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Raquel Del Angel, Georges Mouchaham, Farid Nouar, Antoine Tissot, Christian Serre. Robust and environmentally friendly MOFs. Patricia Horcajada Cortés; Dr. Sara Rojas Macías. Metal-Organic Frameworks in Biomedical and Environmental Field, Springer International Publishing, pp.1-31, 2021, 978-3-030-63379-0. 10.1007/978-3-030-63380-6_1 . hal-03098238

Chapter 1.
Robust and environmentally friendly MOFs

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Abstract.
Metal-organic frameworks (MOFs) are one of the most prominent families of porous materials. With their great chemical and structural versatility, MOFs have shown to be suitable for a great number of applications related to energy, environment, or medical fields. Nevertheless, in order to expand their potential into wider horizons, some limitations must be overcome. MOFs with higher stability (robust MOFs) and greener more efficient synthetic routes are among the main targets that must be achieved in order to promote their use in industry. In the last years, these two aspects have been broadly studied. This chapter presents, firstly, a discussion of some of the most relevant strategies that can be employed to improve chemical, thermal and/or mechanical stabilities of MOFs. Approaches to strengthen/preserve the coordination bond, as well as some other structural factors that can enhance the stability of MOFs are discussed throughout some relevant examples. Finally, some environmentally friendly synthetic pathways for MOFs production are presented.

Table of Content:

List of abbreviations:

ABTC	3,3′5,5′-azobenzenetetracarboxylate
BDC	1,4-benzenedicarboxylic acid
BET	Brunauer–Emmett–Teller

BPDC	4,4′-biphenyldicarboxylate
DABCO	1,4-diazabicyclo[2.2.2]octane
DMF	Dimethylformamide
DUT	Dresden University of Technology
HKUST	Hong Kong University of Science and Technology
HPLC	High-Performance Liquid Chromatography
IBU	Inorganic Building Unit
ICP	Inductively Coupled Plasma
IRMOF	Isoreticular MOF
MDIP	3,3′,5,5′-tetra- carboxylatediphenylmethane
MIL	Materials of Institute Lavoisier
MIP	Materials of the Institute of porous materials from Paris
MOF	Metal–Organic Framework
NMR	Nuclear Magnetic Resonance
NU	Northwestern University
PCN	Porous Coordination Network
SALI	Solvent-Assisted Ligand Incorporation
TCPP	Meso-tetra(4-carboxyphenyl)porphyrin
TGA	Thermogravimetric Analysis
TzGal	5,5′-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2,3-triolateUiO University of Oslo
XRD	X-ray Diffraction
ZIF	Zeolitic ImidazolateFframework

1. Introduction

Porous materials have attracted the attention of scientists for several decades. The presence of pores and high surface areas make this type of solids propitious for a wide variety of applications such as molecules capture and storage, filtration or catalysis, among others. Zeolites, activated carbons, and silica are examples of benchmark porous materials that have been employed in industries for long time. [1]

The impact of porous materials for industrial and technological applications can be of prime importance. Therefore, many scientists have embarked on the quest of finding new solids with higher surface areas and new properties that can make them appealing for novel applications or to improve the efficiency of current ones. Since the early 1990s a new series of hybrid materials, porous polymeric coordination networks, has emerged as a promising class of crystalline porous solids. [2–5] These solids have been denoted as metal-organic frameworks (MOFs) and have received increasing attention promoting them as a very popular research field among the scientific community. [6–8]

MOFs are a family of porous crystalline materials consisting of inorganic building units or IBUs (metal ion, or, more often, metal-oxo-clusters/-chains) that are bridged together by means of organic building units, also called ligands or linkers (bearing coordination functional groups such as carboxylates, phosphonates, azolates…), through coordination bonds, leading to a periodic porous 2D or 3D structure (Figure 1). [9,10]

