Progress and potential of metal-organic frameworks (MOFs) as novel desiccants for built environment control: a review

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Abstract: The regulation of the balance of the sensible and latent loads remains a critical problem for built environment control. Unlike the traditional vapor compression system that features high-energy consumption and environmental-unfriendly processes, desiccants represent an alternative air-conditioning method that takes advantage of the low-grade energy, decreases the energy consumption and even employs use of water vapor. Though the desiccant-based systems can achieve spatial moisture transfer through the periodic adsorption/desorption process, however, the water-stable desiccants with high water uptake and mildly reversible adsorption are required, and the traditional desiccants cannot meet these requirements. In this respect, metal-organic frameworks (MOFs), possessing a variety of structures and precise functional ability to optimize their properties, are promising porous materials exhibiting high potential for rational design and sorption-based applications. In this review, intrinsic properties and prevalent water adsorption mechanisms of the potential micro/mesoporous MOF desiccants have been elucidated. Subsequently, the selection criteria of the promising MOF desiccants for water loading removal from air in the built environment is proposed and some currently available water-stable MOFs based on different working humidity ranges have been analyzed for the potential humidity control from the aspects of microstructure, isotherms and regeneration conditions. Finally, approaches for screening the well-suited MOFs from material and system levels is presented. Overall, the cases of actual applications in the active or passive

way have confirmed that MOF-based systems can effectively regulate the humidity load within the desirable range, thus, underlining the high potential of large-scale applications in the near future.

Highlights:

1．Research on metal-organic framework (MOF) materials for the built environment control has been reviewed.

2． Special crystal structure of MOF plays an important role in the adsorption mechanism.

3．The selection criteria and classification of MOFs disclose the potential application in solid desiccant systems.

4．Developments of MOF commercialization and system-related technologies (i.e. coating process) are prospected.

Keywords: MOFs, intrinsic properties, adsorption mechanism, screening, active/passive-type, solid desiccant system

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1. Introduction

Benefitting from the scientific inventions of the contemporary era, people's lifestyle has evolved from early open-air living spaces into more comfortable and enclosed air-conditioned ones. The energy consumption by the air conditioning systems represents more than 40% of the total building energy consumption. In the traditional cooling dehumidification, the cooling air below the dew point, used to remove both sensible and latent loads, gives rise to a large extent of energy waste owing to the low trigger temperature for the latent load removal [1, 2]. Therefore, the critical problem in the indoor air-conditioned zones is to achieve an independent control of temperature and humidity [3, 4]. It is to be noted that either moisture accumulation or deficiency will cause discomfort to human beings and damage to building materials, and 45%~65% relative humidity (RH) in residential buildings has been recommended by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) [5]. In this regard, the introduction of desiccant materials is an alternative method to achieve effective humidity control within a desirable range, and extensive studies have been devoted to the synthesis and application of new desiccants possessing high water capacity and gentle regeneration conditions [6, 7].

Desiccants can generally be classified into liquid and solid phase. As the liquid desiccant dehumidifiers suffer from large and complicated systems, metal corrosion, etc., the solid desiccant systems (SDSs) progressively exhibit potential as promising methods for indoor humidity control [8, 9]. Some commercially used materials, like zeolites and silica gels, have been incorporated into the air-conditioning systems, but these are incapable of achieving high-performance dehumidification due to the harsh regeneration condition or low work loading [10, 11]. Therefore, research efforts are going for the development of novel solid desiccants with an ability to improve the whole system performance with respect to the built environment control.

Recently, micro- and mesoporous materials such as metal-organic frameworks (MOFs) have emerged as an effective alternative to the currently used desiccants [9]. The MOFs are constructed by the formation of strong chemical bonds to bridge inorganic metal-related units with organic ligands, thus, creating open frameworks with ordered structure [12, 13]. A high level of structural flexibility and ultra-high porosity make these materials promising desiccants in the sorption-based applications [14]. In addition, most of the MOFs have S-shaped isotherms with a steep rise in a narrow relative humidity (RH) range. The observed steep rise is directly correlated with the special adsorption mechanism of MOFs, however, it does not rely on the formation of strong bonding sites in the crystalline frameworks, thus, partly indicating their gentle regeneration condition [15].

To date, more than 80000 different MOFs have been reported, but only a small number of literature studies have investigated their distinct advantages over traditional materials in the air-conditioning system [16, 17]. One critical challenge appears to be the effective screening of the available MOF desiccants. First, the long-term water stability is the precondition that ensures the conservation of their frameworks [10]. Hydrothermal stability tests over several thousands of adsorption/ desorption cycles have been proven only for a few structures [18-21], while most reports have presented only a few dozen cycles on laboratory scale. Second, the working performance (adsorption and desorption) of MOF desiccants is of importance for the working efficiency. At present, a small number of studies have been reported on the MOF-based open SDSs (directly contacting the ambient air) for humidity regulation in buildings. However, water-harvesting applications [22-24] and explorations of the sorption-based close SDSs (without contacting the ambient air) such as heat pumps [25-31] and adsorption-based refrigeration [20, 32-34] provide more information about the basic hydrothermal properties of MOFs. Third, the intrinsic properties of the MOF chemicals decide the application area. In

general, it is also preferred to use green and safe materials with low cost in the practical applications [35]. Besides, the other challenge is to classify the MOF desiccants. In general, MOFs such as MOF-801 [36], MOF-841 [37], MIL-160 [25], CAU-10 [38], Co_2Cl_2(BTDD) [39], etc., have been investigated for good working capacity in the 0~30% RH range, while MIL-100 (Cr, Fe, Al) [27, 40], MIL-101(Cr) [41],Cr-**soc**-MOF-1 [42], Y-**shp**-MOF-5 [21], UiO-66 [37], etc., exhibit high working capacity in the 30%~65% RH range. Especially, Y-**shp**-MOF-5 [21] and Cr-**soc**-MOF-1[42] demonstrate autonomous humidity control within a desirable range (45%~65% RH) for the building environment. Thus, the ongoing work on the classification of MOFs should be intensively developed.

To the best of our knowledge, there are only a few comprehensive overviews focusing on MOFs for the water adsorption applications [16, 17, 43, 44], not to mention the built environment control. In this review, we will explore in detail the development of MOFs in built environment control from materials and systems. A brief review of the compositions and intrinsic properties of the MOF materials has been presented. Some basic selection criteria of MOFs for humidity load control have been subsequently proposed, and three groups of MOFs have been classified and discussed based on their different trigger point (a turning point P/P_0 before a steep rise in isotherms). At the end of this review, the strategy and design of systems using MOF materials have been provided for either passive or active methods. Though it is hard to review the vast number of literature studies on MOFs and make a well-considered evaluation on this subject, it is still hoped that the review provides some insights into the selection of the most suitable MOFs depending on the different conditions with reference to their application in the built environment control.

2. Compositions and intrinsic properties of MOFs

2.1. Compositions

A specific MOF requires the provision of metal ions derived from the inorganic metal salts, organic ligands, and possibly solvents. MOFs with desirable structures can be prepared through the component exchanges in the metal ions, ligands or solvents.

Metal ions: metal-containing units are used for bonding with organic groups. To date, many metal ions have been reported for developing MOFs with high hydrolytic stability, most of which traditionally are divalent metal ions such as Cu^{2+}, Zn^{2+}, Zr^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+} and Cd^{2+} [30, 39, 45-47], trivalent metal ions such as Fe^{3+}, Cr^{3+} and Al^{3+} [27], and even tetravalent ions such as Ti^{+4} and Hf^{+4} [48, 49]. In past decades, many studies have also been conducted on lanthanide series (i.e., Ce, Pr and Eu), p-block elements (i.e., Ga and In) and even mix-metals [10, 50, 51].

Ligands (linkers): the ligands are used to connect the metal clusters, which shape the crystal framework. The structure of ligands can provide insights about the hydrophilicity/ hydrophobicity of the pore surface. Theoretically, longer ligands bear larger surface area, thus, providing more adsorption sites and storage space, and correspondingly affecting the adsorption capacity. Common ligands used in the synthesis of water-stable MOFs include BTC (1, 3, 5-benzene tricarboxylic acid), TPA (terephthalic acid), TDC (thiophene-2, 5-dicarboxylic acid), fumaric acid, etc. [40, 41, 49].

Solvents: the solvents are not a necessity during the synthesis of MOFs, especially for mechanochemical synthesis. However, the solvents can provide a benign environment for the chemical reactions, resulting in the diversity of the formed structures. Besides, the solvents can also determine the thermodynamics and activation energy for a specific reaction. The commonly used solvents are water and organic solvents such as ethanol, acetone and ethyl

144 acetate. A few non-green solvents (e.g. dimethyl sulfoxide, tetrahydrofuran, toluene, formic
145 acid etc.) can also be used in the large-scale production by strictly following the standard
146 procedures [52, 53].
147
148 2.2. Intrinsic properties
149 The remarkable performance of MOFs has advanced their synthesis, accompanied by the
150 development of geometric topology design, post-synthetic modification and multivariate
151 MOFs. It is to be noted that the interaction between the acceptor and target pairs (i.e. MOF-
152 water vapor) makes the MOFs competent desiccants. Namely, the intrinsic properties of MOFs
153 drive the performance for water uptake and corresponding applications (Table 1 and Table 2).
154
155 2.2.1. Metal sites
156 There are many coordinatively unsaturated metal sites inside the MOF structure, where the
157 guest molecules such as water or other organic solvents can be coordinated after synthesis [54].
158 Prior to the practical usage, activation is needed to help remove these guest molecules from the
159 metal nodes by heating in a vacuum environment. As the exposed sites exhibit strong polarity,
160 MOFs demonstrate relatively high affinity towards vapor molecules even at low vapor pressure.
161 Correspondingly, the amount of the recovered unsaturated metal sites can enhance the
162 adsorption capacity of MOFs for vapor molecules [55, 56].
163
164 2.2.2. Functionality and expansion of structures
165 Apart from metal sites, the combination of functional groups with ligands is also an alternative
166 to improve the hydrophobicity/ hydrophilicity of MOF chemicals, tune the shape of isotherms
167 or move their trigger points (P/P_0). Commonly used hydrophilic functional groups, such as -
168 NO_2 (nitro), -NH_2 (amino), -OH (hydroxyl), etc., have been reported for the synthesis of MOFs

[57-62]. In comparison with the original MOFs without functionalities, the functionalized MOFs demonstrate strong tunability in isotherms, however, at the expense of surface area or pore volume. On the other hand, the exploitation of MOF-based composite materials has also gained interest. In order to facilitate the heat and mass transfer of desiccants, MOFs have also been combined with inorganic salts or carbon substrates to improve the adsorption performance. For instance, $CaCl_2$@UiO-66 and MIL-101(Cr)@graphene oxide have been reported to possess high water capacity [63-67].

In addition, a few research studies have expanded the MOF structures based on the same topology, which indicates that it is possible to develop identically topological and uniquely functional MOFs. An example of such cases is HKUST-1 [$Cu_3(BTC)_2$], which results from the bridging of copper metal ions (Cu^{2+}) with tritopic ligand (BTC^{3-}). Identically topological structures were constructed through ligand expansion from BTC to TATB, and further to BBC. The BBC analog has been reported to possess 17.4 times volume as compared to the original HKUST-1 [68]. Accordingly, the developed extension exhibits the potential to provide more adsorption sites for achieving diverse functionalities.

2.2.3. Porosity, surface area and pore apertures

From the perspective of topology, MOFs consist of the units of nodes (metal ions) and rods (ligands), and the rods generally encompass a number of void spaces therefore making MOFs porous materials. To date, the flexibility of the selection of both metal ion sources and organic ligands has resulted in various internal structures, leading to a wide range of surface area (from hundreds to thousands m^2/g) and porosity up to 90% [69], with pore size in micropore range (~nm) or even smaller [70]. Furthermore, according to the synthesis methods reported in literature, the reaction conditions have a direct correlation with the intrinsic structure through

the control on the residence time, feed mass, reaction temperature, etc., thus, allowing flexibility during synthesis.

Table 1

Reported real applications of MOFs in water adsorption.

Materials	Surface area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Pore diameter (nm)	Uptake (g g^{-1})	P/P_0 of the steep adsorption	Possible regeneration condition	Refs.
CAU-10(Al)	635	0.43	0.7	0.36	0.15-0.25	70℃	[32, 38]
MIL-53-FA(Al)	1080	0.49	0.6	0.53	0.2-0.35	90℃	[52, 71]
MIL-100 (Fe)	1917	1.0	2.5/2.9	0.77	0.25-0.45	<70℃	[27, 72]
MOF-801(Zr)	990	0.45	0.48/0.56/0.77	0.36	0.05-0.15	80-85℃	[37, 73]
MOF-303(Al)	-	0.54	0.6	0.48	0.1-0.25	85℃	[22, 74]

Table 2

Promising MOFs in water adsorption applications.

