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Short communication

On the general water harvesting capability of metal-organic frameworks under well-defined climatic conditions

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ABSTRACT

The ability of some highly porous materials to adsorb and desorb water vapor under atmospheric conditions without the use of external power sources could become a promising methodology for the capture and release of water in arid or desert regions of the world.

Here, the use of some readily available metal-organic frameworks as water harvesting materials has been tested and compared with other porous materials. Water adsorption experiments were conducted at 25 °C and at a relative humidity (RH) of 40%, while the desorption process took place at 45 °C with a RH of 10%. These experimental conditions are in good accordance with the climatic conditions being present in the Sahara desert during the summer season.

In all experiments, UiO-66 derived MOFs showed the best water harvesting efficiency, releasing up to 89% of the adsorbed water at 45 °C and 99% at 60 °C. Though, the adsorption capacity of UiO-66 is noticeably lower than that of more hydrophilic materials such as the MOF compound HKUST-1 and the zeolite A3. The latter, however, are only able to release water when they are heated up to at least 60 °C.

Finally, the stability of the investigated MOFs after adsorption-desorption cycles have been confirmed through XRD and FT-IR analyses.

1. Introduction

The capture of water vapor raised a considerable attention in the last years due to the increasing water shortages [1]. From this perspective, materials that are able to reversibly adsorb and desorb water – as they have been developed for clean energy applications such as adsorption heat pumps – are extremely interesting [2–4]. However, the concept of harvesting water from atmospheric humidity has been already developed by nature in geographical areas where the water availability is extremely limited. For example, the Namib Desert beetle is able to collect water from the morning fog with high efficiency [5,6].

For technical applications, the development and manufacturing of materials that can deliberately adsorb water from the air and desorb it under opportune conditions may greatly contribute to the delivery of water in arid and desert areas [7]. Several scientific works have been already reported and different materials have been tested [8–14], However, the performances achieved so far are not yet satisfactory and some fundamental research is still needed. In particular materials which allow a higher working capacity, in terms of amount of harvested water per mass of adsorbent, should be introduced. In this context metal-organic frameworks (MOFs) have the potential to provide a remarkable contribution to this research field [15–17]. Until now several MOFs have been already investigated as potential adsorbents for cycling heat transformation processes. Within these works the stability over several hundreds of cycles has been tested [18–21].

MOFs are porous crystalline materials constituted from organic and inorganic building blocks with exceptional surface area (up to 7000 m^2/g) which can, theoretically, host a considerable amount of water within their pores [22–24]. Additionally, by tailor-made synthesis or post-synthetic modifications the properties of MOFs can be fine-tuned preparing materials with defined porosity and affinity to water [25–27]. Some preliminary studies have already proved that MOFs could potentially be used to deliver drinking water in arid areas. Yaghi et al. recently define the three fundamental properties that a material must own in order to be suitable for such applications [28]. Firstly, the condensation of water within the pores of the material must take place at low relative humidity and exhibit a steep uptake behavior. The second property concerns the total uptake capacity, which must be obviously very high to

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ensure the delivery of a considerable amount of water. The last criterion is the recyclability of the material and its water stability [29]. Many MOF materials fulfill the second criterion, while they fail in the first and third one. Several MOFs adsorb water only at a high relative humidity or they only release it at very high temperatures. Other MOFs are not stable against humidity, compromising their implementation in a process that is supposed to be continuously repeated.

The mechanism of water physisorption has been studied for several MOFs. At low water pressure, the water molecules are adsorbed through H-bonding, whereas upon increasing of pressure, more water molecules get confined in the cavity by forming new hydrogen bonds with several of the adsorbed molecules at the primary binding sites. Such further adsorbed molecules provide additional binding sites to facilitate the adsorption in the larger cavities and subsequent water condensation in the framework. This physisorption mechanism seems to be somewhat similar to those known from activated porous carbons for which surface water molecules first adsorb onto oxygenated/hydroxylated surface sites. These adsorbed water molecules then act as nucleation sites for the formation of larger water clusters. Eventually, these clusters connect either along the surface or across the pore, leading to pore filling [16].

Adsorbents with larger pores are associated with pore condensation phenomena that lead to hysteresis during desorption cycles and therefore pose a hurdle in the efficient water harvesting from the atmosphere [16].

Several Zr-MOFs have shown good water adsorption capacity, like for example MOF-808 and UiO-66 [28]. Moreover, this capacity can be further enhanced by tailored modifications on the porous materials, for example by increasing the hydrophilicity of the MOF with the introduction of hydroxyl groups into the organic linker molecules [30]. Similarly the presence of some coordination defects in UiO-66 has been associated with a higher water uptake [31,32]. Nevertheless, a hydrophilic material will be inclined to hold water molecules also at higher temperatures, compromising the possibility to use it in a real application scenario. Additionally, the presence of coordinative unsaturated sites (*cus*) in the framework facilitates adsorption on metallic clusters as they modify the first coordination sphere of the metal ion (chemisorption). Chemisorbed water molecules can be only desorbed at high temperatures (≈ 200 °C) thus preventing the use of *cus* containing MOFs as water harvesting materials, at least for the here discussed scenarios [16].

