1 **Recent Progress of Atmospheric Water Harvesting Using**
2 **Metal-Organic Frameworks**

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Abstract Atmospheric water harvesting based on vapor adsorption is a newly emerged and potential technology to supply portable water for arid areas. To efficiently harvest vapor from the air, sorbents are required to have considerable adsorption capacity, easy regeneration and high stability. With the advantages of porous structure, tunable pore size and tailorable hydrophilicity, metal-organic frameworks (MOFs) have demonstrated excellent performance in vapor adsorption and water generation. In this review, we first discuss the degradation mechanisms of MOFs exposed to water and summarize the structure-stability relationship; by centering on the adsorption isotherms, the connection between the structure of MOFs and the water adsorption property is illuminated; finally, some prospects are suggested in order to push forward the progress of this technology.

Keywords Metal organic frameworks; Atmospheric water harvesting; Hydrolytic stability; Water adsorption isotherms

1 Introduction

Water shortage is one of the most urgent global challenges, which is threatening the development of human society. It is estimated that two-thirds of the population will live in water-stressed countries by 2025^[1], environmental pollution and increasing population further exacerbate this situation. Although most of the earth's surface is covered with water, 96.5% of them is salt water and cannot be utilized directly, only 2.5% is fresh water, while just 0.3% of them is in liquid form^[2]. To exploit new fresh water resources, desalination is the most commonly used method to get fresh water nowadays^[1]. Seawater can provide a steady supply of fresh water, however, the construction of infrastructure needs a large cost of capital and the process is energy-intensive^[3,4]. Besides, most arid regions are inland, thus it is necessary to develop distributed water-harvesting devices to offer fresh water for these areas.

Atmospheric water is a potential water resource that has unfortunately been ignored for a long time. It accounts for about 10% of all fresh water in lakes^[2] and opens a new path to solve the current dilemma. The water in air mainly exists in three forms: cloud, fog and vapor. To collect water from cloud and fog, fine meshes are utilized to capture the microscopic droplets, however, the preconditions

of this method are high relative humidity ($RH \approx 100\%$) and light wind, meaning that it is geographically dependent^[5]. Except the microscopic water droplets existing in fog and cloud, most atmospheric water is in the form of vapor. And this part of atmospheric water existing in a molecular state is everywhere, even in the driest desert area^[6]. Water vapor can be harvested by chilling-based condensation and adsorption-based concentration. Condensation is conducted by cooling down moist air below its dew point^[7], which is energy-intensive and humidity-dependent, and will become impractical at $RH < 50\%$ ^[6]. Absorption-based concentration is a technology using desiccants to harvest vapor from air in the shade, then adsorbed water is released by low-grade energy (e.g. solar energy and waste heat) and is finally liquefied to droplets. In comparison, the adsorption-based method is more convenient and energy-efficient.

Currently, typical desiccants including: hygroscopic salts^[8,9], polymers^[10-12], zeolites^[13] and silica gel^[14]. However, they are suffering from drawbacks of slow kinetics (for salts), or hard regeneration (for polymers), or weak adsorption capacities (for zeolite and silica gel). Metal-organic frameworks (MOFs), as a new type of porous materials, are connected by metal nodes and organic ligands. They are characterized by unprecedentedly high surface areas and porosities, tailored microporous structure, and tunable surface property, which endow them with great potential in harvesting water from air^[15]. Although MOFs have been extensively and intensively investigated as sorbents for the storage and separation of different gases, such as CO, CO₂, CH₄ and H₂^[16-18], it is not until recent years that they have been applied to adsorb H₂O, because most MOFs have poor ability to withstand structural degradation in the presence of water or vapor^[19]. With the development of more and more water-tolerant MOFs, their use in water harvesting has aroused increasing research attention.

In this review, we first introduce the degradation mechanisms of MOFs exposed to water and the corresponding structure-stability relationship. In the following section, we center on water adsorption isotherms of MOFs, discussing how the isotherms reflect MOFs' water adsorption behaviors and thus their water harvesting performance in correlation with MOFs' structural property, with the aim to provide guidance for the design and fabrication of the next generation of water harvesting materials. Lastly, some prospects are provided in order to push forward the development of MOFs in the area of atmospheric water harvesting.