Materials	Surface area (m^2 g^{-1})	Pore Volume (cm^3 g^{-1})	Pore diameter (nm)	Uptake (g g^{-1})	P/P_0 of the steep adsorption	Possible regeneration condition	Refs.
BIT-66(V)	1417	0.87	0.65/2.58	0.71	0.6	-	[75]
BUT-46A(Zr)	1550	0.69	1.6-3.5	0.52	0.44-0.49	-	[76]
BUT-46B(Zr)	1430	0.65	1.6-3.5	0.49	0.51-0.55	-	[76]
BUT-46F(Zr)	1563	0.71	1.6-3.5	0.59	0.39-0.43	-	[76]
BUT-46W(Zr)	1565	0.71	1.6-3.5	0.63	0.27-0.37	-	[76]
CAU-1(Al)	1300	0.55	0.5/1.0	0.55	0.38	-	[77]
CAU-23(Al)	1250	0.48	-	0.37	0.3	60℃	[20]
CUK-1(Co)	510	0.26	-	0.28	0.12	-	[30]

CUK-1(Mg)	580	0.28	-	0.36	0.23-0.28	-	[30]
CUK-1(Ni)	520	0.26	-	0.3	0.12	-	[30]
Cr-soc-MOF-1	4549	2.1	-	1.95	0.58-0.72	25℃, RH<45%	[42]
DUT-67(Hf)	810	0.33	-	0.29	0.25-0.45	-	[49]
DUT-67(Zr)	1064	0.44	-	0.41	0.25-0.45	-	[49]
DUT-68(Hf)	749	0.34	-	0.29	0.38-0.42	-	[49]
DUT-68(Zr)	891	0.41	0.8/1.3/ 1.4/2.8	0.34	0.38-0.42	-	[49]
DUT-69(Hf)	450	0.22	-	0.2	-	-	[49]
DUT-69(Zr)	560	0.31	-	0.26	-	-	[49]
MIL-100(Al)	1814	1.14	2.5/2.9	0.5	0.25-0.45	-	[27]
MIL-100 (Cr)	1517	-	2.5/2.9	0.8	0.25-0.42	-	[40]
MIL-101(Cr)	5900	2.0	2.9/3.4	-	-	-	[41]
	4150	-	-	>1.5	0.4-0.5	70℃	[78]
+NO_2(Cr)	2146	1.19	<2.9/3.4	1.08	0.41-0.52	-	[57]
+NH_2(Cr)	2509	1.27	<2.9/3.4	0.9	0.37-0.44	-	[57]
+SO_3H(Cr)	1920	0.94	<2.9/3.4	0.62	0.28-0.36	-	[57]
MAF-7(Zn)	1870	0.67	-	0.43	0.26-0.3	-	[79]
MIL-160(Al)	1070	0.398	-	0.37	0.05-0.16	90℃	[25]
MIL-125-NH_2(Ti)	1509	0.66	-	0.68	0.2	-	[48, 80]
MIP-200(Zr)	1000	0.4	-	0.46	0.17	65-70℃	[46]
MOF-74(Mg)	1250	0.53	1.11	0.75	0-0.05	-	[37]
MOF-808	2360	0.84	1.84	0.6	0.28-0.32	-	[37]
MOF-841(Zr)	1390	0.53	0.92	0.5	0.26	80℃	[37, 81]
Co_2Cl_2(BTDD)	1912	-	2.2	0.97	0.28	55℃	[39]
Ni_2Cl_2(BTDD)	1752	-	2.2	0.77	0.3-0.32	-	[39]
Ni-BPP	2039	0.88	1.7	0.72	0.08-0.32	-	[33]
Ni-TPP	1975	1.14	2.3	0.84	0.26-0.64	-	[33]
Ni-IRMOF74-III	-	-	-	0.35	0-0.05	<65℃,	[82]

NU-1500(Cr)	3580	1.28	1.4	1.09	0.45-0.49	25℃, RH<20%	[83]
PIZOF-2(Zr)	1250	0.68	2.0	0.68	0.7-0.74	-	[37, 84]
SIM-1(Zn)	570	0.3	0.65	0.14	-	-	[51]
UiO-66(Zr)	1290	0.49	0.74/ 0.84	0.44	0.3-0.35	-	[37]
+NH_2(Zr)	1328	0.7	0.75/ 1.2	0.38	0-0.3	-	[80]
Y-shp-MOF-5	1550	0.63	1.2	0.45	0.55-0.72	25℃, RH<45%	[21]
ZJNU-30(Zr)	3116	1.24	0.7/1.4/ 2.1	1.2	0.21	<60℃	[81]

3. Mechanisms and selection criteria of MOFs to the application in the built environment

Considering the operational performance of traditional desiccants, solid desiccant technology suffers from the bulky systems and low efficiency, thus, leading to limited applications [11]. Some efforts have also been made to mix the inorganic salt with desiccants (i.e. silica gel) to improve the working capacity. However, the regeneration condition is closely related to the nature of the desiccants, not to ignore the corrosion hazard of the inorganic salts on the metal framework. It is expected that the novel desiccants could well overcome these drawbacks. In the following section, the detailed information about the promising MOF-based desiccants has been presented. The adsorption mechanisms are also noted to disclose the moisture transfer within the MOF desiccants (Section 3.1). Based on their properties, the selection criteria of available MOFs have been discussed to further elucidate the advantages of MOF desiccants in practice (Section 3.2).

3.1. Water adsorption mechanisms in MOFs

Owing to the remarkable features of MOFs, the water adsorption mechanism has drawn significant research attention, which can be divided into three subgroups: I) chemisorption in metallic clusters, II) reversible physisorption in layers or cluster adsorption, and III) irreversible capillary condensation.

Chemisorption in metallic clusters: Due to the accumulation of charges, the unsaturated metal sites in MOFs evolve into strong adsorption nodes [85]. These strong adsorption nodes can form initial adsorption sites, followed closely by the weaker nodes. However, to regenerate MOFs to their full adsorption capacity, extensive extent of thermal energy is needed, which is undesirable for sorption-based applications. Besides, some studies have reported that the repeated adsorption/desorption of vapor molecules on these sites may lead to gradual degradation [56, 86].

Physisorption in layers or cluster adsorption: Surface water molecules initially gather at the hydrophilic surface sites (i.e. hydroxyl), followed by the adsorbed water molecules acting as nucleation sites to grow into large water clusters (nucleation growth process). As these clusters connect with each other through the surface or pores (pore filling process), the continuous moisture transfer is observed to occur [87]. This mechanism is similar to other conventional materials like activated carbon, and observed in some MOFs as well.

Capillary condensation: As some porous materials have a hysteretic capillary condensation phenomenon, the definition of critical diameter indicates that the capillary condensation in desiccants with certain pore size is generally accompanied by a hysteresis loop in the isotherms [51]. In contrast to pore filling, it should be noted that the capillary condensation is an

irreversible process. As for MOFs with pore size <2nm, the presence of hysteresis is generally assigned to the deformation of inner frameworks [88].

3.2. Selection criteria for MOF desiccants

MOFs with special intrinsic properties and adsorption mechanisms have been identified in the previous sections. Here, the selection criteria were discussed in detail to further elucidate the assessment of MOFs. To do so, some criteria related to material properties have been presented, namely stability, performance and safety. Other factor such as scalability belongs to the manufacturing technologies depend on the improvement of industrial level.

3.2.1. Stability

In many cases, the employment of MOF materials is held back due to the weak long-term stability. In built environment, the MOF material may quickly break down after moisture exposure, thus, it is preferable to identify the promising candidates based on the stability studies reported in literature. Previously, the stability of MOFs upon exposure to water in vapor and liquid phase has been reviewed in ref. [14], based on which the relationship between the structure and stability has also been discussed with respect to metal-ligand bonds and degradation mechanisms (including ligand displacement and hydrolysis) [29, 89-96]. Moreover, a comprehensive review of heat pumps using MOF desiccants is also available [16]. Burtch et al. have expediently identified MOF water stability in the thermodynamic and kinetic regimes, as shown in Fig. 1 [17]. However, the balance between thermodynamic and kinetic control over MOF water stability remains under debate [97].

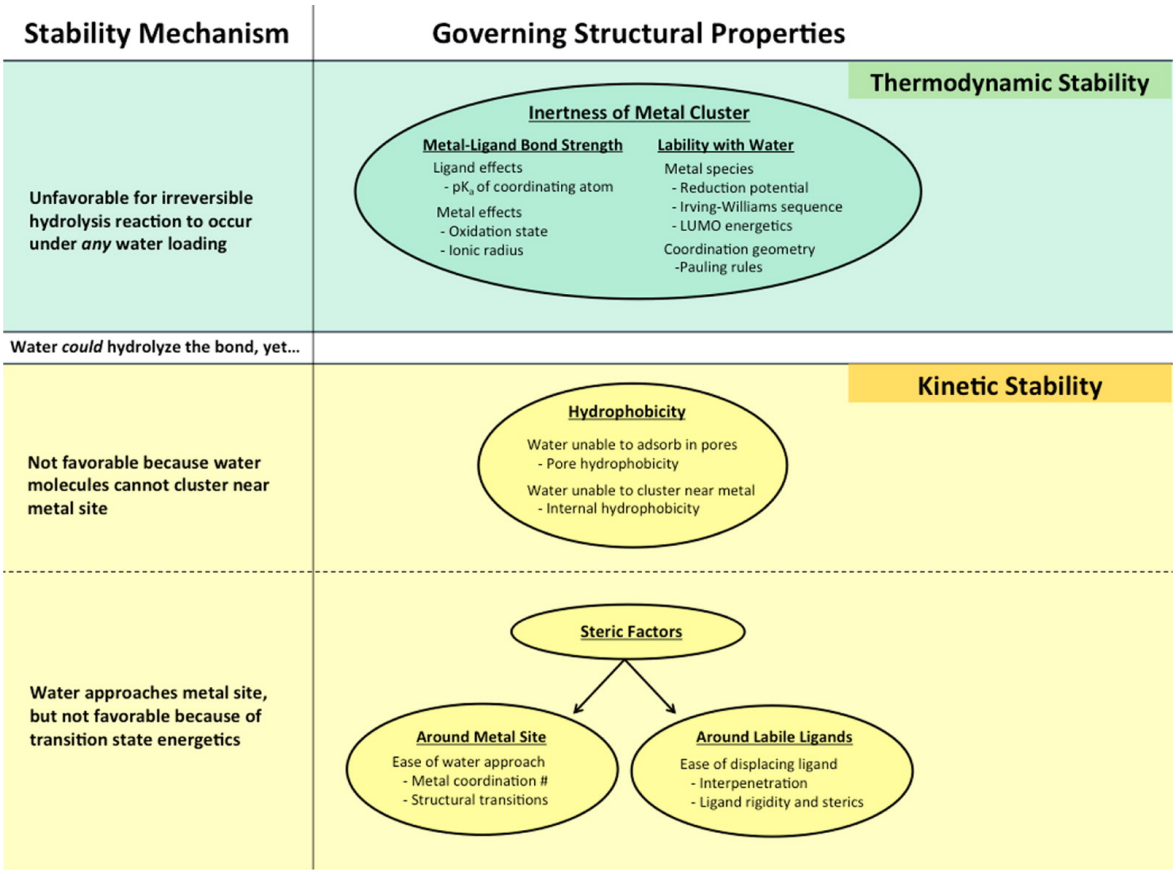


Fig. 1. Structural factors affecting MOF water stability [17].

Thermodynamic stability relates the free energy in a hydrolysis reaction to the structural properties of MOFs. In other words, the inert degree of the metal cluster directs the coordination with water, followed by the destruction of the crystal structure. It is believed that a thermodynamically stable MOF can maintain the framework avoiding breakdown after a long-time exposure to moisture, and it is concluded to contribute to the strength of metal-ligand bond [89, 95, 98] and the lability with water [92, 99]. Under a built environment, the thermal stability of MOF materials during moisture transfer still requires further exploitation.

Kinetic stability is dependent on the activation energy barrier related to the specific reaction. Even if a structure may not be thermodynamically stable, high activation energy can still restrict the hydrolysis reaction and keep the structure stable in the presence of water. Here, the

kinetic stability represents the material resistance to water in the vapor phase [100]. In addition, some MOFs have been reported to effectively perform in humid air without any degradation, though breakdown is observed after exposure to liquid water [101]. These MOFs still exhibit strong potential of use in humid air [38, 78, 102].

3.2.2. Performance

With respect to the assessment of a practical system, it is inevitable to mention the water capacity, regeneration condition and sorption dynamics of the desiccant employed. Some research studies have indicated that a regeneration temperature less than 80℃ can lead to significant improvement in the system performance [20]. High water capacity and dynamic sorption instead can reduce the time spent in the periodic cycles or system volume. Consequently, it is desirable to select MOFs with high water capacity and dynamic sorption, along with gentle regeneration condition.

Isotherm is a vital tool for characterizing the water capacity and affinity to water vapor for the desiccant materials [51]. It is known that the water capacity and affinity to water vapor can affect the adsorption and desorption process. High affinity between the water vapor and desiccants indicates the difficulty for the adsorbed water molecules to break away from the formed chemical bonds, thus, signifying a strict regeneration condition. In Fig.2, IUPAC (International Union of Pure and Applied Chemistry) has classified isotherms for thermodynamic analysis [103]. However, only desiccants (e.g. MOFs) with type V isotherm (sigmoidal or S-shaped curve, which enables a sharp change within a narrow P/P_0) are the optimal candidates for sorption-based systems [11]. A sharp increase in adsorption capacity at low RH is the characteristic of highly hydrophilic desiccants, as presented in Type I, II, IV and step-like Type VI isotherms. These desiccants (e.g. zeolite (I) and silica gel (II)) generally

require more energy to drive the regeneration process. Type III isotherm belongs to the hydrophobic group, which is not suitable for the system operation due to the higher trigger point (P/P_0). Thus, the selection criteria should at least meet >0.2g_{H2O} g-1 water capacity and <90℃ regeneration condition.

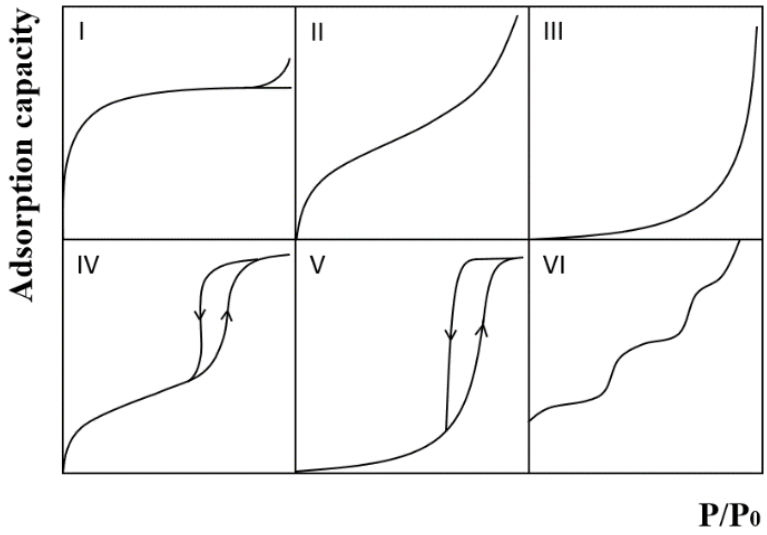


Fig. 2. Classification of isotherms based on IUPAC (International Union of Pure and Applied Chemistry) [103].

