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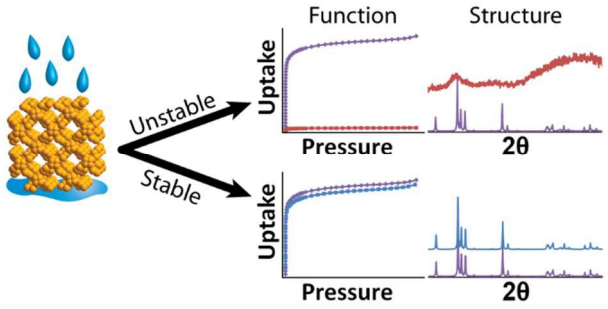
Water stability of MOFs is reviewed including exposure techniques, characterization methods, and ultimately more consistent definitions of water stability.



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PERSPECTIVE

Parameterizing and Grading Hydrolytic Stability in Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are a class of porous solid, which have a variety of potential applocations. Unfortunately, MOFs often lack hydrolytic stability, which hinders their use as viable materials for large scale applications. Though there have been an increasing number of reports proving water stability, this aspect is often ignored and negative results often remain unpublished. As a result, this report has been produced to offer common benchmarks for stability of MOFs to moisture. This will be done by discussing what water stability means – both with regards to the exposure methods and the means of assessing the MOF after exposure. Based on these two criteria, definitions are proposed in order to allow MOFs to be discussed more consistently. The purpose of this report is not to rank existing MOFs based on water stability or for potential application but to promote and facilitate discussion about hydrolytic stability of MOFs.

1. Introduction

According to the IUPAC recommendation, metal-organic frameworks (MOFs) are "...[a] coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions...with an open framework containing potential voids."[1] Though crystallinity is often included in a MOF definition, IUPAC has chosen not to. This definition also recognizes that MOFs are often dynamic with their structure depending on the current environment. MOFs can be systematically tuned based on the choice of organic ligand and metal, which can allow them to be used for a variety of applications, such as gas separation and storage,[2–7] catalysis,[8] luminescence and sensing,[9] and ion conduction.[10,11]

Water is omnipresent in the environment. For materials or processes that cannot function in a wet atmosphere, excluding water will add cost to its implementation and upkeep. For most industrial applications, excepting inert atmosphere catalysis, they will require hydrolytic stability. Moreover, for simple storage and stability for any widespread application, moisture stability is critical. While MOF stability has been a serious concern in the past, the last decade has seen increasing reports of water stable MOF materials. There have been two recent review articles on hydrolytic stability in metal-organic frameworks;[12,13] this report is meant to complement these reviews in order to allow a standard reference to be adopted.

Though MOFs are being investigated for the storage and separation of a variety of fluid phases, some of the most researched are pre- and post-combustion CO_2 separation[2,14–18] and H_2 storage.[19–22] In a post-combustion CO_2 capture system, from a power plant burning low sulfur coal, the gas stream after combustion contains 5-7% water by volume and any capture material needs to be stable to these conditions.[23] Pre-combustion CO_2 capture is removal of CO_2 to make a cleaner H_2 fuel, typically from the steam reforming or the water-gas shift conversion.[24,25] Steam reforming produces H_2 fuel in the form of syngas, which can contain over 20% water by volume.[25] Similarly, in the water-gas shift conversion, carbon monoxide and water are converted to CO_2 and H_2, the amount of water present varies from approximately 18-38% by volume depending on the exact process used.[25] Based on the inevitable presence of water in industrially produced gas streams, stability to humid conditions is a criterion that must be met for MOFs to be effectively utilized in these processes.

MOFs are actively being explored for use in catalysis[8] and can be used in two main ways – directly as the catalyst (using either the metal centers or functionalized ligands) or as a scaffold (entrapment of nanoparticles or molecular catalyst acting as a rigid, shape/size selective support).[26–36] Although many catalyzed reactions require water to be excluded, there is a growing drive to use water as the medium for catalysis. Though there are limitations, water is considered to be an ideal solvent for catalysis for economic, environmental, and safety reasons.[37,38] Catalytic reactions not carried out in water, will benefit from a hydrolytically stable MOF as aqueous extractions are commonly employed in the purification of products and water is often used to hydrolyze intermediates, by-products, or unwanted products to make purification easier.

MOFs are also investigated for their luminescence, often for sensing.[9] The origin of this luminescence is through ligand-based luminescence[39–42], metal (typically lanthanide) luminescence[43–51], charge-transfer[39,52–55], or guest induced (usually lanthanide ions or organic dyes).[56–58] Depending on the purpose of a MOF for sensing, water may or may not be present. There are MOFs, which have distinct fluorescent shifts dependant on the solvents present, including water.[55,59] Water can also be used as the medium for guests to be absorbed into a MOF, allowing for fluorescent sensing of various ions,[56,60–62] pH[51], aromatic compounds[39,45,55], and others.[57–59,63] For luminescent sensing in biological applications MOF stability in aqueous

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conditions is crucial. For MRI (magnetic resonance imaging) and other imaging techniques a contrast agent needs to be able to safely circulate the body, which has led to the development of several MOFs for this application. [48,64–66]

MOFs are also being investigated as a means of drug delivery, which may require the framework to be fully or only partially stable to biological conditions.[57,67] A hydrolytically stable MOF would be used to transport drug molecules through the body, before being released at the target. A partially stable MOF would likely be used to gradually introduce a drug to the recipient; this drug could either be a guest in the framework, or a constituent of the framework. Tuning of the MOF's hydrolytic stability would allow for faster or slower release of the drug in question, which could allow for drug delivery over a long period of time. In this regard, establishing more defined strata for MOF stability is important.