2 Hydrolytic Stability of MOFs

The prerequisite of using a MOF for capturing water from the air is that it is structurally stable in the presence of water. Therefore, it is crucial to understand the hydrolytic stability and degradation mechanisms of MOFs for developing MOF-based sorbents for water harvesting.

2.1 Degradation mechanisms

Through experimental testing and molecular modeling, Low et al. proposed that the reaction of MOFs with water involves two pathways: hydrolysis and linker displacement^[20]. Hydrolysis reaction occurs by breaking the metal-ligand bond, in which the hydroxyl groups dissociated from water would be added to metal nodes with free protonated linkers being formed simultaneously (Equation (1)):

In contrast, the linker displacement involves the insertion of water into metal-ligand bond, forming a hydrated cation interacting with a deprotonated linker as indicated in Equation (2):

It is conceivable that the reaction pathway in water solution is pH-dependent. For instance, UiO-66 is degraded in HCl solution following the mechanism which is similar to hydrolysis (Figure 1a), while in NaOH solution or pure water, it is degraded by linker displacement^[21] (Figure 1b,c). As regards water harvesting from air, it is obvious that linker displacement should be the main degradation mechanism if the air is clean and unpolluted. Besides, it is also reported that solvation can promote the degradation process. At higher water loading (four water molecules per unit), the degradation of hydrophobic MOFs built from basic zinc carboxylate SBUs is mainly attributed to the linker displacement by one water molecule, while additional three water molecules would stabilize the state with one bound water molecule by solvation^[22]. Understanding the degradation mechanisms would guide us to fundamentally improve the hydrolytic stability of MOFs.

Figure 1. Proposed mechanisms of the degradation of UiO-66 in HCl solution (a), NaOH solution (b) and pure water (c), Carbon (gray), hydrogen (white), oxygen (red), zirconium (light blue), and chlorine (green) atoms can be seen; hydrogen atom are omitted for clarity^[21].

2.2 Relationships between structure and stability

In view of the degradation mechanisms mentioned in 2.1, there are two general ways to design hydrolytically stable MOFs from the perspective of thermodynamics and kinetics respectively.

Thermodynamically, the binding groups of organic ligands and the metal nodes can be regarded as Lewis acid-base pairs. On the one hand, their interaction would be strengthened by increasing the acidity of the metal nodes or the basicity of the organic linkers. As demonstrated by Choi and Park, linkers containing pyrazolate and imidazolate with high pK_a values are conducive to forming water-stable MOFs^[23,24]. Highly charged metal ions (such as Zr^{4+} , Ti^{4+} , U^{6+} , etc.) with small pK_a values are also beneficial to enhance the hydrolytic stability^[25-27]. Besides the pK_a value, polarizability is another factor for designing a stable structure. Considering linkers with high pK_a values are usually hard bases, thus on the basis of the hard-soft acid-base theory, stable MOFs can be constructed by matching hard base linkers (e.g., carboxylate, pyrazolate, or tetrazolate) to metal ions which are defined as hard acids (e.g., Al^{3+} , Cr^{3+} , Ti^{4+} , Zr^{4+}).

In addition, reduction potential of the metal ions also plays a crucial role in MOFs' stability, those with lower reduction potential are less hydrolytically stable^[28]. Kizzie and his colleagues synthesized different coordination polymers M/DOBDC with Mg, Ni and Co for CO₂ capture, after exposure at 70% humidity and further thermal regeneration, Mg/DOBDC only recovered 16% of its original capacity, while Ni/DOBDC and Co/DOBDC recovered 60% and 85% of its initial capacity^[29]. The weakest stability of Mg/DOBDC is attributed to the lowest reduction potential of Mg (-2.372 eV) compared to the other two metals (Ni (-0.25 eV) and Co (-0.28 eV)).