With respect to dynamic sorption that indicates the adsorption and desorption equilibrium in cycles, Thomas et al. initially investigated the adsorption performance of traditional desiccants [104]. Afterwards, many research studies have reported experimental analysis on activated carbon and silica gel [105, 106]. Recently, the dynamic nature of the MOF materials has been evaluated by means of *in-situ* EDXRD [58], thermogravimetric analysis [107], etc. Solovyeva et al. have reported the high potential of MOF-801 in adsorption cooling through water adsorption dynamics [73]. In this regard, the dynamic nature of MOFs correlated to material properties of heat and mass transfer can help to anticipate the future applications [64, 72, 108, 109].

3.2.3. Scalability

The translation of novel materials into practical technologies faces the challenge to produce MOFs at the required scale and quality. For the built environment, an open SDS generally requires MOFs at the kilogram or ton scale to regulate the latent load, which is quite different from the gram-scale production of MOFs in laboratory. Recently, factors affecting the scale-up methods have been comprehensively reviewed, and two aspects can be concluded [110]: synthesis process and raw materials. Normally, a complete synthesis process includes synthesis and post-synthesis. The development in the chemical synthesis methods of MOFs have been discussed for the past 20 years (See Fig. S1, Supporting Information). It is desirable that the emerging methods are capable to significantly reduce the time spent in the chemical reactions [111]. After synthesis, careful processing is required in order to qualify the materials, as shown in Fig.3. Here, processes such as washing and activation lead to the extension of the cycle time. Thus, meaningful studies on shorting the post-synthesis processes are needed. On the other hand, raw materials correspond to the possibility of large-scale preparation of MOFs. It is encouraged to use cost-effective and environmentally friendly raw materials to obtain the functional MOF materials. To date, large-scale production of some MOF materials has been reported [6, 16, 44,112,113].

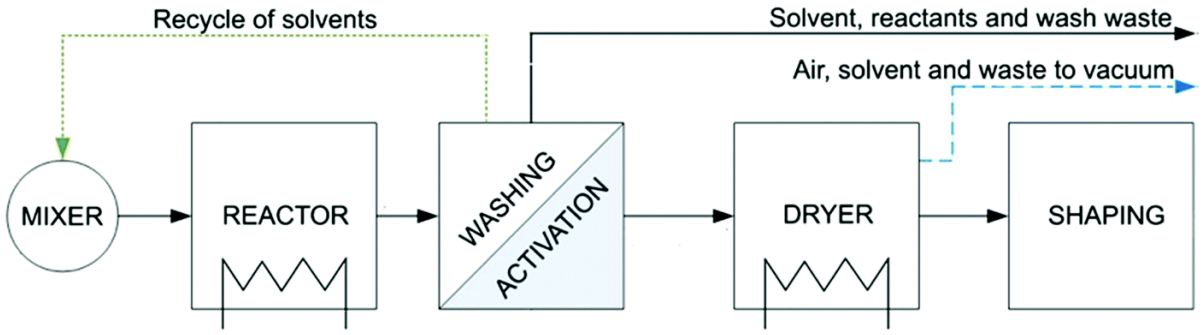


Fig. 3. Basic processes for MOF production [110].

340 3.2.4. Safety

341 Toxicity of MOFs is one of the most important concerns, as these materials may be harmful to
342 human health on direct contact. The selection of green materials should be of high priority for
343 specific applications. Thus, among the raw materials for MOF synthesis, the use of
344 environmentally unfriendly ingredients should be reduced or avoided. Green transition metals
345 such as Al, Fe, Zr and Cu have been widely recognized as alternatives to Cr-based MOFs due
346 to the low toxicity and cost [35, 114-116]. Green solvents are also employed during MOF
347 synthesis. Some of the accepted green solvents such as water, ethanol, ethyl acetate, etc., are
348 highly recommended, and less green solvents including formic acid, dimethyl sulfoxide,
349 dimethyl formamide, etc., should be used in moderation [32, 35]. In short, natural or biomass-
350 based products are good candidates to generate ideal MOFs using low-toxicity metal clusters.
351 Besides, it is noteworthy that other safety hazards such as inflammability and bacteriostatic
352 activity all have certain effects on the quality of the built environment.

353

354 **4. Material-level water vapor capture of MOFs**

355 As many MOFs have desired water uptake and regeneration condition, care is necessary to
356 screen the MOFs suitable for the specific use under specified conditions. Many literature
357 studies have reported the MOF materials for water harvesting in water scarcity regions and heat
358 transformation in heat pumps [23, 27, 32, 81, 117]. As an open SDS employed for humidity
359 regulation of the built environment, it is noteworthy that different MOFs may correspond to
360 different trigger points, corresponding to different climate conditions. Based on the
361 classification of the trigger point, MOFs with the following features are focused in this section
362 (*material level*): 1) high water uptake (more than 0.2 g g^{-1}) and stability, 2) gentle regeneration
363 condition, and 3) steep rise in water uptake.

4.1. Low range (<30% RH)

Desiccants with high water uptake at the low relative pressure have strong affinity towards water molecules, generally requiring strict regeneration conditions. In comparison with the traditional desiccants such as silica gel, zeolites, etc., many MOF materials with low trigger point can still have a low regeneration temperature and high water uptake. With these properties, active SDS can significantly improve the system performance, while passive SDS can maintain the low RH level, which is a requirement in some special installations. The humidity control can effectively avoid, for example, ageing of the batteries in battery factories and deterioration of artefacts in museums [118]. Thus, the search for MOFs with low trigger point P/P_0 in isotherms deserves more intensive efforts.

CAU-10 (CAU: Christian Albrechts University) is a kind of porous aluminum isophthalate, which combines aluminum clusters with BDC (1,3-benzene dicarboxylic acid) ligand. As a commercially available MOF, the synthesis method has been greatly improved by substituting toxic DMF-water solvent (dimethylformamide) with green options [32]. In the framework of CAU-10, corner-sharing AlO_6 polyhedra are connected with each other, forming a helical arrangement and square channels with up to 0.7nm pore diameter [19, 38]. Fröhlich et al. [119] were the first to investigate the hydrothermal stability through 700 adsorption-desorption cycles with no observed irreversible degradation, as shown in Fig.4 (a). A 0.34 g g^{-1} of water uptake at thermodynamic equilibrium has been observed, accompanied by 0.18 P/P_0 trigger point in the isotherm. CAU-10 coated adsorption chillers [32] have been subsequently prepared, which indicates that a regeneration temperature of 70℃ can generate a specific cooling power over 1200W kg_{ads}^{-1}. Additionally, several functional groups in the ligands have also been

investigated, such as CAU-10(-OH, -OCH_3, -NO_2). Reference [38] presents different shapes of isotherms with even less water uptake at adsorption equilibrium, as shown in Fig.4 (b), probably resulting from the change in pore volume and heterogeneous character.

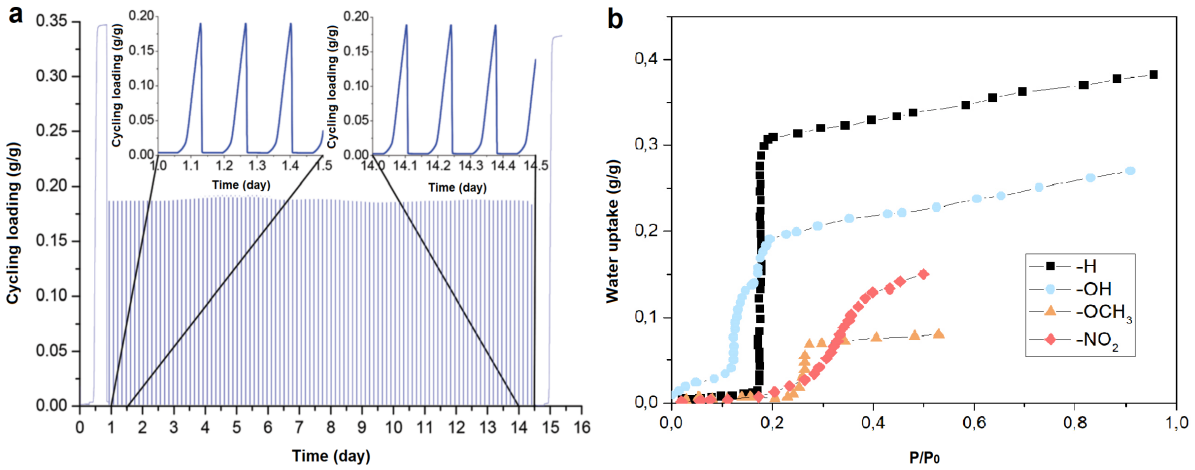
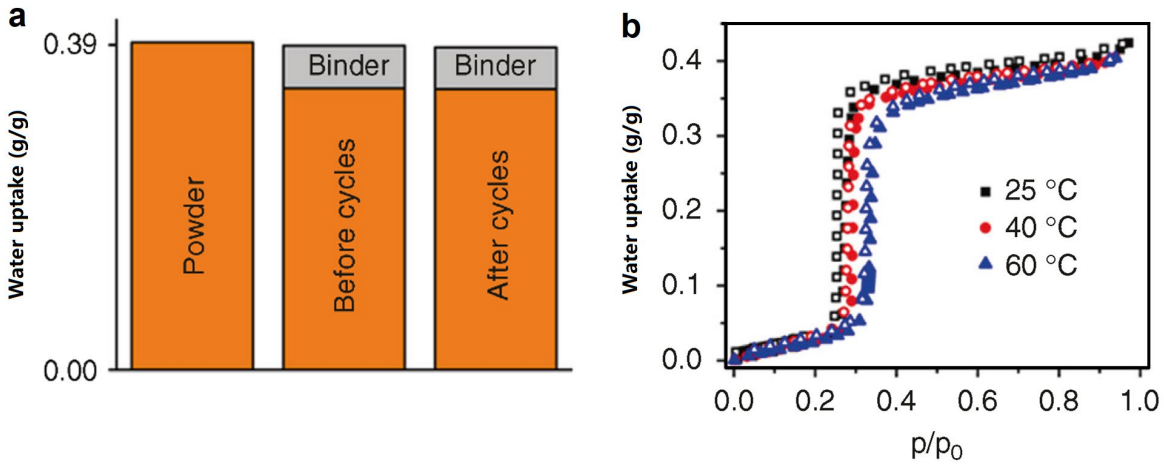


Fig. 4. (a) Cycling performance of CAU-10 [119] and (b) water adsorption isotherms with different functional groups (25℃) [38].

CAU-23 is a new class of Al-based MOF with TDC (thiophene-2, 5-dicarboxylic acid) as its ligand. A recent study has indicated that CAU-23 can be synthesized using a green and scalable method by using water as the only solvent, and it is stable in air up to 400℃, thus, exhibiting high thermal stability [20]. In the three-dimensional structure of CAU-23, the metal cluster unit comprises of the combination of helix and straight AlO_6 polyhedra, joined with TDC to form square channels. CAU-23 has been tested for 5000 cycles with nearly no loss in water uptake as shown in Fig.5 (a). Water isotherm indicates that a maximum water uptake of 0.43g g^{-1} can be obtained without hysteresis loop at room temperature. Correspondingly, the trigger point is noted to be around 0.24 P/P0. Besides, the findings from the desorption analysis have pointed out an ultralow regeneration temperature of <60℃ for the adsorption-driven chillers, along with a cycling water capacity of 0.37g g^{-1} [20]. As the temperature increases, the trigger point

406 of the isotherms in Fig.5 (b) is observed to move right to a larger P/P_0 with lower water capacity.
407 Other analogues of CAU-23 such as CAU-22 [120], CAU-28 [121] and CAU-39 [122] are
408 more or less limited by the low hydrothermal stability or low uptake capacity.



409

410 **Fig. 5.** (a) Water uptake of CAU-23 coatings before and after 5000 cycles and (b) water
411 adsorption/desorption isotherms of CAU-23 at different temperatures [20].

412

413 MIL-53 (Al, Fe, Cr) [MIL: Material Institut Lavoisier] is one of the most frequently
414 investigated MOF series. Among the various analogs, MIL-53 (Al) is currently produced at
415 industrial levels and features corner-sharing AlO_6 chains connected by terephthalate ligands in
416 the crystal structure. To date, MIL-53(Al) has been prepared at large scale by sole use of water
417 as solvent, however, the recorded water capacity is far less than 0.2 g g^{-1} [123]. Subsequently,
418 Alvarez et al. have investigated a new MOF [114], MIL-53-FA (or aluminum fumarate), which
419 has an isoreticular structure to MIL-53(Al). Although these have similar cornering-sharing
420 aluminum-based octahedra, MIL-53-FA uses fumarate as its ligands. As a commercially
421 available product with green synthesis, MIL-53-FA has been widely applied for gas storage and
422 water vapor capture [71]. Henninger et al. [18, 52] also reported the highly stable nature of the
423 hydrophilic MIL-53-FA. As shown in Fig. 6, the cycling adsorption capacity is observed to be

constant at around 0.37g g^{-1} after 4500 cycles. The isotherm shows a steep rise in water uptake between 0.2-0.35 P/P_0. Regeneration at 90℃ achieved the release of more than half of the adsorbed water molecules within several minutes, which is superior to the zeolites (>100℃).