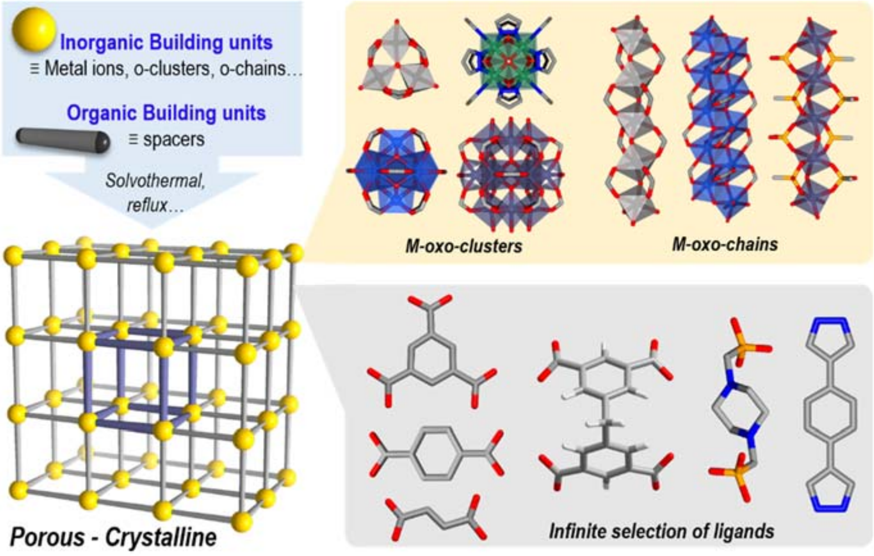

Figure 1. General overview summarizing the modularity and the versatility of the crystalline structures of MOFs.

MOFs have aroused great interest by presenting numerous features that have shown considerable potential of efficiency enhancement in a variety of applications, when compared to conventional porous materials such as carbon, zeolites, clays... Indeed, their highly modular crystalline porous structures, (with tunable surface areas and pore sizes, pore geometries, and chemical tunability) make these versatile materials appealing for a wide range of potential applications related to the environment, energy, health, catalysis, sensing, electronics, gas adsorption and separation. [6–8]

Nevertheless, despite the evident and numerous advantages that these hybrid materials may offer for a plethora of potential applications, most MOFs still suffer from specific limitations that have slowed down their integration into industrial applications. Albeit substantial progresses over the last few years, stability, scalability and sustainability as well as cost limitations remain important barriers that MOFs still shall overcome to reach industrialization. Indeed, their limited stability (chemical, thermal or mechanical) in some cases, the use of expensive and/or toxic chemicals (e.g. precursors, organic solvents) together with the use of sometimes complex and/or energy demanding synthetic conditions (e.g. solvothermal) are among the practical aspects that, for several years, have hampered the great potential of these materials. They have significantly contributed to consider MOFs as "unsuitable" for industrial developments in comparison with commercial activated carbons or zeolites, already in use in industry since decades.

In this regard, significant efforts are devoted, nowadays, to unravel these issues. The discovery of MOFs with enhanced stability is a priority for many scientific groups. In parallel, developing more environmentally friendly scalable synthetic routes is also being increasingly favored. This book chapter provides an overview on the considerable advances that have been made in this line. It gives some insights on the strategies that have been followed to develop robust MOFs and greener synthetic routes, paving the way for MOFs towards higher levels of developments.

2. Stability of Metal–Organic Frameworks

The stability, also called robustness, is one the main feature that any material/compound should present at least in the timeframe of defined operating conditions. Subsequently, it can be designated as a multifold feature (also depending on the required conditions), and its definition can be further divided into three main subcategories. Accordingly, one can associate to a given MOF a chemical, thermal and/or mechanical stability.

Nevertheless, even though the definition of stability seems to be simple and straightforward, the actual concept is, in reality, more subjective. Nowadays, there is no strict parameter/standard to delimit what can be considered, in absolute terms, as a chemically, thermally of mechanically stable MOF. Consequently, the so-called stability of a MOF stands only under certain tested conditions, or, in some cases, that a MOF is more stable relatively to another when tested under similar parameters. For these reasons, one shall consider a MOF as robust when it can retain its crystalline structure and properties (including porosity) after being exposed to the operation conditions required for a desired application.

Assessing the stability of a MOF cannot rely on only one characterization technique but it must be confirmed after corroborating the results of different analyses. Indeed, while X-Ray Diffraction (XRD) is a natural tool to assess the crystallinity of a structure, this is far from being enough. Other techniques are required such as N_2 porosimetry to check if the material has maintained its porosity or not. Moreover, additional analysis such as infra-red spectroscopy, solid-state NMR, thermogravimetric Aanalysis (TGA), especially when studying the thermal stability, can also be of great help. Besides, chemical analysis (i.e., elemental analysis, ICP) and chromatography (i.e., HPLC) can be, for instance, of high need to identify if the MOF degradation is very slow. Finally, electron microscopy is an important tool to verify that the particle morphology (size and shape) has not been impacted throughout the exposition of the MOF crystals during the practical use. Even if all these characterizations are in favor of the stability of the MOF after its exposition, one shall ultimately verify that the properties of the MOF are kept under operating conditions.