Apart from the above thermodynamic parameters, kinetic factors also have influence on the hydrolytic stability of MOFs. The first step of MOF degradation is water approaching to the metal nodes, steric shielding can efficiently limit the diffusion of water and thus improve the stability. It is worth noting that introducing steric shielding is not equivalent to reducing the adsorption capacity or weakening the water affinity, it is a strategy to protect the linkages between metal nodes and organic linkers from water molecules' attack. As a rule of thumb, there are two pathways to introduce steric shielding: metal nodes with high connectivity and bulky linkers. The excellent stability of UiO-66 is attributed to the high coordination of Zr/Hf nodes (12-connected) that provides steric shielding for the framework. In general, highly charged metals, such as Zr and Hf, are often highly coordinated and therefore favoring stability. However, it is worth noting that the coordination number is not the only factor of the steric shielding and the pore size would also make a difference. For example, despite being isostructural, UiO-67 shows markedly lower water stability than UiO-66, because the larger pore size of UiO-67 promotes the accessibility of water to the metal-linker coordination bonds.

Besides, modifying the linker with various functional groups has proven helpful for improving the water stability of MOFs. Jasuja et al. demonstrated that nonpolar functional groups such as methyl groups could prevent the Zn-O bond in [Zn(L)(DABCO)_{0.5}] (L is functionalized 1,4-benzenedicarboxylic acid) from the attack of water, and they attributed this result to the steric shielding effect instead of the hydrophobicity of the framework, considering its high water uptake at low RH^[30]; Interestingly, polar functional groups such as amines and alkoxy groups could also improve the stability by drawing water away from the metal nodes^[31].

Modifying the framework with hydrophobic functional groups is likewise an effective strategy to strengthen the hydrolytic stability of MOFs by water exclusion. Fluorination and methylation are two

most commonly used methods. Pal et al. found that after partial fluorination, the water uptake of $\{[\text{Zn}_2(\text{L})(\text{H}_2\text{O})_2](5\text{DMF})(2\text{H}_2\text{O})\}_n$ (L is functionalized tetracarboxylic acid) shifted to a higher relative pressure ($P/P_0=0.85$), indicating the formation of hydrophobic pores^[32]. Likewise, decorating the linkers with methyl groups increased the hydrophobicity of $\text{Al}(\text{OH})(1,4\text{-naphthalenedicarboxylate})$, as reflected by the right-shifted inflection point on the water adsorption isotherm^[33]. Notably, although this strategy improves the water stability of MOFs, the price is the loss of water adsorption capacities^[34], and it is therefore not suitable for water harvesting applications.

The kinetic inertness of the metal ions was reported to play a pivotal role in improving the water stability of thermodynamically unstable MOFs. Kang et al. investigated the water stability of three isostructural MIL-53 (MIL-53-Al, MIL-53-Cr, MIL-53-V) and found that the stability decreases in the order of $\text{MIL-53-Cr} > \text{MIL-53-Al} > \text{MIL-53-V}$ ^[35]. This result cannot be explained by the bond strength that follows a reversed order of $\text{V-O} > \text{Al-O} > \text{Cr-O}$; it is not associated with the coordination and oxidation state of the metal ions either, as the three materials are identical in these aspects. However, it may be explained by the inertness of their central metal which follows the order of $\text{Cr}^{\text{III}} > \text{Al}^{\text{III}} > \text{V}^{\text{III}}$, and correlates well with the rank of water stability.

In summary, in order to gain hydrolytically stable MOFs for water harvesting while at the same time not producing negative effects on water uptake capacity, one approach is to increase the bond strength between linkers and metal nodes thermodynamically using the indicators of $\text{p}K_a$, polarizability, and reduction potential; another widely applied strategy is to introduce steric shielding to prevent the bond from the attack of water molecules, by choosing highly charged metals with high coordination number or kinetically inert metal ions to synthesize corresponding MOFs.

