xylene isomers and ethylbenzene. An elution order of p-xylene, m-xylene, ethylbenzene and o-xylene was obtained for MIL-101(Cr) and UiO-66, while HKUST-1 gave m-xylene stronger retention than p-xylene, ethylbenzene and o-xylene. The IRMOF-coated capillaries have been applied for successful high-resolution GC separation of polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs) and hexachlorocyclohexanes (HCHs) [2].

Up to now, a large number of MOFs, like MOF-5 [24], HKUST-1 [24,25], MIL-47(V) [25–28], MIL-53(Al/Fe) [25,28–32], MIL-100(Fe) [32,33], MIL-101(Cr) [32,34,35], MIL-125(Ti) [36], MIL-125(Ti)-NH2 [37], and a mesoporous Cd MOF ((Cd(abdc)(bpy)) [38] and even homochiral MOFs, in particular a Zn-organic framework [39] and a chiral analoque of UMCM-1 (Bn-ChirUMCM-1) [40], have been shown to be promising as a stationary phase in high-performance liquid chromatography (HPLC) in the form of powder packed columns. Remarkable results are achieved for the separation of relative "small" molecules, compared with the typical analytes in HPLC applications (e.g. peptides or protein digests). In liquid phase, the separation of substituted aromatics on MOFs has been studied by several authors: difunctionalized benzene homologues (e.g. position isomers of xylene [27,29–31,35–37], ethyltoluene [27,29,37], cymene [29,37], dichlorobenzene [25,27,30,35], chlorotoluene [30,35], chloroaniline [32,33], toluidine [27,32,33], cresol [27], nitrophenol [30], nitroaniline [32] and aminophenol [32]), alkylnaphthalenes [25] and very large polycyclic organic molecules (e.g. polyaromatic hydrocarbons [24] and organic dye mixtures [38]) were used as probe molecules. In most cases, columns packed with MOF crystals result in relative high pressure drops, pronounced peak broadening and unsatisfactory performance due to the non-spherical, irregular shape and the polydispersity of these MOF particles. To circumvent high pressure drops, single-pulse experiments were performed on columns packed with pellets, using MIL-53(Al) [41] and UiO-66 [42] as adsorbent for the separation of xylene isomers. Use of pellets in analytical chromatography however decreases the resolution of the separation dramatically. Hybrid column packing materials [43–46], such as silica-MOF composites [43–45], hold great promise as separation medium for chromatographic separations. They combine the good packing quality properties of silica with the separation ability of the MOF material. The first silica-MOF composite was synthesized by Ameloot et al. [43], where the authors proposed a new synthesis method for the formation of HKUST-1 inside the mesopores of the silica beads, leading to the formation of monodisperse silica-MOF composite spheres. Another possibility to reduce these frequently occurring shortcomings of MOF-packed columns is the use of capillary liquid chromatography (cap LC), as was already demonstrated in our previous work on the flexible framework MIL-53(Al) [47]. As an alternative for a particulate packed bed, Huang et al. [46] developed a MOF-polymer monolith as stationary phase in cap LC with MIL-101(Cr) as adsorbent. More recently, enantiomeric separation using homochiral MOFs became an important research subject in gas and liquid chromatography [14–16,39,40,44]. Another kind of stereoisomer separation relates to the separation of cis/trans mixtures, which is rarely explored in MOFs. HKUST-1 [25] and MIL-96(Al) [48] were able to make a distinction between cis and trans isomers of mono- and di-olefins (piperylenes), respectively.

In this work, we investigated the potential of the UiO-66 metal-organic framework as chromatographic stationary phase. UiO-66 was originally reported by Cavka et al. in their work on the synthesis of the isostructural Zr-MOF series UiO-66, UiO-67 and UiO-68 materials, based on the inorganic brick $Zr_6O_4(OH)_4$ and 1,4-benzene-dicarboxylate (BDC) as organic linker for UiO-66 [49]. The complex structure consists of a small tetrahedral (~7.5 Å) and a large octahedral (~11 Å) cage. The complex structure was elucidated by a combination of XRD, NMR, vibration spectroscopy and computational optimizations [50]. The average number of BDC-X linkers is typically 8–10 and not the theoretical achievable 12. The UiO-66 framework shows remarkable thermal (up till 648 K), chemical (organic solvents, water, strong acid and base conditions) and mechanical stability [49–51]. The UiO-66 framework was evaluated for gas based applications (H_2, CH_4, CO_2) [52–65], water adsorption [51,62,66] and hydrocarbon separation [23,42,67,68] by several groups. Previously Chang and Yan reported on the use of UiO-66 as a stationary phase in capillary GC for the separation of C6, xylene and propylbenzene isomers [10]. Here we report on the application of the zirconium metal-organic framework for packed bed columns in gas and liquid phase for shape selective separations by exploiting confinement effects.

2. Experimental

2.1. Synthesis

UiO-66. and functionalized variants (UiO-66-Me and UiO-66-NO$_2$) were synthesized according to published methods [69–71]. Structure was verified by XRD (Fig. S1). Chromatographic experiments were performed for a set of probe molecules, listed in Table 1.

2.2. Inverse pulse gas chromatography

Adsorption equilibrium Henry constants were calculated from the first order moment of the chromatographic response curves in the range of 473–573 K for UiO-66, 473–573 K for UiO-66-Me and 473–553 K for UiO-66-NO$_2$ using the gas phase inverse pulse chromatographic method. The UiO-66 material was pelletized and packed in 30 cm, 1/8 inch steel columns; UiO-66 (501 mg), UiO-66-Me (458 mg) and UiO-66-NO$_2$ (532 mg). It was shown that the experiments were performed in the linear part of the isotherm by injecting different amounts (Fig. S2). Absence of diffusion limitations was confirmed by using different carrier flow rates. A detailed explanation of the experimental setup and procedure was previously reported [29].

2.3. High-performance liquid chromatography

A 10 wt% slurry of the stationary phase was prepared in an appropriate solvent (UiO-66 in water and UiO-66-Me in ethanol) by sonication in an ultrasonically agitated reservoir. Using a slurry packer, stainless steel columns (for UiO-66: length 100 mm, inner diameter 2.1 mm; for UiO-66-Me: length 50 mm, inner diameter 2.1 mm) were packed and allowed to settle at 400 bar for a few hours. Afterwards the columns were flushed with acetonitrile (ACN). HPLC experiments were performed with an Agilent Technologies 1100 series apparatus with different mobile phase compositions (based on volumetric fractions) of ACN and methanol (MeOH). Diluted solutions of the analytes with a concentration of 10 v% were injected (injection volume: 2 μl for UiO-66 and 0.5 μl for UiO-66-Me) and UV absorption at 254 nm or RID was moni-