In the following sections, a general overview will be given in terms of the aforementioned three subcategories of stability. Definitions for each type of stability will be drawn up together with an outline of structural features that can potentially confer to a MOF an enhanced chemical, thermal or mechanical stability. It is worth mentioning, though, that the given stability cannot be absolute but depends on the complex interplay between the chemical natures of the building units, their arrangement (topology of the MOF), the shape and the size of the cavities, as well as a series of sub-factors such as the coordination geometry of the cation, the nuclearity and the connectivity of the IBU, the rigidity and the topicity of the linker, the hydro-phobic / -philic character of the network (particularly with water), the redox behavior, the presence of open metal sites or defects, framework catenation, inter- and intramolecular interaction, the particle size and so on.

2.1. Chemical Stability

The chemical stability of a MOF can be defined as the resistance of its structure to degradation (or coordination bond breakage) when exposed to a certain chemical environment. This latter may include the presence of water, either as a liquid or as a vapor, other molecules or ions, corrosive or not, such as phosphates, carbonates, ammonia, SOx, NOx, etc., or even different ranges of pH, temperatures or concentrations. In general, the chemical stability of a MOF strongly depends on the strength of the iono-covalent bond that links organic and the inorganic parts of the structure. In other words, a stronger coordination bond between the organic linker and the metal oxo-cluster is expected to lead to the formation of a more chemically stable structure.

This section will discuss, although in a non-exhaustive manner, the different approaches that have been followed to enhance the chemical stability of MOFs, with particular attention dedicated to the stability in aqueous media. It will be divided into two main categories: the first will focus on strategies allowing strengthening the interaction between the metal cation and the organic ligand, while the second will be showing alternatives aiming to preserve the coordination bonds.

2.1.1. Reinforcing the coordination bond

Because water (or humidity) is an essential element of our environment, this part will address strategies leading to enhanced chemical stability through examples mostly dealing with aqueous conditions (neutral, acidic and basic). However, stabilities toward other species than water will be also highlighted in some cases. [11–14]

Indeed, stability of MOFs under aqueous conditions (or hydrothermal stability) becomes of great importance for numerous applications, due to the fact that most of the processes (at room temperature or higher) take place in atmospheres where a certain degree of moisture (if not liquid water) cannot be prevented. This is, for instance, the case for water purification/desalination (the most prominent one), [15–17] for gas/vapor separation (although corrosive contaminants are also present), [18, 19] or even for drug delivery and other biomedical applications, where the robustness toward humid environments under different pH and in presence of highly complexing species (i.e., phosphates, enzymes…) becomes critical. [20, 21]

The main reason for which a MOF would present a low stability under an aqueous environment is the existence of a competitive reaction between the linker (or the metal-ions) and the water molecules or any other species present in it, such as hydroxide ions. This competition reaction can be easily explained considering the strength of the Lewis pair –metal-ion as acid and ligand as base– that forms the link between the building units of the MOF. Subsequently, a hard base, such as a carboxylate group, exhibits a stronger bond with a hard acid (metal-ion with high valence state) such as Zr^{4+}, Ti^{4+}, and Cr^{3+}, rather than divalent cation such as Cu^{2+} or Zn^{2+}. Similarly, low-valence metal-ions (soft acids) such as Zn^{2+}, Cu^{2+} and Ni^{2+} give stronger bonds when combined with soft ligands such as imidazolates, triazolates or pyrazolates. One can give, for instance, the striking example of zinc-carboxylates MOFs, such as IRMOFs, highly unstable in water, while Ni-pyrazolates MOFs remains intact after exposure to water or even very harsh conditions. [22, 23]

In fact, when MOF particles are in contact with water, this molecule enters into the pores of the MOF and gets in competition with organic linker, resulting in a possible break and hydrolysis of the metal-ligand bond. This phenomenon is even further amplified in a non-neutral pH. In a basic medium, hydroxide ions (hard base) present in the solution can easily react with high-valence metal ions, resulting in the replacement of the organic linker to produce metal oxides or hydroxides. In a similar scenario, in acidic media, MOFs formed via a low-valence metal and N-donor linker are expected to be more easily degraded due to the affinity between the azolate groups and the protons present in solution. [24]

	High-valence metal ion (M) + Carboxylate (L)	**Low-valence metal ion (M) + N-containing linker (L)**
Acidic medium	Higher resistance	$M^nL^- + H^+ \rightarrow M^n + LH$
Basic medium	$M^nL + nOH^- \rightarrow M(OH)_n + L^-$	Higher resistance

Moreover, one should also remind that the complexing ability of the functional group has also a considerable effect on the strength of the interaction: the higher the pKa, the stronger is the interaction and, hence the less vulnerable the bond is. In this regard, three approaches have been followed (where at least one of the building unit is showing high complexing potential) to reinforce the metal-ion/organic ligand interaction and hence, enhancing the chemical stability:

i. the use of high-valence cations or high-charge density cations (directly related to the charge over the ionic radius of the metal-ion);
ii. the use of organic linkers bearing highly complexing functional groups (showing higher pKa values than that of carboxylic acids (~4.5));
iii. the combination, when chemically possible, of both cations of high oxidation states and highly complexing ligands.