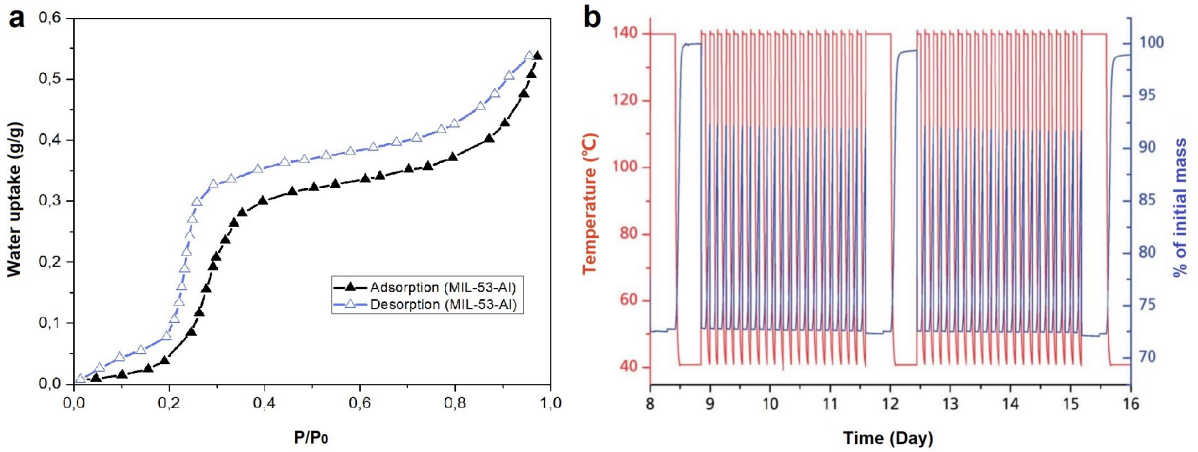


Fig.6. Water adsorption/desorption isotherms of MIL-53-FA at 25℃ [48] and cycling tests [52].

Serre et al. reported hydrophilic MOF (MIL-160), a promising material for heat reallocation, which consisted of aluminum ions and FDCA (2, 5-furandicarboxylic acid, derived from renewable biomass feedstock) ligand [25]. As an isostructure to CAU-10, hydrothermally stable MIL-160 has helically cis-connected chains with four surrounding carboxylates forming square-shaped channels as shown in Fig. 7. The subsequent studies indicated that MIL-160 with 0.5nm pore size outperforms CAU-10 in surface area and pore volume [25]. Though the water uptake of MIL-160 is almost identical to CAU-10, its 0.05 P/P_0 trigger point exhibits better hydrophilicity than 0.16 P/P_0 for CAU-10 due to the presence of many hydroxyl groups at the pore surface. The measured water uptake is around 0.37 g g^{-1}, and most of the water adsorption is below 0.18 P/P_0. The high water affinity enables a heat source around 363K (90℃) to achieve the release of 75% of the water molecules (regeneration). Lately, the authors

have also investigated the energy-storage capacity and cycling loading lift of MIL-160, which are noted to be 6 times as compared to zeolite 13X [124]. Based on these features, MIL-160 is a promising desiccant for adsorption heat transformation (i.e. heat pump) [125] and even in places requiring an ultralow relative humidity with gentle regeneration condition.

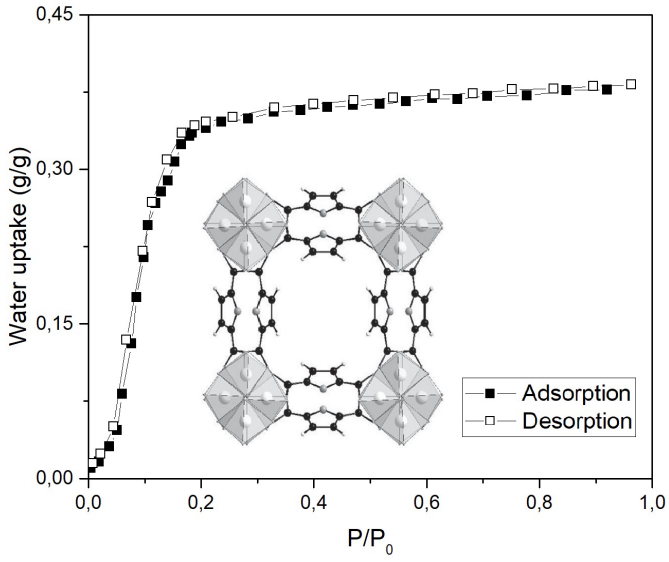


Fig. 7. Water adsorption/desorption isotherms for MIL-160 [25].

MIL-125-NH_2 is a Ti-based MOF comprised of titanium clusters and BDC-NH_2 (2-amino benzene dicarboxylic acid) with two types of cages (0.51nm and 1.25nm). Since Dan-Hardi et al. [126] reported the synthesis of highly porous MIL-125, the ligand functionalization has been applied to generate MIL-125-NH_2 [127, 128]. MIL-125-NH_2 has a three-dimensional bipyramidal structure with $Ti_8O_8(OH)_4$ as metal node connected with eight BDC-NH_2 ligands. It is reasonable to expect a reduction in pore size and surface area owing to the introduction of the amino group, but isotherms exhibit an obvious increase in the water uptake for MIL-125-NH_2 compared to unusual adsorption and desorption behavior of MIL-125. This indicates that MIL-125-NH_2 is more hydrothermally stable in presence of water [129]. A recorded 0.67 g g^{-1} water uptake with 0.2 P/P_0 trigger point in Fig.8 confirm the competence of MIL-125-NH_2 for

hygrothermal control at low RH range. Kim et al. have investigated its potential use in the adsorption heat transformation, and regeneration at 80℃ with a constant cycling water capacity of 0.45 g g^{-1} at working conditions confirm its superiority as compared to most of the currently used desiccants [48].

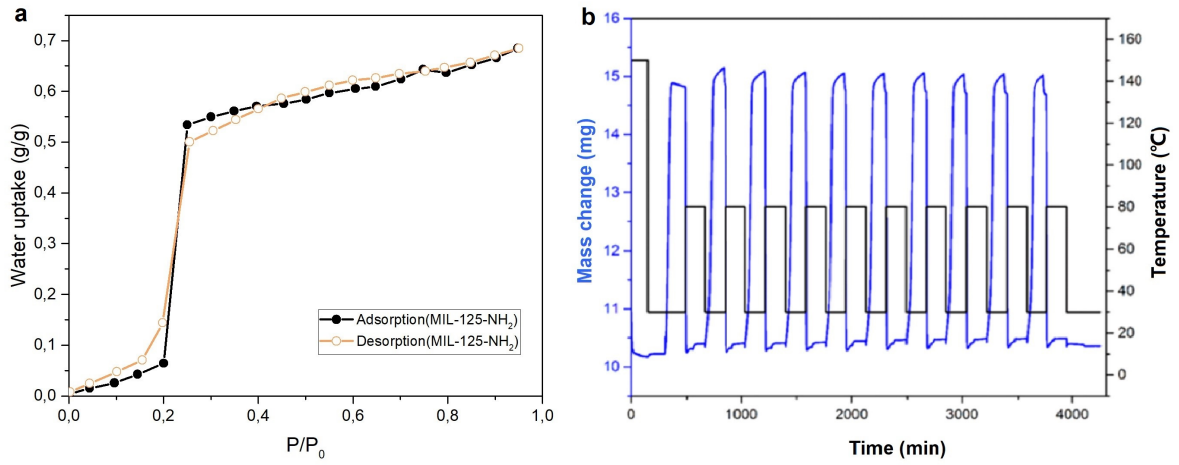
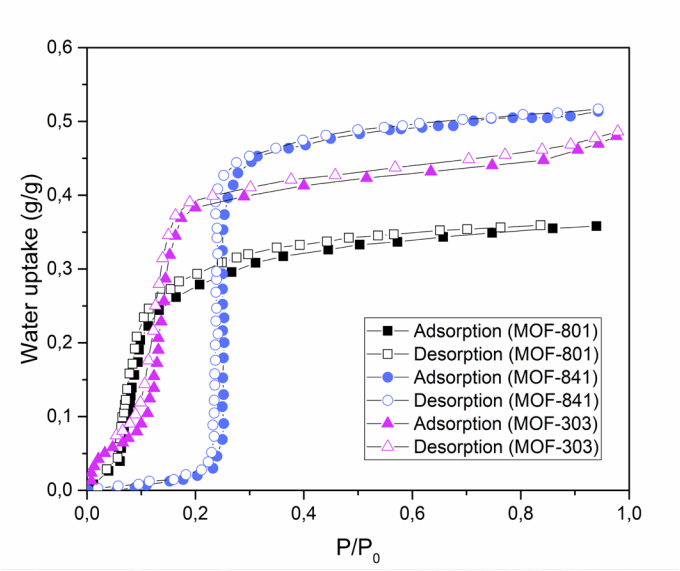


Fig. 8. (a) Water adsorption/desorption isotherms for MIL-125-NH_2 and (b) dynamic water uptake with adsorption at 30℃ and desorption at 80℃ [48].

In recent years, MOF-801 has attracted research attraction for use in applications requiring low RH range, such as water harvesting in deserts. Behrens et al. [36] first reported the preparation of MOF-801 by combining a zirconium cluster (Zr^{4+}) with fumaric acid. The structure of MOF-801 is composed of cubic spaces with three independent cavities, two tetrahedral cavities of size 0.56nm and 0.48nm, and one octahedral cavity with a diameter of 0.74nm. MOF-801 has been demonstrated to be stable in hygrothermal conditions, and its cycling water uptake remains stable after five adsorption-desorption cycles [37]. The adsorption isotherm in Fig.10 displays a steep rise around trigger point (P/P_0) of 0.05 and reaches a saturated state around 0.5, from which a water uptake capacity of 0.36g g^{-1} at room temperature can be observed, greatly outperforming the traditional desiccants (i.e. silica gel). Subsequently, Yaghi et al. have

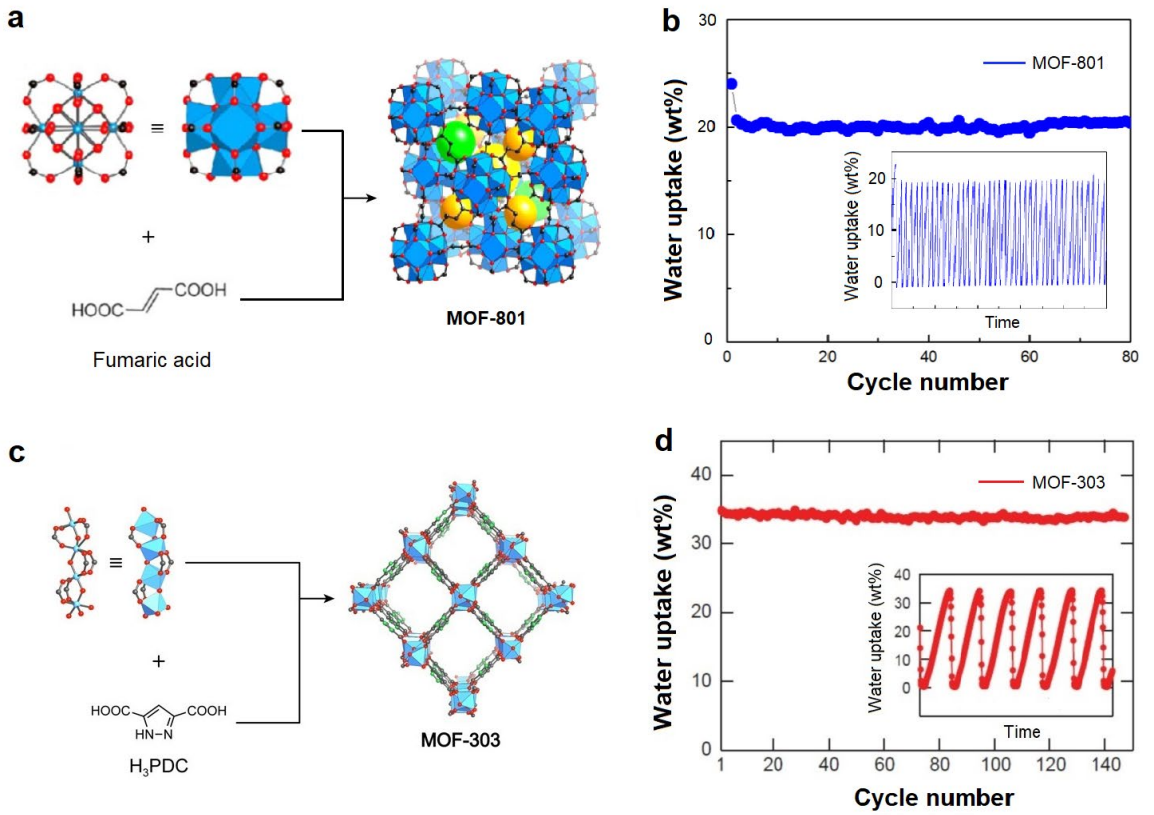
prepared MOF-841 and other analogs such as MOF-802, MOF-805, MOF-806 and MOF-808, however, the latter ones demonstrate unstable water adsorption during initial cycles owing to the loss of porosity [37]. MOF-841 is prepared by employing MTB (4,4',4'',4''-methanetetrayltetrabenzoic acid) as connecting ligand. In the three-dimensional framework of MOF-841, the metal cluster bound with eight ligands constructs the basic structural unit. Cycling performance indicated that MOF-841 exhibits relatively constant adsorption after several cycles. Its steep rise in Fig.9 occurs around 0.26 P/P_0, and it reaches saturation around 0.3 P/P_0, at which the water uptake accounts for nearly 90% of total water uptake (0.5g g^{-1}). Recently, Yaghi et al. [23, 117] applied MOF-801 for water harvesting from air. The experiments were conducted with a regeneration temperature of 65℃, and the set-up was predicted to produce a 2.8L_{water} kg_{MOF}^{-1} each day at 0.2 P/P_0. Based on this study, the authors also developed a next-generation desiccant MOF-303, synthesized by using aluminum-based metal cluster and HPDC [1H-pyrazole-3,5-dicarboxylate] [22]. The green hydrophilic MOF featured pore volume and pore size of 0.54cm^3 g^{-1} and 0.6nm, with up to 0.48g g^{-1} of water capacity. The trigger point is noted to be around 0.15P/P_0, which is comparable to its predecessor MOF-801. In addition, 150 cycling experiments verified the hydrolytic stability of the material owing to no measurable mass loss. Fig.10 shows the evolution and cycling performance of the crystal structure from MOF-801 to MOF-303. MOF-303 with higher cycling water lift is theoretically superior to MOF-801 for humidity regulation.