3 Water adsorption isotherms of MOFs

In addition to hydrolytic stability, the MOFs applied in water harvesting also need to satisfy the following fundamental properties: tailorable hydrophilicity, high adsorption capacity, and easy regeneration^[36]. These criteria can be evaluated by the parameters of adsorption isotherms, including Henry constant K_H (slope of the isotherm in low-pressure range), the relative pressure α at which half of the adsorption capacity is reached, the maximum water adsorption capacity q_{max} and the hysteresis

loop between adsorption and desorption branches^[37]. K_H and α are related to hydrophilicity of MOFs, higher K_H and lower α mean stronger hydrophilicity; $q_{\max}$ is connected with the pore volume and the hysteresis loop reflects the regeneration capacity of MOFs. According to the updated IUPAC report in 2015, physisorption isotherms can be classified into six types (Figure 2)^[38]. Type I represents very hydrophilic sorbents with steep increase at low relative pressure (high K_H value). Sorbents with type II, IV and VI isotherm shapes are classified as materials with medium hydrophilicity. These sorbents all have considerable adsorption capacity at low relative pressure. In contrast, sorbents with type III and V isotherms are considered as less hydrophilic materials that have small adsorption capacity at low relative pressure. Among them, type I, II, III, IV(b) and VI are fully reversible and their adsorption capacity has high sensitivity to the changes of RH, while type IV(a) and V are not fully reversible with hysteresis loops in certain relative pressure range. A large hysteresis loop is usually undesirable because it means a large amount of energy is required to regenerate water from the sorbent. Isotherm type can reflect some adsorption/desorption properties of the materials. For the applications of atmospheric water harvesting, optimal sorbents should be selected based on the specific RH condition. For example, in the rigid area (e.g., desert regions), ideal sorbents should have a high affinity to water to enable water uptake at low RH (10%–20%), while for areas with high RH (e.g., seaside regions), sorbents having high adsorption capacity at high RH (60%–80%) are applicable. Note that an over strong affinity between the sorbent and water, which can be a consequence of ultrasmall pore size or super hydrophilicity of the pore surface, is not favorable for water regeneration, because it requires high energy input to release the adsorbed water and is difficult to be realized by low-grade energy like solar thermal or waste heat. The sorbents' performance is evaluated by the working capacity, which is the amount of water (g) generated per gram of sorbent in one adsorption/desorption cycle. The working capacity is determined by the property of sorbents and the specific adsorption/desorption conditions. To achieve full working capacity in short time, fast adsorption/desorption kinetics is needed, but this point has not been carefully taken into account in the current literature. The adsorption/desorption behaviors of MOFs can be adjusted by controlling their structural and compositional parameters, such as metal nodes, organic ligands, defects, and framework flexibility, as elucidated below.

Figure 2. IUPAC classification of adsorption isotherms^[38].

3.1 The effect of metal nodes

Metal nodes in MOFs have great influence on their water adsorption properties. Studies revealed that producing open metal sites by activation can increase the affinity of MOFs to water. In 2009, Küsgens et al found that HKUST-1 exhibits an adsorption isotherm of approximate type I^[39]. Due to unsaturated coordination, the open metal sites of HKUST-1 showed high affinity towards water, thus the adsorption capacity increased quickly at low relative pressure range (0~25%) (Figure 3a). Schoenecker et al also discovered the same phenomenon in MOF-74 whose maximum (saturated) adsorption capacity $q_{\max}$ was reached at low relative pressure ($\sim 10\%$)^[19]. However, the binding of water to the uncoordinated metal sites was so strong that it was difficult to release all the adsorbed water even at a lower relative pressure, as shown in Figure 3a. Functionalizing the metal cluster in MOFs can also exert influence on their water adsorption behaviors. Zhang et al decorated the metal cluster of BUT-46X with functional groups of different sizes and hydrophilicity (size: $\text{H}_2\text{O}/\text{OH}^- <$

$\text{HCOO}^- < \text{CH}_3\text{COO}^- < \text{PhCOO}^-$, hydrophilicity: $\text{PhCOO}^- < \text{CH}_3\text{COO}^- < \text{HCOO}^- < \text{H}_2\text{O}/\text{OH}^-$) to achieve precise tuning of its water uptake capacity (Figure 3b)^[40]. They found that replacing HCOO^- with different groups have significant effects on the size and hydrophilicity of the pore windows and thus the K_H and $q_{\max}$.