Strengthening the interaction between the metal-ion and the organic bridging ligand is however not without any consequence on the formation of MOFs. Indeed, a stronger interaction is associated to a faster kinetics of crystallization between the chemical species (ligands and solvent), hence decreasing the possibilities of a controlled MOFs nucleation and growth. To circumvent this problem, reaction combining high-valence cations and polycarboxylic acids are generally performed under slightly acidic conditions (such as in the presence of HF [25, 26] or HCl [27]). This is done in particular when the metal-ion is highly oxophilic in order to limit the formation of metal oxides or hydroxides and to maintain a minimal concentration of metal cations needed for the formation of hybrid frameworks in solution. Moreover, the use of monotopic carboxylic acids [28] or more recently oxalates [29] has also shown to be very useful for a better control of the MOF crystallization. These molecules (generally monotopic ligands, but not limited to) are known as modulators (or inhibitors) that are not expected to bridge the IBUs but to compete with the polytopic linker helping in controlling and slowing-down the nucleation-growth processes and yielding to larger crystallites. One would also notice that strategies using less reactive precursors such ester form of the ligand, [30] metal oxides, metal hydroxides [31] and even pure metal [32] have been in some cases reported to be successful in controlling the crystallization process.

Since the early 2000's, trivalent metal-ions (such as Cr^{3+}, Al^{3+} and Fe^{3+}) have proven to be prone to yield relatively highly chemically stable MOFs suitable for many applications. Materials of Institute Lavoisier (MIL*n*) compounds are prominent successful examples of this strategy. One can cite for instance the benchmark MIL-53 [22, 33–35] and MIL-100 [36–38] ($M = Al^{3+}$, Fe^{3+}, or Cr^{3+}) analogues that are built of benzene-1,4-dicarboxylate (terephthalate) and M-oxo-chains for the former, and M-oxo-trimers and benzene-1,3,5-tricarboxylate (trimesate) for the latter; showing 1-D microporous channels or mesoporous cages, respectively (Figure 2). They have shown very good stability in aqueous media, at different pH (ranging from 2 to 12 in the case of MIL-53(Cr)), and turned to be successful candidates for dehumidification or separation [39]. More recently, the Al dicarboxylate MIL-160 has also proven to be a very promising material for application related to water. [40] It is constructed from Al-oxo-chains and furan-2,5-dicarboxylate (Figure 2) and its synthesis can be easily scaled up in green conditions and at high space time yields. Due it is very high stability in water and inherent properties towards water uptake, it has shown high promises for application in heat reallocation. [41]

Other relatively hydro-chemically stable MOFs based on more extended ligands and/or higher topicities than the aforementioned ones have also emerged more recently. [42–44] This is for instance the case of MOFs constructed from meso-tetra(4-carboxyphenyl)porphyrin (TCPP) and the Al-oxo-chains [45] or Fe-oxo-trimer (labeled PCN-600) [46] that have been reported to be stable in water as well as into slightly acidic pH (~5) and pH values ranging from 2 to 11, respectively. Moreover, MIL-127(Fe) (also known as *soc*-MOF(Fe) or PCN-250), built-up from Fe-oxo-trimers and 3,3′5,5′-azobenzenetetracarboxylate (ABTC), has been shown to be hydrothermally resistant. [47–49]