Previously, it was noted that crystallinity is not a condition for a material to be considered a MOF though potential porosity is.[1] Factoring in the range of potential conditions (temperature, humidity, duration of exposure) to which researchers could subject a MOF material, there is a lack of clarity around the precise meaning of a given statement on MOF stability. Does stability refer to structure retention, function retention, or both? If there is an attenuated loss of function, is this acceptable? Both of these questions will be discussed as they pertain to hydrolytic stability of MOFs. In this review, kinetic and thermodynamic water stability will only be discussed briefly as this has already been discussed in depth.[12,13] This will be followed by a literature overview of the different methods to expose MOFs to water followed by the methods to assess their stability. Finally, definitions will be proposed to quantify hydrolytic stability in MOFs in order to clarify and standardize descriptors, both in an academic and an industrial setting.

2. Kinetic and thermodynamic water stability

2.1 Definitions

A comprehensive review on water stability and sorption in MOFs has been published in 2014 by Burtch *et al.*,[12] that does an excellent job discussing the thermodynamic and kinetic stability of MOFs. In this review, the authors define thermodynamic stable MOFs based on their inability to hydrolyze due to either metal-ligand bond strength or the stability of the metal clusters in the presence of water. They then define kinetic stability based on hydrophobicity or sterics around the metal-ligand bond, which provides varying degrees of stability to humid conditions. Using these classifications, the authors separate nearly 200 previously reported MOFs into thermodynamically stable ("stable after long-term exposure to aqueous solutions: week or greater in pure water, day(s) in acidic/basic or boiling conditions"), high kinetic stability ("stable after exposure to high humidity conditions: decomposes after short exposure times in liquid water"), and low kinetic stability ("stable under low humidity conditions").The review by Burtch *et al.* as well as another review in 2015 by Qadir *et al.*[13] both discuss the common trends in water stable MOFs and ways of improving the hydrolytic stability of existing MOFs. For the most part, the methods discussed involve creating stronger metal-ligand bonds – increasing the thermodynamic stability – or creating sterics around the metal-ligand bond – increasing the kinetic stability. Though vague definitions are given by Butch *et al.* for exposure methods, they lack precision and could not solely be used for implementing a standard discussion of hydrolytic stability in MOFs.

2.2 Retention of structure versus retention of crystallinity

Crystallinity is not a prerequisite for a MOF to have porosity and have a function. Imparting hydrolytic stability via thermodynamic routes has the outcome of decreasing the bond reversibility between the ligand and metal and generally leads to less crystalline materials. While most MOFs reported in the literature are (single) crystalline, there are reports of porous coordination polymers with poor or no crystallinity, though these are not always referred to as MOFs in the publication. Often times, these are formed from a combination of organopolyphosphonates and highly charged (≥ 3+) metals. Gagnon *et al.* have written a review on these "Unconventional MOFs (UMOFs)", addressing many important properties for a class of materials that remains less explored due to their lack of crystallinity.[68] Though there are relatively few reports of the quantitative assessment of the hydrolytic stability of these UMOFs, this is not so likely an indication of their instability. More likely, this stems from the fact that these materials are highly robust and zeolite-like as many are prepared from aqueous solutions and demonstrate high insolubility, leading the authors to presume that these materials possess high levels of hydrolytic stability.

3. Types of water exposure

In the past, various research groups have utilized different methods for examining a framework's stability to water as both liquid and vapour. Depending on the intended application and available resources, there may be different tests and practical considerations for how to determine the framework's hydrolytic stability. This section will give an overview of methods currently employed for testing a MOF's water stability.

There are two separate issues when discussing water exposure in MOFs. The first involves the harshness of the condition (e.g.: temperature, relative humidity, pH), which will be used to determine the level of stability of a MOF. The second issue is the means of controlling and delivering the exposure - while some simple methods may be portrayed as less precise or definitive, it should be kept in mind that these techniques can provide fast-screening that the more thorough methods cannot. Given that many of the exposure methods can provide the same degree of humidity exposure, this section will be organized based on the methods used to expose a MOF to a given condition.