496

497 **Fig. 9.** Water adsorption/desorption isotherms of different MOFs used for water harvesting

498 [22, 37].



499

500 **Fig.10.** Crystal structure (a and c) and cycling performance (b and d) of MOF-801 and MOF-

501 303 [22, 37].

MIP-200 is a newly developed MOF material constructed using the zirconium cluster and H_4mdip ligand (3, 3', 5, 5'-tetracarboxydiphenylmethane). In the three-dimensional structure, Zr-based metal cluster is connected with eight carboxylate groups and four formate groups, thus, forming a triangular tunnel of 0.68nm and a hexagonal channel of 1.3nm. A surface area of 1000m^2 g^{-1} as well as a pore volume of 0.4cm^3 g^{-1} were measured as well. Serre et al. [46] explored the application of MIP-200 in adsorption-based chillers. From isotherm in Fig. 11, MIP-200 is noted to exhibit high water capacity of around 0.46 g g^{-1}, however, a two steep rise occurred at 0.01P/P_0 and 0.17 P/P_0, respectively. It is also found that the material is stable against different chemicals and temperatures over 300℃. One intriguing property is the facile regeneration temperature below 70℃, which outperforms most of currently reported desiccants, such as MIL-160 (90℃), SAPO-34(~90℃), aluminum fumarate (90℃), etc. [20]. Other family members such as MIP-202, MIP-203 and MIP-204 have also been synthesized. However, the ultra-small porosity limits their application [130].

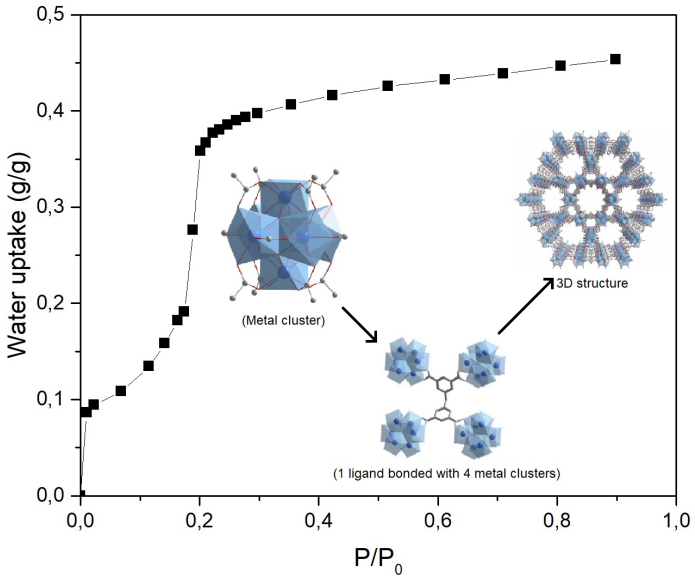


Fig. 11. Water sorption isotherms of MIP-200 at 25℃ [20, 46].

The MOFs described so far represent both widely used desiccants as well as newly developed desiccants. These desiccants feature low trigger point (0-30%), exhibiting great potential of application for the control in built environment. In addition, other promising desiccants such as M_2Cl_2(BTDD) (M=Co, Ni) [26, 39], mixed-metal MOF [10], ZJNU-30 [81], CUK-1[30], etc., demonstrate strong capability for humidity control. The exploitation of these MOFs is still an ongoing research.

4.2. Medium range (30~65% RH)

In the past few years, a few MOFs have been reported with a medium trigger point. Though these MOFs may have weak affinity towards water molecules, the water capacity and regeneration condition are still significant. Hydrophilic MOFs might be preferred for the active systems due to high working efficiency. However, a few studies carried out by using these neutral MOFs have also indicated that these desiccants are well capable of sorption-based heat transformation [27]. One the other hand, as ASHRAE has recommended the comfort zone of relative humidity, >65%RH and <30%RH to a degree make human beings to feel uncomfortable. Materials that can adsorb water vapor at higher humidity levels and desorb it at lower humidity levels can well meet the demand for humidity control in a passive way. Traditional materials have limited performance in both active and passive SDS. Many research studies have focused on exploring neutral desiccants and most of these deserve further study.

CAU-1 was first synthesized by the combination of H_2N-H_2bdc (aminoterephthalic acid) and $Al_8(OH)_4(OCH_3)_8$ (aluminum-based octameric cluster) by Stock et al. [131]. The AlO_6-based octameric clusters are connected to other units to form two types of cages, an octahedral cage

of 1nm and a tetrahedral cage of 0.5nm. The remarkable water uptake at 25℃ is recorded around 0.55g g^{-1} [77, 132], and the TGA data exhibit that the material can keep stable under hygrothermal conditions and preserve its framework up to 310℃ [131]. Subsequently, a new Al-based MOF named CAU-3 has been synthesized, which exhibits water uptake of up to 0.51 g g^{-1}. However, the thermal stability tests indicate that the decomposition of framework may occur in air under 200℃ [133]. Reinsch et al. have reported the green synthesis of CAU-15-Cit [134]. CAU-15-Cit exhibited a 23.8% water uptake at the trigger point of 0.5P/P_0, and the powder X-ray diffraction (PXRD) disclosed the reversible de- and rehydration behaviors, which greatly outperform the unstable form CAU-15 [135].

As a member of DUT series (DUT, Dresden University of Technology), DUT-68 has been synthesized by using TDC (2, 5-thiophenedicarboxylate) as ligand with different metal clusters (Z-based and hf-based). Senkovska et al. [136] reported the structure of DUT-68 to contain a complicated pore system with four types of pore size (0.8nm, 1.25nm, 1.39nm and 2.77nm). From water adsorption studies, it is observed that a steep rise in water uptake takes place at 0.38P/P_0 exhibiting a value of 0.29 g g^{-1}, along with structural stability verified by using repeated water adsorption tests. Besides, it is noted to adsorb nearly 40% of total water uptake at <30% RH, which may result from the complex hierarchical pore system. Recently, an insight into water adsorption by DUT-67 has been proposed for exploring its potential in adsorption-based heat transformation. Bon et al. [49] conducted more than 20 adsorption-desorption cycles to prove its stability and investigated the pore filling process through neutron powder diffraction. In comparison with the other Zr-based DUT-68, Fig.12 indicates that DUT-67 has a water capacity of 0.44g g^{-1} at 0.6 of P/P_0 with a steep rise in relative pressure range 0.3-0.4. In this respect, DUT-67 is confirmed to be potential desiccant for water adsorption [31]. Other

DUT series such as DUT-52, DUT-53 and DUT-69 have been prepared. Though a few of these may have S-shaped adsorption isotherms, the shape of desorption branch is significantly different from Type-V isotherms, thus, these are not suitable for humidity control [49, 136].

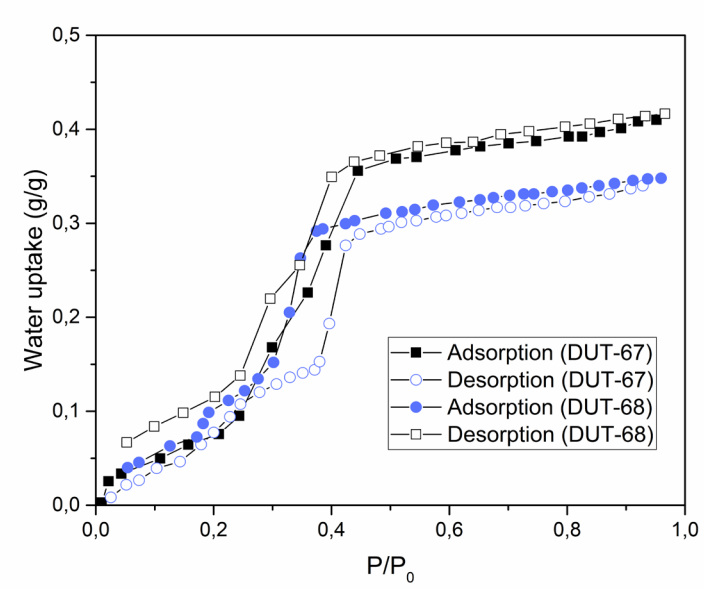


Fig.12. Water adsorption/desorption isotherms of water-stable DUT series [49].

MIL-100 is one of the most studied MOF benchmarks for water adsorption applications. To date, three metal elements such as Fe, Al and Cr have been mostly used with BTC (1,3,5-benzene tricarboxylic acid) as ligand to prepare MIL-100 series. Since Férey et al. [137] reported the three-dimensional (3D) structure of MIL-100(Cr), a corner-sharing tetrahedral MOF(Cr) with 2.5-3nm and 0.65nm sized mesopores and micropores respectively, many research studies have reported the stability for water adsorption, along with its application in sensible and latent load control [40, 138]. Kitagawa et al. [40] conducted more than 2000 adsorption-desorption cycles with no observed structural decomposition, and the water uptake was maintained at 0.8g g^{-1}. However, the undesirable isotherms have also driven the efforts to graft some hydrophilic groups on the coordinately unsaturated metal sites to tune the isotherm shape of MIL-100(Cr). The introduction of hydrophilic groups tunes the hydrophilicity of MIL-

583 100(Cr), however, decreases the surface area and pore volume, thus, resulting in different
584 trigger point (P/P_0) as well as water uptake capacity [139].

585

586 In addition, considering the potentially harmful chromium compounds, Horcajada et al. have
587 successfully synthesized Fe-based MOF, MIL-100(Fe) with non-toxic nature [140].
588 Subsequently, Henninger et al. [27] have used MIL-100(Al, Fe) for heat transformation
589 applications. From the comparison of isotherms in Fig.13, the water uptake of 0.77g g^{-1} for
590 MIL-100(Fe) is noted to be superior than 0.5g g^{-1} for MIL-100(Al) with, and all of the studied
591 MOFs bear hydrothermal cycling stability under 40 cycling experiments (6.4% loss for MIL-
592 100(Fe) and 6.6% loss for MIL-100(Al)), as shown in Fig.14. From the adsorption behavior, it
593 is interesting to find two step steep rise at 0.24 and 0.35P/P_0 for MIL-100(Fe, Al), respectively,
594 which is similar to 0.24 and 0.38P/P_0 observed for MIL-100(Cr). The observed behavior is
595 explained as follows: the open metal sites start adsorbing a fraction of water molecules below
596 0.2P/P_0, and subsequently the two steep rise steps contribute to the sudden adsorption in the
597 cage of different size [45]. The resulting features therefore render MIL-100 series very
598 interesting alternatives for sorption-based heat and humidity control.

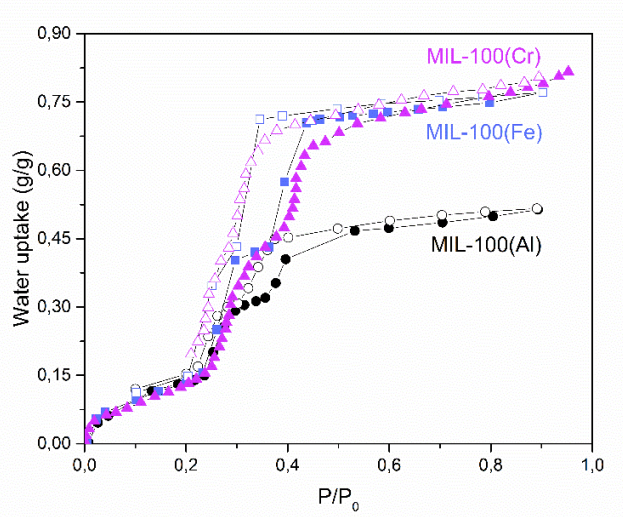


Fig. 13. Water adsorption/desorption isotherms of MIL-100 (Al, Cr, Fe) [27, 40, 138].

