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Water sorption performance of the zeolitic metal azolate framework MAF-7

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Water sorption isotherms of $[Zn(tmz)_2]_n$ (MAF-7) were collected over a wide temperature range (15 – 45 °C) and its water sorption performance was assessed in terms of water uptake, sorption kinetics, recyclability, and regeneration temperature. Additionally, molecular simulations were conducted to elucidate the locations of water molecules within the pore cavity of MAF-7.

Water, H_2O, despite its chemical simplicity, is vital to all known forms of life. It is ubiquitous on earth in the form of atmospheric water vapor, although its distribution is geographically uneven. Water vapor in the air serves as a natural and self-supplementing water reservoir, with a total estimated amount of around 1.3×10^{13} ton, surpassing the combined volume of all the rivers on our planet (~2.1×10^{12} ton).[1] Nevertheless, relative humidity (RH), which represents the water vapor concentration, varies widely worldwide, ranging from as low as 10 % in arid regions to over 90 % in tropical regions. This variation impacts at least two societal demands: freshwater security and air dehumidification.[2,3] In desert regions, water scarcity arises due to insufficient rainfall, depletion of underground water resources, and distance from the sea, leading to a primary demand for freshwater security. Conversely, tropical regions experience a strong demand for air dehumidification.

The principle underlying potential solutions to address or mitigate these demands can be similar: extraction of water vapor from the atmosphere under different conditions. Atmospheric water harvesting in arid areas typically occurs under 30 % RH, while air dehumidification in tropical areas typically occurs above 60 % RH. Porous materials offer significant potential in water sorption-based applications.[4,5] However, it is crucial to evaluate the performance of these materials across the full range of RH levels, including water uptake, sorption kinetics, recyclability, regeneration temperature, in addition to synthesis costs. For instance, activated carbons and zeolites have been widely used as desiccants for many decades, particularly throughout the 20th century. However, they often suffer from either low water uptake, slow sorption kinetics or high regeneration temperatures.

Metal-organic frameworks (MOFs),[6-8] also known as porous coordination polymers/networks (PCPs/PCNs),[9-11] represent a diverse class of metal-organic materials (MOMs),[12,13] distinguished by their ordered structures, high surface area, tunable pore size/shape/chemistry, and modularity to crystal engineering or reticular chemistry.[14,15] MOFs have found extensive applications in gas storage, hydrocarbon separation, catalysis, sensing, drug delivery and more recently, water harvesting and air dehumidification.[16-24] Notably, the emergence of metal azolate frameworks (MAFs) or zeolitic imidazole frameworks (ZIFs) over the past two decades has introduced a variety of MOF materials with high hydrothermal stability, low synthesis cost, and diverse pore chemistry (e.g., hydrophobicity or hydrophilicity).[25-27]

Among MAFs/ZIFs, $[Zn(mim)_2]_n$, MAF-4/ZIF-8 (Hmim = 2-methylimidazole),[26,28] is one of the most extensively studied MOF materials, partly thanks to its hydrophobic nature that is desirable for gas storage and separation applications. Through pore surface engineering, where one N atom replaces the C-H in the Hmim ligand of MAF-4/ZIF-8, a different MOF material, $[Zn(tmz)_2]_n$, (MAF-7, Htmz = 3-methyl-1,2,4-triazole),[29,30] can be readily synthesized. The structure of MAF-7 (SOD topology) is analogous to that of MAF-4/ZIF-8, but MAF-7 exhibits stronger host-guest interactions due to the uncoordinated N atom in the linker ligand, which acts as a Lewis base active site for guest binding.[29-31] This property also renders MAF-7 hydrophilic, allowing it to adsorb up to 43 wt% of water.[29] Such characteristics make MAF-7 potentially useful for water sorption-based applications such as atmospheric water harvesting, air dehumidification or combination thereof.

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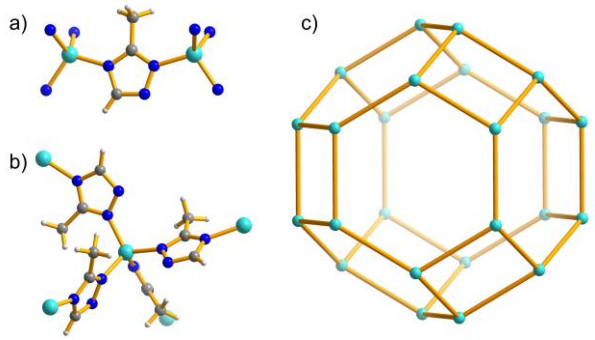

Fig. 1. a, b) Coordination geometry and c) skeleton of the secondary building unit of MAF-7. Zn: aqua, N: blue, C: grey, H: light grey.

However, to our knowledge, the water sorption performance of MAF-7 has not been thoroughly investigated, although a preliminary water sorption isotherm has been reported.[29] In this study, we examined the water sorption behaviour of MAF-7 across a broad temperature range and assessed its water uptake, sorption kinetics, recyclability, and regeneration temperature using dynamic water vapor sorption. Additionally, molecular simulations were conducted to elucidate the locations of water molecules within the pore cavity of MAF-7.