3.1 Exposure to ambient air

Some papers have reported that a MOF is water stable, despite only testing its stability towards activation and exposure to ambient conditions. This is a dangerous conclusion to draw as it is highly dependent on the local conditions present during the "stable" time; these can include ambient relative humidity (which is directly affected by temperature and pressure), degree of activation, and storage method. Since relative humidity is calculated based on the external pressure and temperature to give the concentration of water vapour in air, which can be highly dependent on location and time, it is not always a consistent method for establishing water exposure. Typically, most well ventilated buildings are held at around 21°C and have a relative humidity of 20-60%, which corresponds to the partial pressure of water varying from 0.064 to 0.191, drastically changing the amount of water that a framework is exposed to. In regards to degree of activation, a material that has not been fully activated will have remaining guests in the pores. These can interact more strongly with the pores, hindering the accessibility of water into the pores and imparting stability

that may appear to be intrinsic to the MOF. The presence of these guests can either be checked by placing the MOF under vacuum and determining if the material is still outgassing (usually done at or above the boiling point of the guest) or by running a thermogravimetric analysis (TGA) on the material and looking for a mass loss. If the MOF is stored in a closed system, a new equilibrium between absorbed water in the MOF and water vapor in the surrounding environment will be established, resulting in a relative humidity different to the ambient relative humidity. While activating a MOF and exposing it to ambient conditions does not necessarily mean that the material is water stable, it does not preclude it. Doing this, however, makes accurate comparisons of water vapour concentration in air very difficult, especially if pressure, relative humidity, and temperature are not measured continuously.

3.2 Immersion in liquid water

Another method reported to test water stability is immersing a MOF in water at various temperatures.[69–72] Some studies report water stability for MOFs if it was synthesized in water. It should be noted that synthesizing a MOF in water does not necessarily demonstrate water stability as the solution is in equilibrium with its components , the MOF can be kinetically insoluble, or there may be other constituents (e.g.: organic solvents or salts) that decrease the MOF's solubility in solution. That being said, a MOF synthesized in water may still possess water stability, though these materials' stability should be further investigated.

Bezverkhyy *et al.* demonstrate this with method of exposure with MIL-53(Al), [Al(OH)(Bdc)]. Upon boiling in water, MIL-53(Al) shows a slight decrease in the pore volume (0.57 cm^3/g to 0.50 cm^3/g) as a thin layer of γ-AlO(OH) forms on the surface of the MOF particles.[73] Further boiling of these MOF particles resulted in a thicker layer of γ-AlO(OH) to the point where the material no longer shows porosity. This work is important as it does an excellent job in characterizing the decomposition product and continuing the exposure to learn about whether the pore volume attenuates at a metastable product or continues to degrades, which many reports do not consider.

3.3 Uncertain relative humidity exposure

One method of exposing a material to a definite temperature but an unknown amount of humidity is using the vial in vial method.[18] In this method, a vial of MOF is placed inside a larger vial containing water, which is then placed in an oven at elevated temperatures. This method does not allow the water content to be accurately determined since internal pressure is unknown. While this method does have uncertainties in the relative humidity exposure, it does provide a valuable fast screening method for determining if a MOF has the potential for hydrolytic stability and merit further testing.

3.4 Certain relative humidity exposure

There have also been tests of MOFs' stability towards humid conditions by exposing the material to varying degrees of relative humidity, at different temperatures, and for various lengths of time.[18,74–76] This test allows for the stability of internal pores to be investigated as it ensures that water vapour can enter the pore system without having to overcome cohesion of bulk water on the surface. In order to bring a more consistent discussion on MOFs and water stability, it becomes necessary to use more precise methods of determining the humidity that a MOF is exposed to. The following methods are listed in no order – each has its own benefits and drawbacks to utilization.

3.4.1. Saturated binary salt solutions

Saturated binary salt solutions are one method to produce a specific relative humidity at a given temperature.[77–79] This method is particularly useful at room temperatures where the relative humidity can be easily and systematically controlled between 4% and 97% depending on the choice of salt used to make the saturated solutions.[77–80] As temperatures increase, less data is available regarding the relative humidity produced by saturated binary salt solutions – still at temperatures of 50°C, there still exists a large pool of data, allowing for a range of relative humidity to be targeted between.[79] A summary of potential salt solutions, based on the recommendations in Section 5.5, can be found in Table 1.

Table 1. Binary salt solutions capable of achieving a desired relative humidity at a specific temperature. The numbers below the salt indicate the actual relative humidity achieved (in percent).

R.H.	20°C	50°C	100°C
20%	$CaBr_2$[79] 19	KF[79] 21	$MgCl_2$[79] 22
50%	$LiNO_3$[78] 49	$CoCl_2$[79] 50	NaI[81] 50.4
90%	$MgSO_4$[80] 90.0	KNO_3[77] 85.0	Pb(NO3)2[81] 88.4

*for many some many of these salts, a solution just above 100°C was used, see references for specifics.

3.4.2 Water sorption experiments

In an effort to test and standardize MOFs water stability, the Walton Group[82–85] along with other groups[70,74,76,86] routinely run water sorption isotherms to assess stability. This allows an exact relative humidity to be reached along with gaining insight to the pore hydrophobicity/hydrophilicity. One issue with water sorption experiments is that condensation of water vapour inside the instrument often prevents testing high levels of relative humidity and this can be very difficult to remove. Despite this, water sorption experiments provide an excellent means of testing a MOF's water stability.