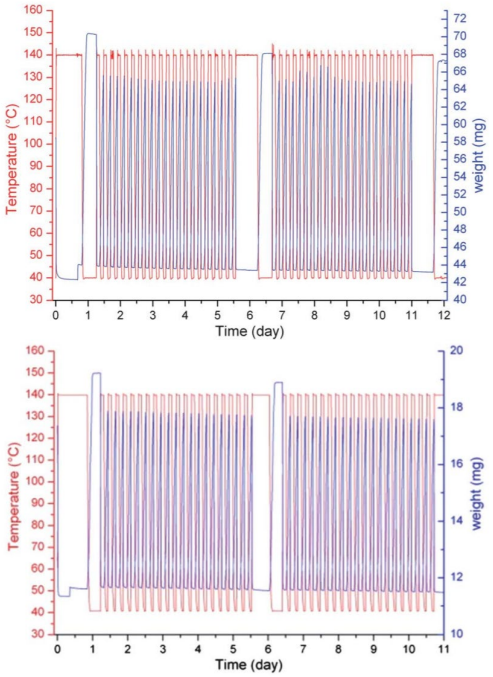
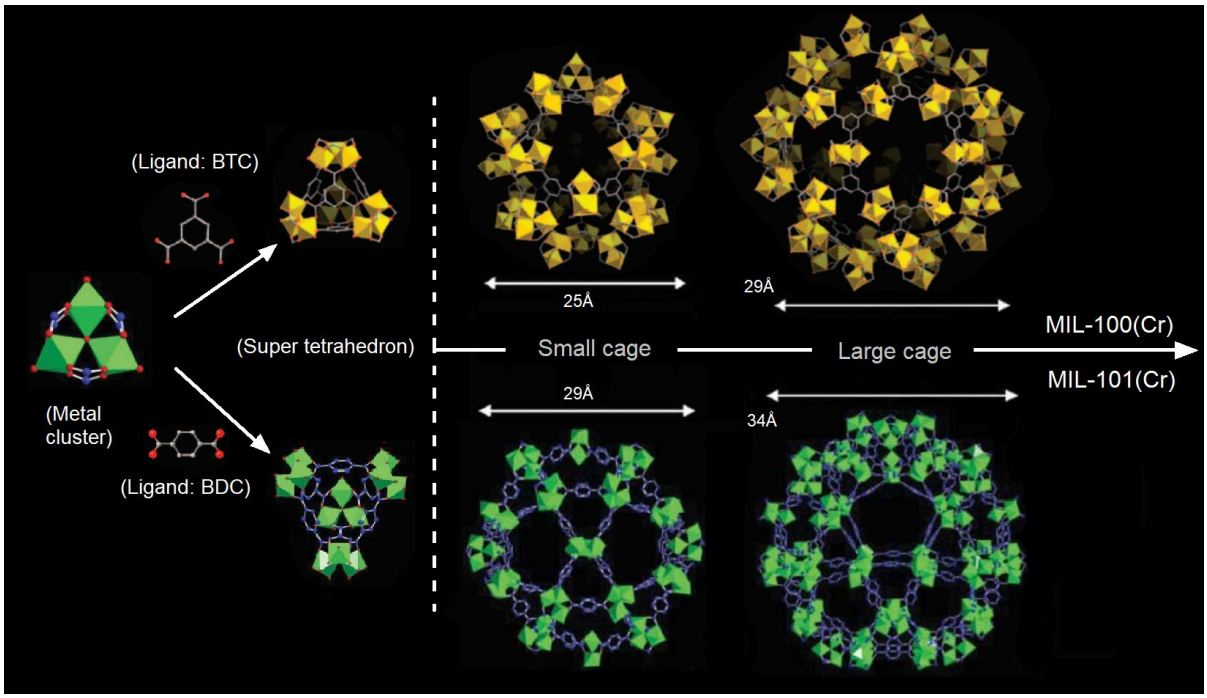


Fig. 14. Temperature profiles and mass loading of MIL-100 (Al, Fe) in cyclic tests [27].

599

600 MIL-101 was first prepared and reported by Férey et al. [41] with 5900 m^2 g^{-1} surface area and
601 2.9-3.4nm pore size. The three-dimensional structure is constructed by joining Cr-based
602 inorganic trimers (octahedra) with ligand 1, 4-BDC (1, 4-benzenedicarboxylate) to form a super
603 tetrahedron, which is closely related to the structure of MIL-100, as seen in Fig.15. With an
604 aim to surpass its predecessor's merit of reversible water adsorption, Henninger et al. [29]
605 evaluated MIL-101(Cr) and pointed out its more desirable isotherm, with a steep rise at $0.4P/P_0$.
606 The results indicated nearly 1g g^{-1} of cycling water loading under a typical condition with only
607 3.2% of loading loss after 40 cycles on applying MIL-101(Cr) in a heat-transformation cycling
608 system. Thus, MIL-101(Cr) is confirmed to demonstrate high water loading along with strong
609 hydrothermal stability. Fig.16 shows several isotherms extracted from the literature studies
610 indicating ultrahigh adsorption capacity of MIL-101(Cr) with a maximum value reaching up

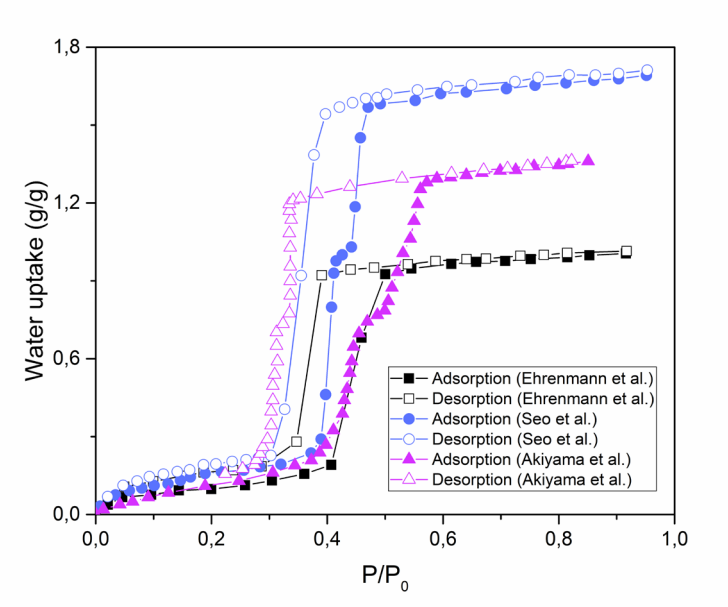
611 to 1.6g g^{-1} [28, 57, 78]. Owing to the larger pore size (>2nm), hysteresis loops occurred in
612 isotherms, therefore reducing the usable loading lift in active SDSs. Kitagawa et al. [57] also
613 examined the adsorption/desorption behavior of functionalized MIL-101 derivatives. These
614 compounds with different substituents (-NO_2, -NH_2, -SO_3H) are noted to reach a water capacity
615 in the range 0.8-1.2g g^{-1} with great stability and regeneration under 80℃ [28, 57]. Different
616 from MIL-100 series, little research has been carried out on MIL-101 analogues with different
617 metal clusters (i.e. Fe^{3+}, Al^{3+}) due to the hydrolysis.



618

619 **Fig.15.** Structure of MIL-100(Cr) and MIL-101(Cr) [6, 141].

620

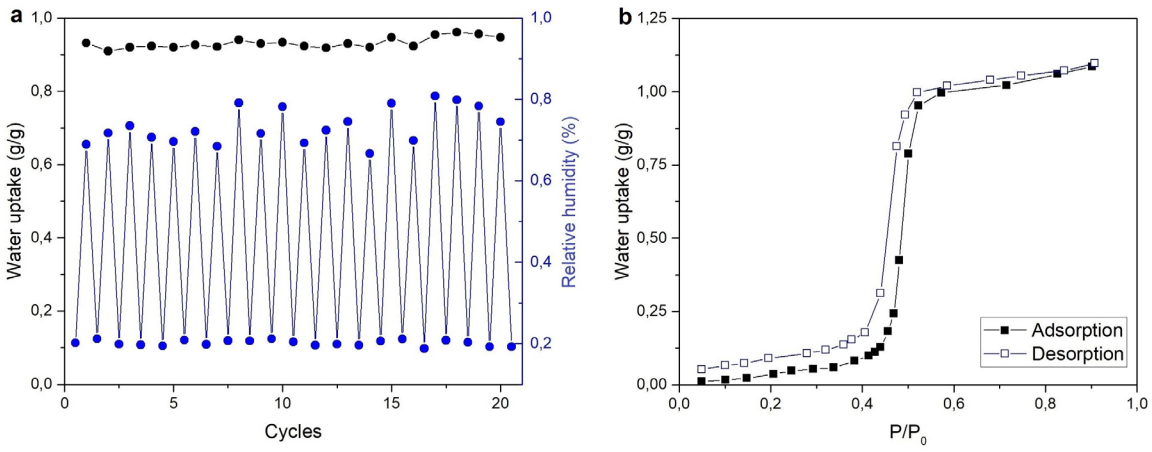


621

622 **Fig. 16.** Water adsorption/desorption isotherms of different MIL-101(Cr) samples [29, 57,
623 78].

624

625 Many MOFs based on NU series (NU, Northwestern University) have emerged recently,
626 however, their use for water adsorption has been limited except NU-1500 [142, 143]. Farha et
627 al. [83] reported that NU-1500 consisted of trivalent trinuclear metal cluster (Fe^{3+}, Sc^{3+} and
628 Cr^{3+}) and trigonal prismatic ligand, while the Cr-based NU-1500 was also noted to exhibit
629 water stability after 20 cycling experiments. In Fig.17(a), water adsorption capacity of NU-
630 1500 is observed to approach 1.09g g^{-1} without hysteresis loop between the adsorption and
631 desorption branches. This may have resulted due to only one kind of small hexagonal channels
632 with a 1.4nm of pore size. The trigger point in Fig.17(b) is around 0.45P/P_0 followed by a
633 narrow steep rise. Consequently, compared with more hydrophilic MOFs (low trigger point),
634 it is reasonable to predict that NU-1500 can be desorbed using a gentler regeneration condition
635 in heat-transformation application.

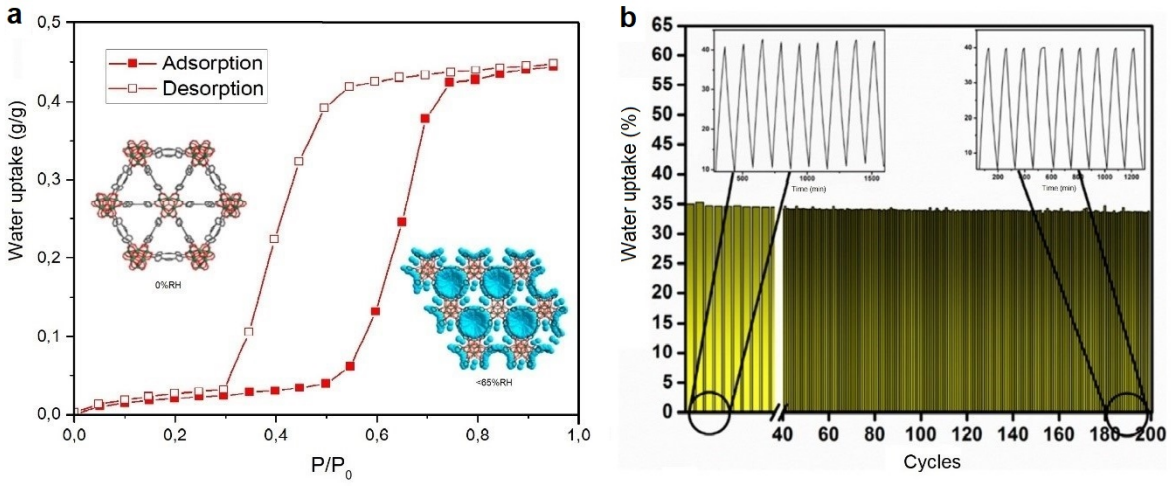


636

637 **Fig.17.** Water adsorption/desorption isotherms and cycling tests between 20%-80%RH [83].

638

639 Recently, two excellent MOFs aimed towards autonomous indoor humidity control have been
640 proposed, namely, Y-shp-MOF-5 and Cr-soc-MOF-1. Y-shp-MOF-5 is the rare earth metal-
641 based MOF composed of the yttrium-based metal cluster and tetratopic ligand [BTEB, 1,2,4,5-
642 tetrakis(4-carboxyphenyl) benzene]. Eddaoudi et al. [21] have evaluated the water
643 adsorption/desorption isotherms and cyclic behavior of hexagonal prism-shaped Y-shp-MOF-
644 5. The trigger points of adsorption and desorption branches are 0.56 and 0.47P/P_0 respectively,
645 as shown in Fig.18(a), after which two steep rise steps occur within 30%-47% RH and 56%-
646 70%RH. The water uptake is noted to reach up to 0.45g g^{-1}, which indicates superior
647 performance as compared to most traditional desiccants. In addition, 200 adsorption-desorption
648 cycles display its stable water uptake variation for relative humidity between 25%-85%
649 (Fig.18(b)), exhibiting the capacity to regulate the humidity within a desirable range.



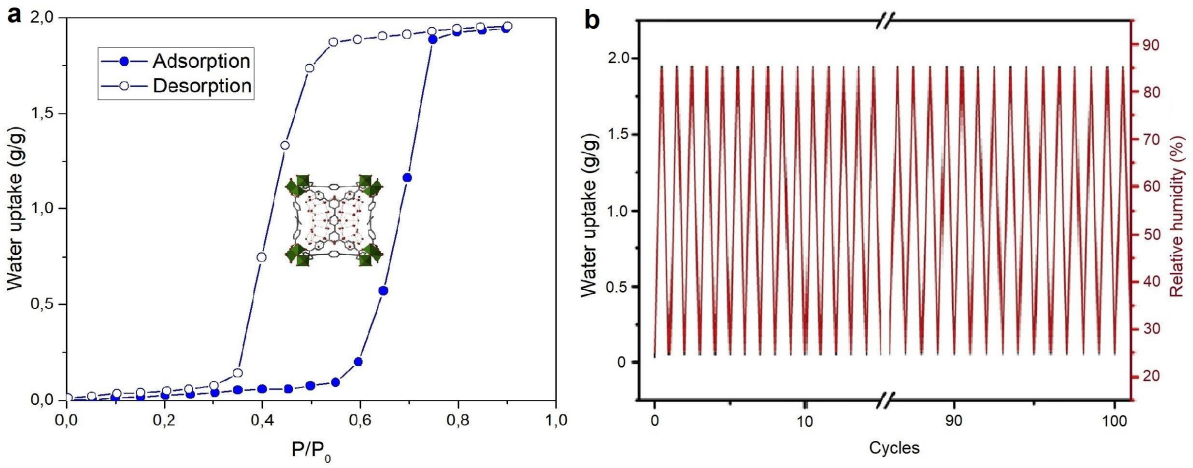
650

651 **Fig.18.** (a) Water adsorption/desorption isotherms of Y-shp-MOF-5 and (b) 200 cycles in the
652 relative humidity range between 25% and 85% [21].