To efficiently harvest water from air, MOFs not only need to show favorable water adsorption capability but also should have easy regeneration property. Creating open metal sites can increase the affinity of MOFs with water, but often leading to over strong interaction that makes water desorption difficult. By comparison, functionalizing the metal nodes with suitable functional groups might be a more feasible and flexible means to tune the sorbent/water affinity for atmospheric water harvesting under specific climate conditions.

Figure 3. (a) Water adsorption (filled symbols) and desorption isotherms (open symbols) of HKUST-1 at 298K^[39]; (b) Water adsorption (filled symbols) and desorption isotherms (open symbols) of four BUT-46-X MOFs at 298K (BUT-46-F, -A, -W, -B are separately grafted with HCOO^- , CH_3COO^- , $\text{H}_2\text{O}/\text{OH}^-$, PhCOO^-)^[40].

3.2 The effect of organic ligands

The organic ligands have also been modified with different functional groups to finely tune MOFs' hydrophilicity. Reinsch et al investigated the effect of various functional groups attached to the organic ligands on the water uptake of CAU-10-X based on the adsorption isotherms (Figure 4a)^[41]. The original CAU-10-H exhibited a type V isotherm; after functionalization with $-\text{NH}_2$ or $-\text{OH}$, the obtained materials (CAU-10- NH_2 and CAU-10- OH) had increased K_H values, and the adsorption isotherm of CAU-10- NH_2 even changed from type V to type I, indicating strong hydrogen bonds formed between water and the framework. Besides, α shifted to lower relative pressures because of the

enhanced hydrophilicity. In contrast, CAU-10-NO₂, CAU-10-CH₃ and CAU-10-OCH₃ were more hydrophobic as seen from their increased α . ZIF-8 is a hydrophobic MOF that has low water uptake at $p/p_0 < 0.9$ (0.0125 g·g⁻¹ at $p/p_0 = 0.5$). After decoration with aldehyde groups, ZIF-8 shows a 8-fold increase in its water uptake under the same conditions (0.1 g·g⁻¹ at $p/p_0 = 0.5$)^[37]. Although grafting polar functional groups is demonstrated to increase the hydrophilicity of MOFs, the occupation of free pore volume by the substituents, in turn, would decrease the maximum adsorption capacity. As seen in Figure 4a, $q_{\max}$ of CAU-10-NH₂ and CAU-10-OH were much smaller than that of unfunctionalized CAU-10-H.

Figure 4. (a) Water adsorption isotherms at 298K of CAU-10-X (X=H, -CH₃, -OCH₃, -NO₂, -NH₂, -OH)^[41]; (b) Structure of Co₂Cl₂BTDD projected along the c axis^[42].

Increasing the length of organic linker and expanding the pore size can offer a higher maximum adsorption capacity. However, the increase of the pore size may sometimes change the water adsorption mechanism from pore filling to capillary condensation. A hysteresis loop may occur and the desorption process would become less sensitive to the change of RH, when the pore size is larger than the critical diameter of water D_c . That is to say, more energy needs to be input to lower RH and desorb all the water, which is also unfavorable for the application of water harvesting. The critical diameter of water is calculated according to Equation (3):

$$D_c = \frac{4\sigma T_c}{T_c - T} \quad (3)$$

Where σ is the van der Waals diameter of water, T_c and T are respectively the critical temperature of

271 water and the adsorption temperature, thus leading to a D_c of 20.76Å at 298K. The occurrence of
272 capillary condensation can be verified from the change of adsorption heat (Q_{st}) calculated from
273 Clausius-Clapeyron equation. Adsorption heat decreased from 80 kJ mol⁻¹ to 45-50 kJ mol⁻¹ (close to
274 the evaporation heat of water at 298K, which is 44 kJ mol⁻¹) when the coverage increased from 0 to
275 20%, indicating water-water interaction becomes dominant over the water-sorbent interaction^[43].
276 Reversible pore filling/evaporation (no hysteresis loop in the isotherm) is desirable for water
277 harvesting applications because this means a full use of the pore volume in combination with easy
278 regeneration of the sorbent. On the basis of such a consideration, Dinca's group synthesized a
279 mesoporous Co₂Cl₂BTDD with controlled pore size of 22Å; water adsorption on its open metal sites
280 at low RH decreased the effective pore size to ~20Å, which is ideal for reversible pore
281 filling/evaporation to take place (Figure 4b), enabling water uptake at the reversible limit to achieve a
282 record water capture capacity^[42].