3.4.3. Humidity ovens

Humidity ovens present an alternative means of exposing MOFs to humidity. Though humidity ovens provide less information about a pore interior than water sorption experiments, they can be considered as a more practical alternative. Humidity ovens allow exposure to higher levels of relative humidity than water sorption experiments. Furthermore, humidity ovens allow for multiple parameters of temperatures and relative humidity to be explored. Unlike water sorption experiments, humidity ovens are more ambiguous as to whether a sample has equilibrated with the water vapour.

3.5 Exposure to bulk water versus water vapour

When discussing a MOF's stability to water, it is important to differentiate between liquid water and water vapour. For example, talc shows hydrophobicity to bulk water, by beading water droplets, while showing hydrophilicity by strongly binding water on its surfaces.[87] At low relative humidity (R.H.), adhesion and entropy are the deciding factors for surface coverage by water; while at saturation, adhesion and cohesion of water

molecules determine the surface's hydrophobicity. This means that a material may appear to be stable to water, when actually only the external surfaces of the particles are being exposed to water, rather than water being absorbed into the pores and interacting with the internal surfaces. This is certainly not going to be the case for all MOFs especially given that some are shown to absorb water preferentially over organic guests. However, stability to liquid water is important to many applications and long term stability to aqueous solutions or short term stability to harsh aqueous solutions is a condition to be considered thermodynamically stable according to Burtch *et al.*[12]

4. Methods of probing water stability

Just as there are different methods for exposing a MOF to water/humidity, there are different methods for assessing the post-exposure stability. Often these methods focus on one property of a MOF and base conclusions of stability on how that property was affected. Common properties investigated are retention of structure and retention of gas sorption properties, though others may be investigated. Although it is less commonly measured, repeated humidity exposures should be performed to determine whether decomposition of a MOF continues or if it plateaus to a stable state.

4.1. Mass Balance

Ensuring that a MOF is not dissolving should be the first parameter explored when determining if a MOF is hydrolytically stable. This can involve weighing of the sample pre- and post-water stability tests or by monitoring the parent solution. Monitoring the parent solution can be done using nuclear magnetic resonance (NMR) (metal depending) to see if the ligands have dissolved or using UV-VIS (ultraviolet-visible light) spectroscopy to look for small changes in the absorption of the solution as its components dissolve (assuming they meet the necessary criteria). This also serves as a check for materials grown in solution as they are typically in a saturated solution of their respective components and may appear to be hydrolytically stable.

4.2. Powder X-ray Diffraction

Powder X-ray diffraction (PXRD) provides a quick method for comparing a sample before and after exposure to some humidity treatment as described above. This is a common way of determining if a MOF is stable to certain treatments, including stability to liquid or vapor phase water.[18,70,71,74,82–85,88–91]The post-treatment PXRD pattern could be identical, reflect slight changes or show a greater variation from the parent sample. When a MOF exposed to water gives a PXRD pattern that is apparently unchanged from the pristine MOF, this itself does not confirm stability. The PXRD pattern may be identical but without retention of mass balance and proof of lack of dissolution, this point is irrelevant. Depend on the extent of humidity treatment, a fraction of a sample may change to amorphous while the remaining sample is as yet unperturbed. This is essentially an incomplete experiment but may give the impression of stability arising from the retention of the parent peaks in the PXRD. Peak broadening or a thicker baseline would be expected in this scenario. Another subtle change not largely captured by PXRD reflects surface defects arising from humidity treatment. PXRD is a bulk characterization tool and surface defects can block access to pores rendering a solid with comparable long range order largely non-porous. Changes in the PXRD to another ordered structure can mean aquo ligation or intercalation of water and these can possibly be reversible. The aquo ligation or intercalation options also exist in the case of conversion to a more amorphous structure. Finally the formation of an amorphous phase is typically associated with collapse of the structure however, this more accurately simply conveys loss of long range order, porosity may still be partially retained. Given all these possibilities, and the lack of strong crystallinity in UMOFs, PXRD as a means of determining hydrolytic stability should only be used in conjunction with further characterization techniques to definitively classify the stability of a MOF.