653

654 Cr-soc-MOF-1 is the other MOF with potential for autonomous humidity regulation. Eddaoudi
655 et al. [42] reported this hydrolytically stable material together with its remarkable water
656 capacity (~1.95g g^{-1}), much better than the MOFs reported so far. Cr-soc-MOF-1 consists of
657 the trinuclear chromium cluster and deprotonated organic ligand (TCPT; 3, 3'', 5 , 5''-
658 tetrakis(4-carboxyphenyl)-p-terphenyl), developed through post-synthetic modification of Fe-
659 soc-MOF-1. The isotherm in Fig.19(a) indicates its intriguing ability for the passive control of
660 indoor humidity load in view of the strong hydrolytically stable nature, with 3 times higher
661 working capacity (1.95g g^{-1} at $0.7P/P_0$) than the predecessor, Y-shp-MOF-5, at room
662 temperature (298K). The rectangular hysteresis loop with two trigger points in adsorption
663 ($0.6P/P_0$) and desorption ($0.42P/P_0$) branches comply with the recommended comfort zone by
664 ASHRAE. Besides, the adsorption-desorption cycles were conducted to confirm the durability
665 of the material within 25%-85% humidity level at room temperature. After 100 cycling
666 experiments as shown in Fig.19(b), the water capacity remained unchanged, which indicated
667 that the adsorbed water molecules can be desorbed at 298K by lowering the humidity level.

668 However, the hydrothermal stability at different temperatures is required for active control in
669 SDSs.



670

671 **Fig.19.** (a) Water adsorption/desorption isotherms of Cr-soc-MOF-1 and (b) 100 cycles in
672 relative humidity range between 25% and 85% [42].

673

674 On the basis of the previous discussion, the relatively hydrophobic MOFs have less affinity
675 towards water molecules, thus these theoretically allow swift release of the adsorbed water
676 molecules. In fact, little research has been carried out to investigate the active heat
677 transformation owing to the low water uptake at the low relative pressure range. Moreover,
678 most of these MOFs have an unwanted hysteresis loop, which reduces the actual loading lift.
679 Luckily, the design and synthesis of these MOFs with hysteresis loop is potentially qualified
680 for the autonomous humidity regulation in a built environment. The benchmark material Y-
681 shp-MOF-5 [21] and its successor Cr-soc-MOF-1 [42] have been the most mentioned for the
682 passive control of indoor humidity load in open SDSs due to their desirable isotherms, high
683 hydrolytical stability and water uptake. However, these materials have undesirable metal
684 clusters (i.e. Y, Cr), which may limit their application range. Moreover, further cycling
685 experiments under different temperature pairs (adsorption-desorption) are needed to be

conducted to evaluate their hydrothermal stability for active SDS systems. Besides, other water stable materials such as MAF [79], DMOF [89], Ni-BPP [33], BUT [76] and functionalized MOFs [62, 144] have been developed, all of which need further intensive studies for passive and active humidity control.

4.3. High range (>65%RH)

Some MOF materials with the adsorption process starting after 0.65 P/P_0 trigger point have also been synthesized. Compared to the earlier-mentioned MOFs, these ultra-hydrophobic MOFs are less competitive towards the sorption-based humidity regulation due to their low efficiency for passive (adsorption at >65%RH) and active control (<30%RH) in SDSs. To date, it is reported that PIZOF-2 [23, 37] initiates water vapor adsorption after $0.7P/P_0$ and reaches 68wt% of water capacity at $0.9P/P_0$. Kitagawa et al. [123] investigated MIL-53 (Al) with different functional groups, and isotherms show a steep rise of water uptake after $0.7P/P_0$ in MIL-53(Al)-OH. Though these MOFs exhibit more or less good stability and S-shaped isotherms with high water uptake, the hydrophobicity makes them ineffective to take up the water vapor molecules at the desirable humidity range. It is expected that modification/ functionalization of these MOFs can tune their inner structure, enabling them to exhibit improved performance based on water adsorption.

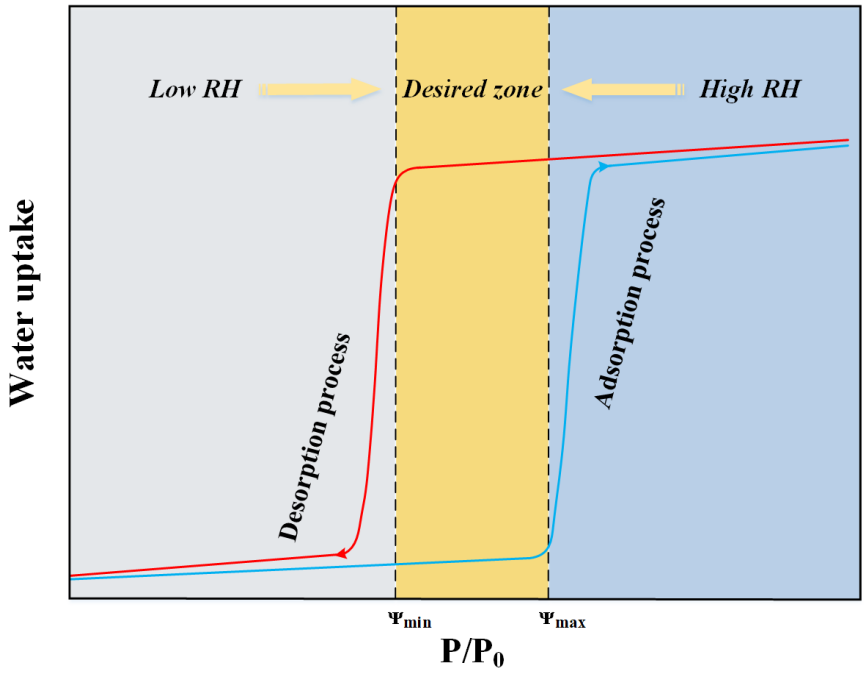
5. System-level screening and applications for the built environment

5.1. Working principles of the open solid desiccant system (SDS)

In general, an open SDS is designed to deal with the hygrothermal load in air, in which the desiccants directly contact with the indoor air to regulate the sensible and latent load. Open SDSs based on different working principles can be classified into active and passive types. The

passive-type SDS can remove the moisture fluctuation by virtue of the nature of the desiccant materials that autonomously adsorb or release the water vapor under high or low indoor humidity levels. As the intrinsic properties of the desiccant decide the operational performance, limited progress has been made in passive-type SDS systems [145-148]. As for active-type SDS, the adsorption loop forces the process air to flow through the desiccant and dehumidifies the air to the desired room temperature. The regeneration loop can reject the trapped water vapor out of the desiccant so that the desiccant can be recovered and utilized in the next operation loop. In this regard, the regeneration can be achieved by heating the desiccant to the regeneration temperature, which relies on the intrinsic properties of the desiccants (i.e. zeolite, ~100℃; MOF, 50~90℃) [11, 20, 72].

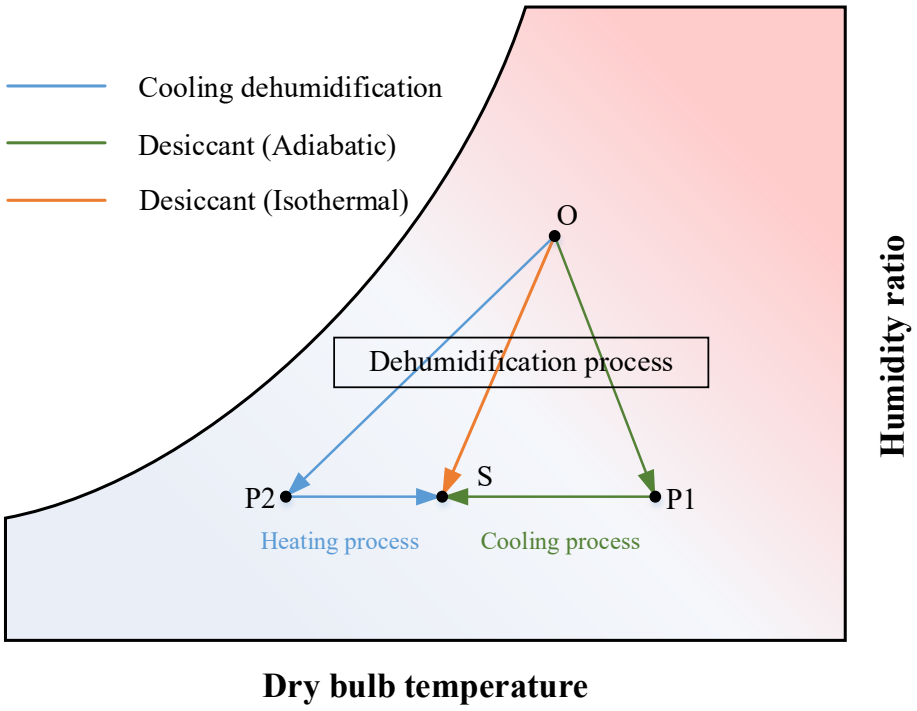
To date, passive-type SDS systems (Fig.20) primarily act as moisture buffer for building environment control, which contains only desiccant materials such as wood, plasterboard, etc. [149]. In contrast, active-type SDS systems (Fig.21) generally have three complex components, namely, dehumidification unit, regeneration unit and cooling unit [150]. The configuration of these units may vary largely based on the desiccant and the employed operation modes, as shown in the following section.



727

728 **Fig. 20.** The variation of water uptake in desiccant materials at high and low RH.

729



730

731 **Fig. 21.** The psychrometric processes of active-type desiccant dehumidifiers in comparison

732 with cooling dehumidification. O: outside air; S: supply air; P1 and P2: medium process.

733

1) Dehumidifier

In the case where SDS has been employed, the dehumidifier can generally work in two different manners: adiabatic [151, 152] and isothermal [9]. The process air stream directly flows through the solid desiccant in the adiabatic dehumidifiers, while in the case of isothermal dehumidifiers, the solid desiccant is not only in contact with the air stream, but is also cooled down by the cooling medium to improve the performance of desiccants. The psychrometric processes are shown in Fig.21. It is clear that the isothermal desiccant system is more desirable than the adiabatic process.

The commonly used dehumidifier types are fixed bed, rotary wheel and desiccant-coated heat exchangers (DCHEs). Since the desiccant can directly affect the performance of SDS, the selection of the desiccant for the above-mentioned systems become a focal point. Traditional desiccants such as silica gel and zeolite have been widely embedded into fixed bed [153, 154], rotary wheel [152, 155, 156] and desiccant-coated heat exchangers (DCHEs) [9, 157, 158]. However, metal-organic frameworks with superior adsorption capacity and gentler regeneration condition have found little evaluation for use in dehumidifiers, thus, presenting a high potential of their application [23, 52, 159].

2) Cooling and regeneration

The cooling medium handles the sensible load in the cooling unit in SDS. In case an adiabatic type dehumidifier is implemented, the adsorption heat released during adsorption process gradually heats up the process air. The cooling unit can cool the air down to the desired supply air temperature. In case an isothermal type dehumidifier is employed, the cooling unit can immediately remove the adsorption heat to keep a high adsorption capacity of the desiccants. To the best of our knowledge, the common cooling unit can be a cold coil, an evaporative cooler

or even an evaporator in the air conditioner.

In addition, the regeneration unit in SDS is of vital significance as it supplies the thermal energy to drain the adsorbed water vapor out of the desiccants. The regenerated desiccant can therefore continue the subsequent adsorption process. As the regeneration condition is primarily decided by the intrinsic properties of the desiccants, SDS makes it possible to use a variety of energy sources, including waste heat, solar energy, electricity, etc.

5.2. Matching the sorption operation with the given condition

Based on the review on the MOF materials, it is confirmed that MOFs exhibit highly tunable structures, thus, laying promising foundation for the sorption-based humidity control. For this application, the optimal MOF materials should possess hydrothermal stability and recyclability. In real life situations, air-conditioning systems usually experience multiple climate conditions during days or years. In MOF-used desiccant systems, hydrothermally stable MOFs with a steep rise in a narrow humidity range (S-shaped isotherm) are expected to maintain the humidity level during the long-term cycling operations [14]. Thus, for SDSs, the ideal MOFs for built environment control should be qualified as follows:

(1) In an active-type system, it is favorable to pick up desiccants with high water lift loading, milder regeneration condition and no or minimal hysteresis loop at the working humidity range.
(2) In a passive-type system, it is desirable that the hysteresis loop of the MOF desiccant formed by the adsorption-desorption branches appears during the working humidity range, and the MOF can be easily regenerated around room temperature. Moreover, these MOFs should not be temperature-sensitive, which implies that these materials are able to maintain almost the same isotherms within a certain temperature range.

In fact, many commercial and laboratory developed MOFs cannot strictly meet these requirements, especially related to hydrothermal stability. Most of heat-transformation studies on MOFs are carried out focusing on the heat pumps, adsorption-driven chillers or water harvesting etc. [23, 28, 32], however, a little knowledge is available on the open SDSs for building humidity control or the introduction of MOF-based system concept [160]. Chang et al. [78] investigated the potential of MIL-100 and MIL-101 for the energy-efficient dehumidification. Obviously, the used MOFs are promising desiccants, however, the study primarily focused on the properties of materials, rather than practical application. Lately, Henninger et al. [52] studied the MOF-coated heat exchanger at full scale considering pretreatment and coating processes. The coefficient of performance (COP) of the cooling system was estimated under different evaporator and heat rejection temperatures, and the results revealed a maximum COP up to 0.72 without heat recovery. As mentioned in the study [52], the preparation and coating processes are arduous for large-scale applications, and the recyclability of the system may need more field experiments. This work thus offers a benchmark for MOF-based open SDSs. Besides, Eddaoudi et al. [21, 42] prepared two novel desiccants with the most favorable isotherms, designed for autonomous humidity control (section 3.2.2) at room temperature. As a whole, the climate conditions, material properties and system requirements determine the design and assembly of an open SDS.