MAF-7 was synthesized following a method described in the literature,[30] with some modifications. 5 mmol of ZnO and 10 mmol of Htmz were dissolved in 10 mL of 25 % ammonia solution and stirred overnight at room temperature to yield MAF-7 (see the supporting information for details). The as-synthesized MAF-7 exhibits a regular polyhedral shape with a particle size range of 5 - 10 µm (Fig. S1). The bulk phase purity was confirmed by PXRD (Fig. S2). Thermogravimetric analysis (TGA) revealed 28.1 % of water loss at 80 °C and the structure remained thermally stable up to 300 °C (Fig. S3), sufficient for most practical applications. The crystal structure of MAF-7 is sustained by Zn(II) ions coordinated tetrahedrally to four tmz linker ligands (Fig. 1a,b), forming a tetrakaidekahedron (truncated octahedron) with 6 four-member rings and 8 six-member rings as the secondary building unit (Fig. 1c). Guest molecules may pass through the window of the six-member rings (d = 3.4 Å) and occupy the pore cavity (d = 11.2 Å). The cavity void is calculated to be around 51.7 % and the Langmuir surface area is approximately 1874 $m^2 g^{-1}$.[29]

The water vapor sorption isotherm collected at 25 °C is shown in Fig. 2, which is comparable yet with some differences to that reported previously.[29] The water uptake remains negligible (1.85 wt%) until 20 % RH, after which it increases dramatically up to 37.4 wt% at 35 % RH. It then gradually increases until reaching saturation at 95 % RH with a 43.1 wt% uptake, corresponding to 5.5 water molecules per unit formula or 66 water molecules per unit cell (Z value is 12). This overall trend is similar to that reported previously.[29] However, in our case, the water uptake can be fully desorbed at 1 % RH, whereas in the previous study,[29] 5.6 wt% of water uptake remained even at 0.5 % RH.

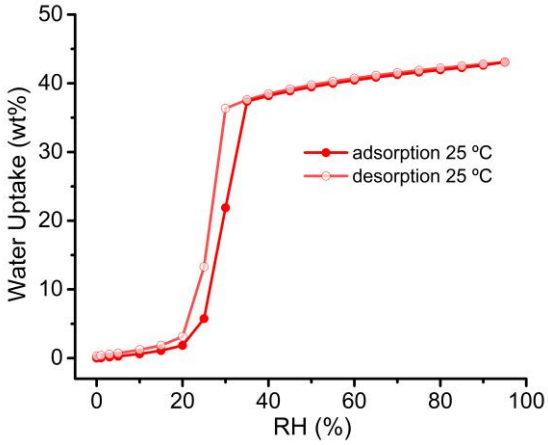

Fig. 2. Water vapor sorption isotherm (25 °C) for MAF-7.

To further investigate the water sorption behaviour of MAF-7, three additional water sorption isotherms were collected at temperatures both below and above 25 °C (Fig. S4). The saturation water uptake ranges from 45.1 wt% at 15 °C to 43.1 wt% at 25 °C, 42.0 wt% at 35 °C, and 39.4 wt% at 45 °C. Furthermore, the hysteresis gap between adsorption and desorption branches gradually decreases with increasing temperature and almost disappears at 45 °C (Fig. S4). The RH values at the inflection/switching point were observed to be 20 % RH, corresponding to 0.340, 0.632, 1.122, and 1.912 kPa at 288, 298, 308, and 318 K, respectively. These temperatures and inflection pressure values were fitted to the Clausius–Clapeyron equation (Fig. S5), to calculate the adsorption enthalpy (ΔH, absolute value) of *ca*. 43.8 kJ mol^{-1}. This ΔH value is slightly higher than the vaporization enthalpy of water (40.7 kJ mol^{-1}),[22] suggesting that physisorption of water dominates in MAF-7.

Water sorption kinetics of MAF-7 were also determined under 90 - 0 % RH and 60 - 0 % RH at 25 °C, respectively (Fig. 3a). It can achieve over 98 % of full capacity within 20 and 30 min under 90 and 60 % RH, respectively, and release the adsorbed water within 40 min at 0 % RH. Elevating the desorption temperature to 30 or 40 °C can reduce the unloading time to 25 or 10 min (Fig. S6). A recyclability test (Fig.3b) was conducted between 60 % RH (30 min) and 0 % RH (30min) for 10 cycles (600 min in total). It demonstrated good recyclability of MAF-7 and a decent working capacity of 35.66 wt%. The theoretical daily deliverability can be calculated to be 8.56 L water per kg of MAF-7. This deliverability can be further improved since the desorption time can be greatly reduced when elevating the regeneration temperature within a reasonable range. For example, if the desorption temperature is set at 40 °C, the required desorption time can be within 10 min, and the daily deliverability will be 12.84 L water per kg of MAF-7, representing a 50 % increase. Nevertheless, we note that in practical the deliverability of sorbents will be highly influenced by several parameters including the device setup, sample packing type (amount, density, thickness), particle morphology (size and shape), heating and cooling rate, and onsite environments.[32,33]