4.3. Gas sorption and related analyses

Measuring gas sorption isotherms, primarily N_2 at 77K to calculate surface area, prior to and after exposure to water is an excellent way of determining stability.[74,75,82–85] Some reports also use CO_2 – or other gases – sorption isotherms at or near ambient conditions to determine water stability.[18,74] At 77K, N_2 sorption isotherms can be used for determining if a material has retained its surface area; however, defects created on the surface of MOF particles may cause a decrease in N_2 sorption at low temperatures as partial blocking of the pore system may occur.[74] Isotherms measured at ambient temperatures may give information about the introduction of surface defects, which would not significantly affect the surface area but may have a drastic effect on the size selectivity for different guests. Furthermore, at ambient temperatures there may be sufficient thermal energy allowing for the framework to vibrate and allow CO_2, or other gases to enter the pore system despite defect formation.[74]

Gas sorption isotherms can also be used to model pore size distribution. These use a mathematical model and can be manipulated based on model choices, it can provide a comparison for semi- or non-crystalline materials and can give further insight over a simple change in surface area or overall uptake in a material. There are many different gases and models that can be used for this type of analysis, so consistency is important. Depending on pore size of the system, different models are used to model the pore size. Typically, pore size analysis uses N_2 sorption at 77K, though there are arguments for using other gas sorption experiments in conjunction.[92] For microporous systems, the Horvath-Kawazoe (HK) method has been traditionally used to estimate pore size.[93] The original form was based on molecular sieves, with the assumption being that they contained slit-shaped pore and that the relative pressure for micropore filling (and the size and shape) is directly related to the adsorbent-adsorbate interactions.[93] The HK method has since been extended to cylindrical and spherical pores, as well as other types of adsorbents.[94–96] More recently, density functional theory (DFT) has been used to model pore sizes as it excludes many of the assumptions associate with the HK method, and other classical thermodynamic derrivations, to provide more reliable results.[97,98]

4.4. Other Methods

Though PXRD and gas sorption analysis are most commonly used to verify that a MOF is stable to various treatments, there have been other methods reported and proposed. When considering which method to use, it is important to consider what properties are relevant for a material's intended application. For example, a material that is used for sensing does not necessarily need to retain the same porosity after water treatment (as determined by gas sorption), as long as it is able to take up the desired guest molecule and display the same type of signal and intensity.

Majumder *et al.* have used single crystal diffraction to show that their material was stable to water.[58] This method may have many of the same

systematic problems as PXRD with regards to production of an unnoticeable amorphous phase.

Tan *et al.* have utilized infrared and Raman spectroscopy to investigate water's interaction with a MOF.[99] In this study, they were able to observe when D_2O absorbs to the framework, the symmetric and asymmetric carboxylate stretching are shifted to higher frequencies. Though on its own, this does not indicate stability, the absence of signals indicating degradation can indicate stability. Furthermore, this technique can give valuable insight into designing water stable materials in order to eliminate known degradation pathways.

For specific applications where water would be present, it would also be beneficial to see how the efficiency of a process (e.g.: sensing, catalysis) changes with varying exposure to water or humidity. Though, to the best of our knowledge, no studies have been performed to look at this, it is expected that these will emerge as MOFs are increasingly employed for these applications.

5. Degrees of water stability

Currently, there are no set definitions concerning the remaining function of MOFs after exposure to water. As such, it is important to develop consistent tests and criteria to discuss this property of MOFs. Because of the vast applications of MOFs, and the resulting criteria to be considered stable, the means of testing and assessing the water stability should be included in the definition. Here, some basic definitions are proposed to allow a common and concise way of discussing water stability and MOFs.

5.1. Degradation and remaining function

When reviewing the literature on water stable MOFs, there is little discussion on partially water stable materials. These partially stable MOFs are typically characterized by a single factor, such as surface area retained after a single exposure, which may ignore a variety of practical properties. Two questions that are often left unanswered in such studies are retained function and attenuation of that function. If a material loses a portion of its surface area (as indicated by, e.g.: N_2 sorption at 77K), this does not preclude it from having retained porosity when studying gas sorption at ambient temperature[74] or retaining its primary function in a given set of conditions, such as sensing or catalysis. The attenuation of a MOF's properties for industrial applications is equally difficult to examine. For partially water stable MOFs, there are few studies that show repeated exposure to water making it difficult to ascertain if they retain a usable function or continue to degrade.

One example is MIL-53(Al), which showed a slight decrease in the pore volume (0.57 cm^3/g to 0.50 cm^3/g) as a thin layer of γ-AlO(OH) formed on the surface of the MOF particles.[73] However, further boiling resulted in growth of a thicker layer of γ-AlO(OH) to the point where the material no longer showed porosity. This is an example of complete degradation over time. Conversely, CALF-28, [$Sn(H_2Tppb)\cdot 4.5H_2O$], showed a loss of surface area (700-800 m^2/g depending on the preparation, to 500 m^2/g) after exposure to 90% R.H. at 80°C for 24 hours.[75] Subsequent humidity treatments showed no further loss in surface area as the material reached a stable state.

5.2. Nature of Water Treatments

It has been shown that a MOF's stability can vary depending on the exposure type (liquid versus vapour) and the temperature of the exposure. As such, it is important to test both these variables and assign them different definitions. For a material to be stable in to either liquid water or water vapour, it should be fully activated first, as discussed earlier.