283 Yaghi and his colleagues compared the isotherms of different MOFs and found that pore size
284 plays a more important role than hydroxyl groups in determining the low-pressure water adsorption
285 behavior for microporous MOFs^[44]. Specifically, in the low-pressure range, the water uptake of MOF-
286 804 and -805 having hydroxyl groups in their frameworks was only ~10% of that of MOF-801, which
287 does not have hydroxyl groups but has more appropriate micropore size for the aggregation of water
288 molecules (Figure 5a, c).

289 It is worth noting that although the modification of organic linkers can tune the hydrophilicity of
290 the MOF for efficient water harvesting under a specific condition, it may cause a substantial decrease
291 of porosity and thus reduce the adsorption capacity. The tradeoff between the surface property and
292 porosity should be considered when modifying the MOFs with functional groups in order to achieve
293 optimal performances.

Figure 5. Water adsorption (filled symbols) and desorption (open symbols) isotherms of zirconium MOFs with small pore (a), large pore (b) and hydroxyl groups (c) at 298K^[44].

3.3 The effect of structural defects

Although the structural defects in MOFs have been extensively studied, most studies focused on how the local defective structures influence the catalytic activity or gas adsorption properties, while there are only a few reports discussing their impact on water adsorption. Yaghi et al compared the adsorption isotherms of MOF-801 in the form of single crystals (MOF-801-SC) and microcrystalline powder (MOF-801-P)^[44] (Figure 5a), the water uptake of MOF-801-P was 1.3 times higher than that of MOF-801-SC. This was because the missing-linker defects increased the hydrophilicity and the pore volume of MOF-801. Choi proved this and further investigated the influence of defects' density and spatial configuration on the adsorption property of MOF-801, and the $\langle 110 \rangle$ direction was

identified to be the preferential direction for water condensation^[45] (Figure 6). UiO-66 was also chosen to study the influence of defects' amount and location on its water uptake^[46], and the hydrophobicity of perfect UiO-66 and defective UiO-66 was clarified by calculating the corresponding adsorption heat Q_{st} . The Q_{st} on perfect UiO-66 was only 15 kJ mol⁻¹ at low water loading, while it was around 60 - 70 kJ mol⁻¹ for defective UiO-66, indicating that water had a strong affinity with the defective sites on the framework.

Introducing defects into a MOF is an effective approach to increase its pore volume and hydrophilicity, leading to a larger water uptake and a smaller α . However, the stability of a defective MOF structure could be a problem for practical applications and should be carefully evaluated.

Figure 6. (a) Five MOF-801 defect structures with different defect densities and/or spatial configurations. The first number in the structure name indicates how many linkers were removed per unit cell, the notations after the underscore refer to different configurations of the defects (par: defects which are perpendicular to each other and located in different planes; 90: defects that are perpendicular to each other and located in the same plane; 180: defects which are in parallel and located in the same plane); (b) Water adsorption isotherms of different MOF-801 (the solid lines are the results of different MOFs obtained from Grand Canonical Monte Carlo (GCMC) calculations; the dashed line is the experimental result of perfect MOF-801 reported by Furukawa et al)^[45].

3.4 The effect of structural flexibility

MOFs with flexible frameworks may exhibit “breathing” or gate-opening effects. Breathing effect refers to the reversible transition of structural phase upon adsorption or desorption, while the gate-opening effect refers to an abrupt structural transition occurs at a nonzero pressure. Generally speaking, flexibility of MOFs cannot be ascertained from the adsorption isotherms alone because the effect of degradation or adsorbate packing change may also result in similarly shaped isotherms. Here, we only discuss the MOFs which has been crystallographically certified that structural transition really occurs

in their framework during adsorption or desorption.