MOF-841 (another Zr containing MOF substance) delivered so far the best performance in terms of reversible water uptake and release. However, its preparation is still too demanding (time, cost of reagents, reproducibility) to anticipate a rapid technological implementation [28].

The potential of MOFs for the collection of atmospheric water has been confirmed by several studies, measuring adsorption/desorption isotherms in laboratory environment and under controlled atmosphere. However, these results have not been validated yet under realistic environmental and climatic conditions. Therefore, in this work the reversible collection and release of atmospheric water is presented employing MOFs and other highly porous materials in a simulated desert environment realized by climatic chambers.

2. Experimental

2.1. Materials and methods

Chemicals and solvents were analytical grade, except methanol which was technical grade (98%), purchased from various commercial suppliers and used without further purification: Basolites® A100 (Aluminum terephthalate), C300 (Copper benzene-1,3,5-tricarboxylate), F300 (Iron 1,3,5-benzenetricarboxylate), Z1200 (2-Methylimidazole zinc salt), Basosiv™ M050 (Magnesium formate) and 4 Å Molecular Sieves were purchased from Sigma-Aldrich; UiO-66 (Zirconium terephthalate) was purchased from STREM Chem; HBea (Si/Al = 75) was purchased from Clariant; Zeolite A3 was purchased from ZeoTech.

Powder diffraction measurements were performed on a Bragg-Brentano Diffractometer, D8 Advance from Bruker AXS, equipped with copper tube, 2.5° Soller collimators, 0.3 mm divergence slit, anti-scatter screen, flip-stick stage and silicon strip detector (LynxEye) with 3° 2θ detector opening. The diffraction patterns were monitored between 5° and 65° 2θ with 0.06° 2θ step width and 3s counting time per step. Crystallite sizes were determined by Rietveld-Analysis.

IR spectra were recorded between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1} accumulating 64 scans using a diamond ATR/FT-IR spectrometer (Thermo Nicolet 6700; ATR-Durascope) with a MCT detector.

Nitrogen adsorption isotherms were measured at −77 K using a Quantachrome NOVA2000e surface area analyser. Samples were degased under vacuum for 5 h at 90 °C prior to the analysis. Relative pressure range varied between $1 \cdot 10^{-1}$ and $1 \cdot 10^{-3}$ p/p_0 for adsorption measurements.

Meteorological simulations were performed in a KS 1000/45 RS-Simulator Climate Chamber (inner volume of 565 L) varying temperature (25–60 °C) and relative humidity (10–40%).

2.2. Synthesis of H_2N-UiO-66 [33]

$ZrCl_4$ (0.634 g; 2.7 mmol) is suspended in DMF (25 mL), concentrated HCl (5 mL) is added and the mixture is sonicated with ultrasound for some minutes, until it becomes clear. Benzene-1,4-dicarboxylic acid (0.338 g; 2.02 mmol) and 2-aminobenzene-1,4-dicarboxylic acid (0.124 g; 0.68 mmol) are dissolved in DMF (50 mL) and poured into the $ZrCl_4$ solution. The final mixture is stirred at 80 °C for 24 h. Afterwards the suspension is filtered off on a PTFE membrane filter; the recovered white solid is suspended in DMF and stirred at r.t. for 24 h. The solid is recovered by filtration, washed with DMF (4 × 20 mL), suspended and stirred at r.t. for 24 h in MeOH. After this the suspension is filtered off again, washed on a polypropylene membrane filter with MeOH (3 × 20 mL) and dried at air (700 mg; 92% yield).

2.3. Synthesis of BDC-SO_3H-Zr MOF [34]

$ZrCl_4$ (1.26 g; 5.4 mmol) is suspended in DMF (50 mL), acetic acid (15 mL) is added and the mixture is sonicated with ultrasound for some minutes, until it becomes clear. Benzene-1,4-dicarboxylic acid (1.00 g; 6.0 mmol) and monosodium-2-sulfobenzene-1,4-dicarboxylic acid ($NaSO_3BDC$) (0.40 g; 2.0 mmol) are dissolved in DMF (100 mL) and poured into the $ZrCl_4$ solution. The final mixture is stirred at 120 °C for 48 h. Afterwards the suspension is filtered off on a PTFE membrane filter; the recovered white solid is suspended in DMF and stirred at r.t. for 24 h. The solid is recovered by filtration, washed with DMF (4 × 20 mL), suspended and stirred at r.t. for 24 h in MeOH. After this the suspension is filtered off again, washed on a polypropylene membrane filter with MeOH (3 × 20 mL) and dried at air (1.67 g; 95% yield).

2.4. Climate simulation tests

The water adsorbing materials were dried at 200 °C under vacuum (10 mbar) for 72 h. In a typical experiment a glass bottle containing 1 g of dried adsorbing material was introduced into the