For a material to be considered stable in liquid water (thermodynamic stability, as defined by Burtch *et al.)*, it should be in pure water (e.g.: no buffers, salts, or other solvents). For biological related research, it is important to choose conditions that are currently used in research labs such that the definition can be easily adopted by those interested in pursuing such research. Hydrolytic stability of MOFs as it relates to biological applications should be studied of *50mM potassium phosphate buffer at a pH 7 and 37°C when discussing hydrolytic stability of MOFs as they relate to biological applications*. Though these conditions are proposed for a definition of stability, it is noted that a variety of applications will use different pH and buffer concentrations to more closely mimic the system of interest. For a material to be stable in water vapour (kinetic stability, as defined by Burtch *et al.)*, both the temperature and the relative humidity need to be brought into consideration. For many processes, being able to withstand a higher temperature and higher relative humidity can be advantageous as less cost would be associated with cooling or drying the system. Temperatures up to 125°C and relative humidity of up to 98% provides a wide range of humid conditions that could be encountered industrially. These humid conditions can easily be achieved using an oven featuring humidity control, an instrument capable of water sorption experiments at variable temperatures, or saturated solutions of binary salts. It is suggested that MOFs water stability to humid conditions be tested at industrially relevant conditions; however, for new MOFs without a specific application, initial tests should cover a wide range of temperatures and humid conditions. *As such, temperatures of 20°C at 20% R.H., 20°C at 50% R.H., 50°C at 50% R.H., and 80°C at 90% R.H. should be tested to simulate ambient, mild, intermediate, and harsh humid conditions.*

5.3. Water Stability Assessments

After exposing a MOF to a given condition, it is necessary to assess changes to the material. Though there are a variety of transformations that may occur, structural and porosity changes are most commonly investigated. Depending on the intended application, other properties should also be used to evaluate a MOF's water stability. For each of the assessments, it is important to continue water treatments if the MOF shows signs of degradation to determine if a stable state has been reached or if it will continue to degrade.

A structural change in a MOF is most commonly and easily observed by changes in PXRD patterns. This method is quick and simple, though it should be used in conjunction with other methods, for reasons discussed previously. For semi- or non-crystalline samples, there are other methods that can be used to infer if structural changes have occurred, though PXRD should also be used to observe if other phases have emerged. Mah *et al.* have used gas sorption isotherms to model the pore size distribution, which can be used to infer structural changes.[75] Infrared (IR) spectroscopy can also be used to determine if there is a chemical change (e.g.: protonation of a coordinating acid group), which can be used in conjunction with other methods to determine if the structure has changed.

5.4. "Acceptable" Levels of Water Stability

Depending on the application of a MOF and its initial proficiency, it becomes difficult to generalize what would constitute an acceptable level of water stability. Even for the same application, it can be argued what an acceptable level of water stability is; one good is example is with CO_2 capture from a flue gas stream. In academia, the concern is often making the best material possible regardless of cost. Conversely, industry will likely not be concerned about whether the MOF is the highest performing or the most water stable. Instead, they will look at the cost and benefit of using a MOF and the conditions that a MOF will be used in. This means that a MOF which loses part of its function may be more financially viable than a different MOF that loses no function. This also means that the conditions the MOF is used in (eg: low versus high humidity) will be dictated by the cost of drying, down time, and replacement rather than the remaining function of a MOF.

5.5. Definitions of Water Stability

While there is currently no standard when discussing the water stability of a MOF, claims are often made based on partial data and thus the conclusions are ambiguous. A meaningful discussion on the true stability of a MOF to moisture would benefit from consistent benchmarks both with respect to how the MOF was treated and the post-treatment analysis. Six levels are proposed to discuss harshness of moisture exposure and summarized in Table 2. These levels correspond to the severity of humidity as mentioned in Section 5.2. E*xposure to Level 1 corresponds to ambient conditions (20°C at 20% R.H.), Level 2 is mild humid conditions (25°C at 50% R.H.), Level 3 is intermediate humid conditions (50°C at 50% R.H.), Level 4 is immersion in water at room temperature, Level 5 is harsh humid conditions (80°C at 90% R.H.), and Level 6 is immersion in boiling water.*

The characterization method to confirm stability is equally important in defining a MOF's water stability and will be split in to four categories, which are summarized in Table 3: *Category A stability is confirmed by both retention of the PXRD pattern and surface area; Category B is the retention of some porosity as confirmed by gas sorption measurements but the loss of crystallinity*; *Category C is the retention of some crystallinity as confirmed by retention of the PXRD pattern, though peak broadening or intensity changes may occur these will still be considered Level C, but the loss of porosity. Category D is the loss of both crystallinity and porosity.* As the exposure conditions exclude any temporal component, and there are also inherent uncertainties in many experimental exposure methods (e.g. variance in ambient relative humidity), there is an unavoidable imprecision in rigidly assigning a grade to a specific MOF. Moreover, there is not a unique descriptor for a given MOF by the methodology to be presented. As such, it is important to note that these are meant as guidelines for discussion and not quantititive metrics.