5.3. Alternative applications

The sorption-based air-conditioning system is a critical technology for achieving energy saving in building environment control. From material to system design, the selected MOFs considering the above-mentioned criteria will be integrated into a real SDS. In this context, most of currently available water-stable MOFs have been classified into three groups, and each

809 of these groups remains a focal point of research. It is noted that significant research efforts
810 have been focused on the some common material properties such as water stability, water
811 uptake capacity and regeneration of MOFs. Some other factors such as processing techniques
812 (i.e. coating process) have been scarcely reported [52, 125, 161], which partly affect the size
813 and performance of SDSs along with initial investment. Thus, it is needed to conduct more
814 field measurements to assess all factors affecting MOF-based SDSs. In the following sections,
815 we propose the case of two MOF-based systems with potential of high energy saving for the
816 built environment control. Here, the promising candidate, MIL-100(Fe), has been applied to
817 the systems working in active or passive mode and detailed parameters have been documented
818 in previous studies [72, 162].

819

820 5.3.1. Active system

821 Through the literature reviews on the development of sorption-based air-conditioning systems,
822 it is clear that the traditional adiabatic dehumidification approaches (i.e. rotary wheel [152,
823 163]) experience the severe effect of adsorption heat, which adversely reduces the total
824 dehumidification efficiency. Therefore, a new system with desiccant-coated heat exchangers
825 may be preferable as shown in Fig.22. The evaporator will remove the sensible load and
826 adsorption heat to keep an isothermal adsorption, which helps to enlarge the usable water
827 loading lift and avoid the low evaporation temperature. Although there is no heat recovery or
828 mixing of new and exhaust air, the ultralow condensation temperature (less than 60℃) has been
829 noted to result in COP of 7.9, which is comparable to the traditional desiccants based cooling
830 systems [164]. As MOF is saturated in the evaporator as well as dried in the condenser,
831 switching of the flow direction can achieve a continuous operation. Besides, the sorption
832 kinetics confirms MIL-100(Fe) to outperform many desiccants in both adsorption rate and

cycling water loading. Apparently, this system can achieve a fast regulation of sensible and latent load.

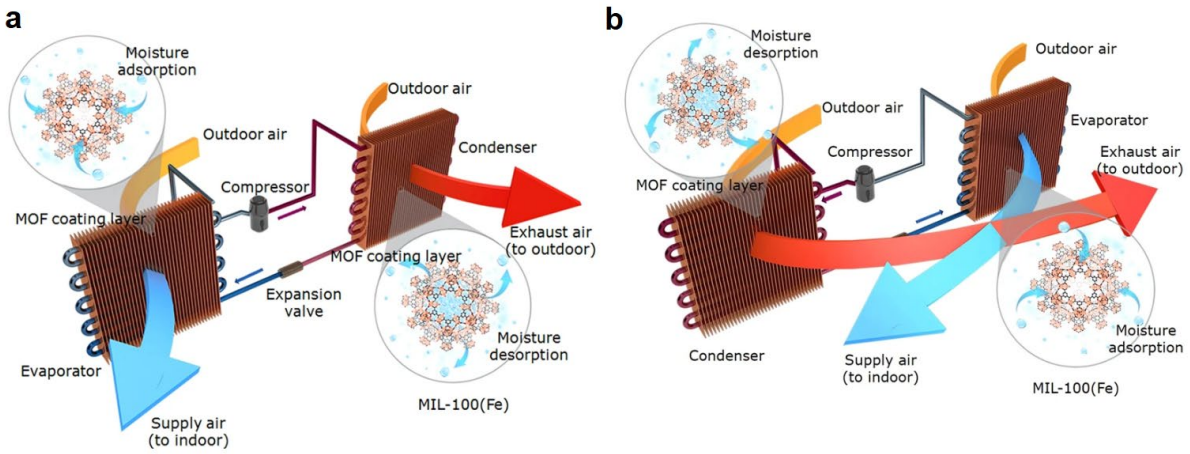


Fig. 22. Configuration of MOF-based cooling system [72]. (a-b) The working operation of the cooling system.

On the other hand, mathematical models of SDS have also been developed for several decades. To date, many research studies have been dedicated to the mathematical prediction of supply air conditioning [158, 165-167]. MOF-based model [159] has also been used recently, which helps to disclose the potential application of MOFs in the low and medium humidity environment.

5.3.2. Passive system

In 2005, Rode et al. [149] introduced a concept of moisture buffer value (MBV), which indicates that the hygroscopic materials can autonomously relieve indoor humidity fluctuation. Since then, many intensive research studies have been carried out for the model development [145, 147, 168, 169] and the assessment of buffer performance of the hygroscopic materials [170-172]. However, MBV test of the traditional hygroscopic materials such as wood, cellular concrete, etc., have been conducted on the laboratory scale, and their low moisture buffer

capacity indicates their inability of effective humidity control. Eddaoudi et al. [21, 42] proposed two promising MOF materials with desirable isotherms, however, these materials need more field experimental verifications at different temperature conditions. Lately, we have applied MIL-100(Fe) as a moisture buffer panel to investigate the changes in indoor humidity load at different climate conditions. The MBV (~10g m^{-2} $RH\%^{-1}$) of MIL-100(Fe) has been measured to be one order of magnitude larger than the traditional hygroscopic material (~1g m^{-2} $RH\%^{-1}$) [162]. The configuration of the room model is shown in Fig. 23.

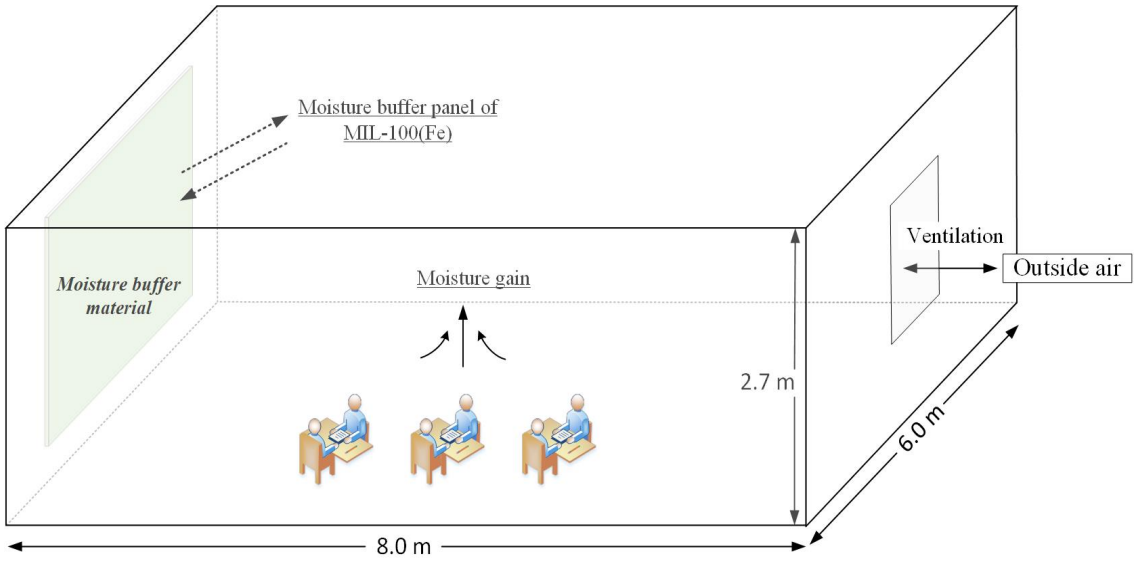


Fig. 23. The room office using a MIL-100(Fe) panel [162].

Considering the inner moisture gain and ventilation, the results indicate that MIL-100(Fe) can remove a majority of the latent load by night ventilation under dry and moderate climate conditions, and more than 70% of the latent load under humid climate is removed with the help of a regenerator driven by the low-grade energy such as waste heat. As the passive control of MOF-based SDSs can remove most of the latent load, it is expected that the COP of air-conditioning system will be raised without cooling dehumidification. Thus, MOFs become promising candidates as hygroscopic materials.

6. Summary and potential

Solid desiccant system is considered as a promising approach to provide a comfortable and hygienic environment, by taking advantage of the low-grade energy. The desiccant is primarily used to remove the latent load in a target room. Therefore, the desiccants with higher water capacity and stable structure become potential candidates. Metal-organic frameworks (MOFs) derived from the combination of metal clusters and organic ligands are one of the potential categories, which possess remarkable microstructure and adsorption mechanisms, together with structural tunability. All of the mentioned MOFs in the review fulfill the basic requirements for SDSs, and some of them have been reported with mild regeneration conditions, usually between 60-90℃ (or even <60℃). Moreover, these MOFs with S-shaped isotherms are also noted to outperform many traditional desiccants, as a sudden tunable change in water uptake can take place in the working humidity range. A comprehensive comparison of the water capacity of MOF desiccants in different pressure ranges is presented in Fig.24.

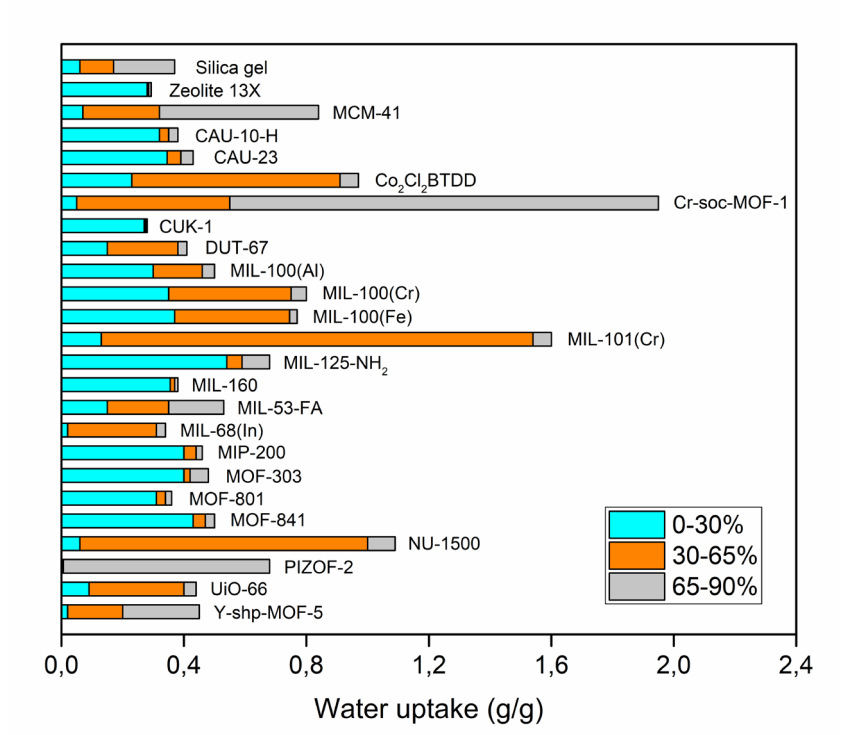


Fig.24. Water uptake of some representative MOFs in different relative pressure ranges.

In the past years, the synthesis and application of MOFs have made significant progress. The balance among the water stability, adsorption capacity and regeneration condition can be achieved through the subtle structure tailoring of the porous MOFs such as functionality or modification. The advances in the development of topology design and synthesis of MOFs [173] raise the chances of large-scale practical applications in both active and passive SDSs, and the research studies devoted to these systems are still increasing (Section 5). Despite the remarkable progresses in MOFs, no single MOF can currently meet all of the requirements owing to the drawbacks more or less related to material or system level. From the reviewed literature studies, some suggestions can be summarized as follows:

1) Chemical synthesis of MOF materials affects their intrinsic structure and material performance. The selection of green and nontoxicity raw materials (metal ions, organic ligand and solvent) is preferable to produce environment-friendly MOFs [35].

2) Conventional synthetic methods for MOF desiccants are considered convenient, however, these may be less productive and time-consuming. Assisted synthesis [174] or flow chemistry [175] can be expected as an alternative way to produce MOFs at large scale.

3) The flexibility of structural tunability makes MOF remarkable intrinsic properties, which helps explain the unique water adsorption mechanisms [14].

4) The screening of the available MOFs based on hydrothermal stability, water adsorption and regeneration, dynamic sorption equilibrium, large-scale production and non-toxicity helps to identify the high priority of MOFs among different MOF series.

5) In a specific environment, open SDSs can sustain the corresponding climate change with superior recyclability. The operation in active or passive way leads to different requirements

for these MOF desiccants, generally focused on the shape of isotherm (i.e. hysteresis loop) and regeneration condition.

6) It is expected that more research studies will be available in future on the heat and mass properties of MOF desiccants, such as thermal conductivity, thermal and moisture effusivity, etc. [125]. Moreover, the applications in the desiccant-coated heat exchangers have been reported, but a little knowledge is available about the rotary wheel or fixed bed systems. In short, these properties and applications of open SDSs can prompt the use of MOF materials in built environment control.

The remarkable advances in the chemistry of MOF materials during the past years have revealed many alluring properties in comparison with the traditional solid desiccants. A systematic exploitation on the novel desiccants for SDSs is the need of the hour. In order to apply an optimal MOF to a specific SDS for the built environment control, it is essential to conduct an intensive research on the material and system levels, from structural design to material preparation, from gram scale in laboratory to ton scale in production facility, from properties assessment to system application. As some studies have confirmed that SDS using MOFs exhibits superior performance over the traditional systems, it is important to conduct further field experiments and identify the appropriate MOFs for safe, cost-effective, and energy efficient processes.

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