Serre and his colleagues first found the breathing effect (more than 5 Å) of MIL-53 between its hydrated form and the anhydrous form in 2002^[47]; Yamada et al also reported the gate-opening effect of the composites which are isostructural to MIL-53^[48]. The flexibility of the framework would exert a significant influence on the isotherms of microporous MOFs because of the structural transformation. Interestingly, Devautour-Vinot found that different metal ions played different roles in the flexibility of the formed MOFs. The magnitude of breathing effect in MIL-53(Cr) was much larger than MIL-53(Fe), and the framework flexibility led to a 40% variation of the volume in MIL-53(Cr) compared to a 10% variation in MIL-53(Fe)^[49], as illustrated in Figure 7a. Functionalizing the organic ligand would help to relieve the structural change caused by the flexibility. Shigematsu et al grafted -NH₂ onto MIL-53(Al)^[50], which made the framework more rigid and the water adsorption isotherm shifted from type V to type I accompanied by the disappearance of hysteresis loop (Figure 7b), because of the formation of internal hydrogen bond between bridging -OH and -NH₂.

The structural flexibility of MOFs provides opportunities for developing novel applications. For example, a flexible MOF structure that responds to external stimuli (e.g., light and temperature) could be useful for atmospheric water harvesting because its adsorption/desorption behavior is easily tunable.

Figure 7. (a) The structural change of MIL-53(Cr) and MIL-53(Fe) upon water desorption^[49]; (b) Water adsorption (filled symbols) and desorption isotherms (open symbols) of MIL-53(Al) (blue), MIL-53-NH₂(Al) (pink), MIL-53-OH(Al) (green) and MIL-53-(COOH)₂(Fe) (red) at 298K^[50].

4 Conclusions and perspectives

MOFs have demonstrated great potential, as high-performance sorbents, for the application of

water harvesting from the air. Their designable and easily tunable structures, porosities, and surface functionalities are particularly advantageous for this application, because the desirable water adsorption/desorption properties of the sorbent varies with the specific climate conditions. The water adsorption/desorption isotherms of MOFs can be used to evaluate their water harvesting performance that is essentially defined by “working capacity”. In general, the MOF materials need to meet the following fundamental requirements: high hydrolytic stability, tailorable hydrophilicity, superior water uptake capacity and easy regeneration. These properties can be tuned by designed synthesis of MOFs’ structures through various aspects, including metal nodes, organic linkers, defects and framework flexibility. A successful example is MOF-801, which has demonstrated a good performance of atmospheric water harvesting in the desert, due to its high water uptake at low RH (about $0.25 \text{ g} \cdot \text{g}^{-1}$ when the RH is 10%) and exceptional stability^[6].

Despite the steady progress made in this field, there remain some challenges to be resolved. Firstly, the working capacity of MOFs needs to be further enhanced to reduce the required mass/volume of the sorbent. As we discussed in the main text, working capacity is closely related to the metal nodes, the organic linkers and the formed pore structure. To design MOFs with ultrahigh working capacity, these three perspectives should be considered comprehensively. Secondly, the water adsorption/desorption kinetics on MOFs, which determines the amount of water generated within a certain period of time and is crucially important for practical applications, has been largely overlooked and unexplored in the literature. Kinetics is not only related to the nature of MOFs, but also is associated with mass transport. Designing rational adsorbent beds to ensure that MOFs can fully contact with air is an efficient pathway to accelerate the kinetics. Thirdly, the mechanical strength of MOF sorbents should be carefully evaluated because in practical applications, they need to be shaped and packed into adsorbent beds. Lastly, the development of smart, stimuli-responsive MOFs for water harvesting remains conceptional but unexploited, which would bring new strategies and opportunities for tuning the water adsorption/desorption behavior to achieve higher working capacities with less energy input.

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