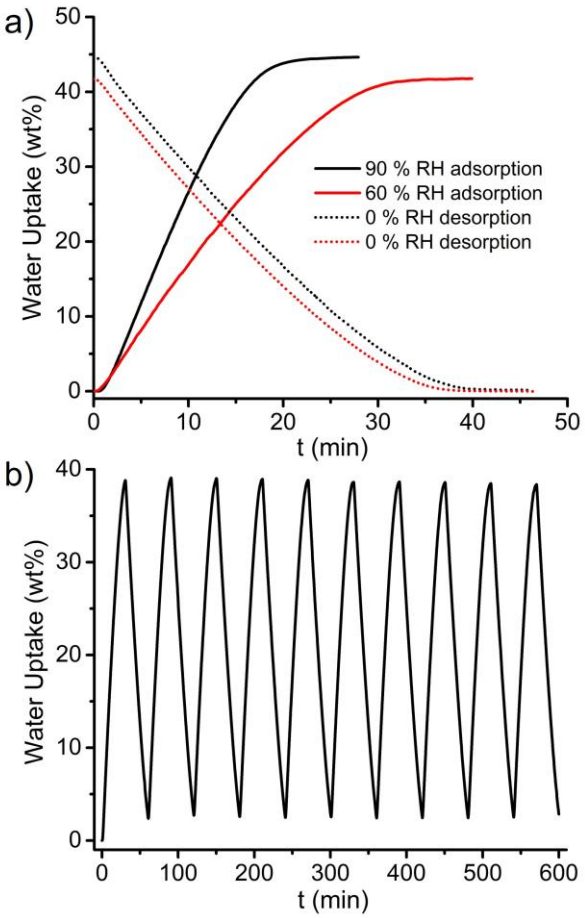

Fig. 3. a) Water sorption kinetics tests under 90 - 0 % RH (black line) and 60 - 0 % RH (red line) at 25 °C; b) recyclability test between 60 % RH (30 min) and 0 % RH (30min) at 25 °C for MAF-7.

It is of importance to understand the water molecule's locations within the pore cavity of MAF-7. Due to the high symmetry of the crystal structure of MAF-7 (cubic, *I43m* space group), it is difficult to accurately determine guest locations in MAF-7 via X-ray crystallography. In order to gain insight into host-guest interactions, molecular simulations were conducted based on the reported single crystal structure of MAF-7 (refcode: EMAPAK). Our results reveal six independent water locations within the cavity of MAF-7 (Fig. 4 and S7). These water location patterns resemble those of gas molecules (e.g. N2, O2, Ar) in ZIF-8.[34] However, it is worth noting that there is no evidence of MAF-7 undergoing the pore opening phenomenon observed in ZIF-8. Additionally, the stepped water sorption isotherms (IUPAC type V) of MAF-7 are attributed to the pore filling effect, likely akin to that proposed for ZIF-90.[35] This differs from the stepped guest sorption isotherms observed in flexible/switching MOFs, which result from guest sorption-induced phase transformations.[36-41]

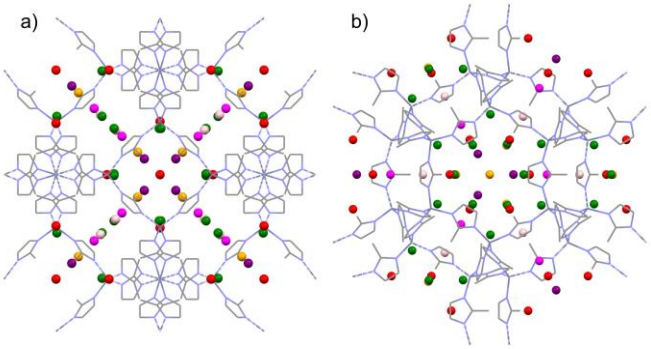

Fig. 4. Six independent water locations within the structure of MAF-7, viewed along a) the four-member ring window and b) the six-member ring window.

In summary, we herein present the water sorption properties of the zeolitic metal azolate framework, MAF-7. Water sorption isotherms were measured at four temperatures (15, 25, 35 and 45 °C) and compared with the previously reported data. Our results indicate that temperature does not affect the RH values of the reflection/switching points, while it does influence the saturation sorption uptakes and hysteresis gap moderately. The water sorption uptakes and kinetics of MAF-7 are comprable or superior to those of other well-known MOFs,[42-46] making it a promising candidate for water sorption-based applications. Moreover, full water desorption can be achieved within 10 min at temperature as low as 40 ºC, suggesting its compatibility with low-grade heat sources. Considering additional factors such as ease of synthesis, low synthesis cost, high hydrothermal stability and good recyclability, MAF-7 represent a prototype of SOD zeolitic-type MOF materials for water sorption. Future studies will explore other sorption behaviour of MAF-7 and investigate water sorption properties of its related MAF/ZIF materials.

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Conflicts of interest

There are no conflicts to declare.

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