When discussing these definitions of water stability, the exposure conditions and time need to be stated; similarly, successive exposures should be performed in order to determine if a MOF reaches a stable state or if it continues to degrade. As a benchmark, 24 hours should be adopted as the initial treatment time, with subsequent treatment times dependant on the initial results. These definitions are not meant to replace those proposed by Burtch *et al.*, but rather to add to them in order to bring a standard set of classifications. On their own, these definitions are insufficient and the exposure type (liquid water or water vapour), condition (temperature, relative humidity), duration, and impact of subsequent exposure (stable state reached or continuous degradation) need to be expressly stated as well. Below, several MOFs are used as case studies to discuss the

Table 2. Harshness of exposure.

Level	Stability to
1	Near ambient conditions (20°C at 20% R.H.)
2	Mild humid conditions (25°C at 50% R.H.)
3	Intermediate humid conditions (50°C at 50% R.H.)
4	Immersion in water
5	Harsh humid conditions (80°C at 90% R.H.)
6	Boiling water

Table 3. Metric used as proof of hydrolytic stability.

Category	Proof of stability
A	Retention of crystallinity and porosity.
B	Retention of some porosity but loss of order
C	Retention of some order but loss of porosity
D	Loss of porosity and crystallinity

experiments performed to prove water stability along with their classifications.

Another potential variable is the activation after water treatment. As there are a wide variety of activation conditions, with many MOFs being activated in several different manners, no activation condition is proposed or suggested as being superior. Depending on future applications, different methods may be more suited and, as a result, it is important to look at several activation conditions and disclose the outcome of each.

With this system, a highly robust MOF would have a stability of 6A, one that degraded at ambient conditions would be a 1D. These definitions are not meant to be exclusive. Due to the nature of treatment, a single MOF may show 3A and 4B (among other combinations) simultaneously and should be reported as such to convey the limits of testing.

6. Case Studies

There are numerous methods for exposing a MOF to water and for asserting that it possesses hydrolytic stability. Here, several MOFs will be discussed in regards to properties that exemplify the previous topics discussed and use the definitions of stability to classify them.

6.1. CALF-25

Taylor *et al.* generated a new, porous phosphonate monoester based MOF, [$Ba(H_2Ptp\text{-}Et_4)$]. This framework has one-dimensional pores lined with hydrophobic ethyl groups. Based on this, they investigated its stability to different hydrolytic conditions. After exposure to 40°C and 95% R.H. for 24 hours, this material shows no change in the PXRD pattern and only a 2% decrease in the N_2 uptake at 77K, indicating a *hydrolytic stability of 3A*. To test the limits of this materials hydrolytic stability, it was then exposed to 80°C and 90% R.H. for 24 hours after which it showed no change in the PXRD pattern or the gas ambient uptake of CO_2, indicating a *5A stability*. However, sub-ambient temperatures show decreased gas uptake – with a 17% decrease in CO_2 uptake at 195K and 40% decrease of N_2 uptake at 77K, indicating *5B stability*. In publications, both of these results should be given; often times it appears as though "negative" results are ignored or omitted but these are equally important when designing functional materials.

Furthermore, boiling the MOF causes significant loss in crystallinity and partial phase change, indicating *4D stability* – gas sorption measurements were not performed on this sample.

6.2. DMOF series

A series of functionalized DMOF, $[Zn_2(Bdc\text{-}X)_2(Dabco)]$, have been studied by Jasuja *et al.* to determine the impact of shielding metal-ligand bonds using an increasing number of hydrophobic groups.[84] In this report, they expose their MOFs to 90% R.H. at 25°C followed by characterization using gas sorption and PXRD. Though this exposure does not match any of the conditions described in Table 3, they are considered mild levels of humidity (Level 2) for clarity's sake though the concentration is roughly between Level 2 and 3 – Level 2 designation has been chosen to describe this report as it is closer to the concentration that the MOFs were exposed to in this. These results are given in Table 4.

6.3. MIL-53(Al)

The previously mentioned study on MIL-53(Al), [Al(OH)(Bdc)], by Bezverkhyy *et al.* provides an excellent example of the shortcomings of using solely PXRD to determine hydrolytic stability.[73] In this report, the authors look at refluxing MIL-53(Al), which begins to show a new phase, similar to the hydrated structure, emerging after four hours and becoming the exclusive phase after ten hours. This new phase is non-porous and exhibits no solvent presence by TGA but does show the presence of protonated H_2Bdc molecules. Given this, the authors began searching for the aluminum, which was formerly bound to the Bdc ligands. They discovered that a small shell of γ-AlO(OH) forms around the product, with increasing thickness over time, but that its portion (~6% weight after ten hours) is too small to noticeably impact the PXRD pattern. By calcining the material, or exchanging it with DMF at 150°C, most of the porosity can be recovered. Based on the experiments performed, MIL-53(Al) can be considered to have *6B stability* – retaining most of its porosity in boiling water. However, this stability classification needs to be further probed - do the shells of γ-AlO(OH) continue to increase in thickness until the whole material is converted to the dense aluminum oxo(hydroxide)?

6.4. HKUST-1

When HKUST-1 (Hong Kong University of Science and Technology), $[Cu_3(Btc)_2]$ where Btc is benzene-1,3,5-tricarboxylate, was placed in water at 50°C for 24 hours, there was a change in the PXRD pattern when compared to the untreated material while the surface area decreased from 1340 to 647 m^2/g (48% retention).[91] This type of behavior is classified as *4B stability*. When exposed to humidity, HKUST-1 can be characterized as *3D stability*, as it degrades in humidity such that it forms a new, non porous phase phase.[100] However, this report shows that the humidity exposed HKUST-1can be partially recovered by stirring in ethanol and reactivation.

6.5. ZIF-8

In its initial report, ZIF-8 (zeolitic imidazolate frameworks), $[Zn(MeIm)_2]$ where MeIm is 2-methylimidazolate, shows *6C stability* when placed in boiling water for one week, as indicated by retention of the PXRD pattern – no gas sorption was reported on this material.[72] A follow-up report shows that ZIF-8 is also retains its uptake and crystallinity after three days at 78% R.H. and 26°C, indicating that it possesses *2A stability* (again, this concentration of water vapour is roughly between Level 2 and 3 but is on the same order of magnitude as 3 and thus is simplified to 3 in the example).[101]

Table 4. Summary of findings from Jasuja *et al.* and the respective stability classification. MOFs are of the form $Zn_2L_2(Dabco)$

MOF L_2	Surface Area Retained (%)	PXRD	Stability Level
DMOF $(Bdc)_2$	0	No peaks	3D
DMOF-MM1 (Bdc-Me)	1	Broad peaks	3D
DMOF-MM2 (Bdc-Me)	0	No peaks	3D
DMOF-DM1 $(Bdc\text{-}Me_2)(Bdc)$	3	Some peak remain. New phase after activation	3D
DMOF-DM2 $(Bdc\text{-}Me_2)_2$	1	New phase	3D
DMOF-TM1 $(Bdc\text{-}Me_4)(Bdc)$	68	crystallinity recovered after re-activation	3B
DMOF-TM2 $(Bdc\text{-}Me_4)_2$	100	No changes.	3A
	NA	New phase after water immersion.	4D
DMOF-TF $(Bdc\text{-}F_4)_2$	0	New phase	3D

6.6. CALF-28

Mah *et al.* have reported a porous, non-crystalline tin-phosphonate framework, $[Sn(H_2Tppb)\cdot 4.5H_2O]$. Various preparations result in materials with surface areas ranging from 700-800 m^2/g with a bimodal pore distribution. Given the strong bond formation between a tetravalent metal and a phosphonate, this material was exposed to 80°C and 90% R.H. for 24 hours and always resulted in a material with a surface area of approximately 500 m^2/g and a unimodal pore distribution. Further exposure to this condition resulted in no change to the surface area or pore distribution. This material can be classified as 5*B stability*, indicating a change in the net structure. Though there are many reports of MOFs retaining a portion of their surface area after exposure to some form of water,[73] there exists few examples where a material shows a decrease in surface area followed by no further loss of surface area.

7. Conclusion/outlook

In order for MOFs to become viable materials for industry, their water stability needs to become a priority. In order to do so, a standard needs to be developed so that comparisons between MOFs become more concise. In order to do so, it is recommended that the suggestions and definitions in this report become adopted by the MOF community. Here, we have

reported methods of exposing MOFs to different conditions and ways of determining and characterizing the product(s) that remains. Using these methods, different definitions have been proposed in regards to both the severity of the conditions and to the remaining materials.

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List of abbreviations

Bdc	benzene-1,4-dicarboxylate
Bdc-F_4	2,3,5,6-tetrafluorobenzene-1,4-dicarboxylate
Bdc-Me	2-methylbenzene-1,4-dicarboxylate
Bdc-Me_2	2,5-dimethylbenzene-1,4-dicarboxylate
Bdc-Me_4	2,3,5,6-tetramethylbenzene-1,4-dicarboxylate
Btc	benzene-1,3,5-tricarboxylate
CALF	Calgary Framework
CALF-28	$[Sn(H_2Ptab)\cdot 4.5H_2O]$
Dabco	1,4-diazabicyclo[2.2.2]octane
DMF	N,N-Dimethylformamide
HK	Horvath-Kawazoe
HKUST	Hong Kong University of Science and Technology
HKUST-1	$[Cu_3(Btc)_2]$
MeIm	2-methylimidazolate
IR	infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
MIL	Matérial Institute Lavoisier
MIL-53(Al)	[Al(OH)(Bdc)]
MOF	metal-organic framework
MRI	magnetic resonance imaging
Ptp-Et_4	pyrene-1,3,6,8-tetraphosphonate tetraethyl ester
PXRD	powder x-ray diffraction
R.H.	relative humidity
TGA	thermogravimetric analysis
Tppb	1,3,5-tris(4-phosphonophenyl)benzene
UMOF	unconventional metal-organic framework
ZIF	Zeolitic imidazolate framework
ZIF-8	$Zn(Im)_2$

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