It should be highlighted that chemical stabilities of MOFs based on trivalent metals can drastically drop from one analog to another. This is due to differences i) in charge density (Z/r^2) between the different ions (i.e., Al^{3+} *vs* In^{3+}) [50], ii) in kinetics of ligand exchange (i.e., $2.4 \times 10^{-6}\ s^{-1}$ for $Cr(H_2O)_6^{3+}$ *vs* $1.6 \times 10^2\ s^{-1}$ for $Fe(H_2O)_6^{3+}$) [51, 52], and/or iii) in their redox behavior (for instance, Al^{3+} *vs* V^{3+}) s [34, 35, 47–49]. Kinetic crystalline phases can also have a lower chemical stability compared to thermodynamic ones. This can be exemplified by comparing MIL-88B(Fe)'s and MIL-101(Fe)'s both built up from Fe-oxo-trimers and dicarboxylates, where building units are arranged in different fashion. These phases tend to be produced using shorter synthesis times and/or lower temperatures and in some cases to undergo phase transition towards denser polymorphs such as MIL-53(Fe)'s [42]. One can also, on the whole, consider that for a given metal and IBU, the chemical stability depends on the number of coordinating groups per organic spacer; one representative example is the lower hydrolytic stability of metal dicarboxylates in comparison with tricarboxylates or tetracarboxylates that is observed for MIL-88B(Fe)'s and MIL-101(Fe)'s *versus* MIL-100(Fe) or MIL-127(Fe) (these two latter being even stable under hydrothermal conditions). This can be further associated to chemical and geometrical constraints such as the nuclearity of the IBUs, (i.e., 0D vs 1D), the presence of "vulnerable" sites (i.e., open metal sites), MOF topology, pore dimensions, etc.

Another considerable breakthrough in the quest for chemically stable MOFs has been accomplished with the discovery of the UiO-66 (UiO stands for University of Oslo), which exhibits a *fcu*-topology built of 12-connected hexanuclear Zr^{IV}-oxo-cluster connected by means of terephthalate ligands. [53] Since then, a great number of MOFs containing Zr_6-oxo-clusters, as well as analogous structures to UiO-66 have been produced. Markedly, to the tremendous number of Zr-carboxylate-based MOFs (such as the chemically stable NU-1000 and PCN's, MOF-801, MOF-808, and some of their analogues), [54] one can cite as highly chemically stable the recent MIP-200 (MIP stands materials of the Institute of Porous Materials from Paris) which presents a high potential for application in water-sorption-driven refrigeration (Figure 2). [55] Formulated $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(MDIP)_2(formate)_4]_n$, this MOF shows a *csq*-topology arising from the association of an eight-connected Zr_6-o-cluster bridged together with a tetracarboxylate ligand (MDIP or 3,3′,5,5′-tetra- carboxylatediphenylmethane). The exposure of MIP-200 to a wide variety of extreme chemical conditions, such as boiling water, highly extremely acidic conditions and even a buffer solution at pH 12, results in the retention of its crystalline structure and N_2 sorption capacity, revealing its astonishing chemical resistance.

Although much scarcer than Zr-carboxylate MOFs based on discrete IBUs, MOFs built of Zr-oxo-chains have been reported to exhibits even higher stability (chemical, mechanical). This is mainly the case of MIL-140's family that can be built with a variety of linear dicarboxylate ligands (Figure 2). [56–58] In this specific case, in addition to the strength of the coordination bond, the fact that IBU is chain-like (rather than discrete) with inaccessible oxo-groups together with hydrophobic channels help considerably enhancing the hydrothermal stability.

Ti^{IV} is another prominent tetravalent ion that, when combined with carboxylate linkers, often results in the formation of chemically stable MOFs such as MIL-125 (based on Ti_8 oxo-cluster and terephthalates) that have shown a very good stability in presence of water at room temperature [59]. However, the number of Ti-MOFs in literature still remains very limited, although an increasing number of examples is observed since the last 5 years. [60–64] The main issue that restricts the synthesis of more Ti-MOFs arises, in fact, not only from the strength of the Ti–O bond, but also from the lack of control of the kinetic of crystallization and polycondensation processes. The high affinity between Ti(IV) and oxygen makes almost impossible the process of bond dissociation that is needed in the mechanism of MOF formation in order to get a crystalline solid. As a result, most of the synthesis attempts result in the formation of either titanium dioxide or powders with a very poor crystallinity. [65] In addition, among the few dozen of Ti-MOFs reported so far, almost all of them exhibit a different IBU, making the design of Ti-MOFs' highly challenging. [60, 66] Recently, the synthesis of a highly stable three-dimensional Ti-MOF was reported, using MDIP as linker. MIL-177-LT (where LT refers to the pristine structure before the calcination step leading the MIL-177-HT), built of dodecanuclear Ti-oxo-clusters and MDIP ligands (Figure 2) presents an outstanding chemical stability under extreme acidic treatments. The obtained results demonstrated no apparent damage to its crystallinity and porosity under boiling water, aqua regia at room temperature, and even under a 6M H_3PO_4 solution at room temperature for one week. Regardless of the excellent stability of the material under acid conditions, 24 h in contact of a NaOH/$NaHCO_3$ buffer (pH=10) solution at room temperature however start to damage the crystalline structure. [67]

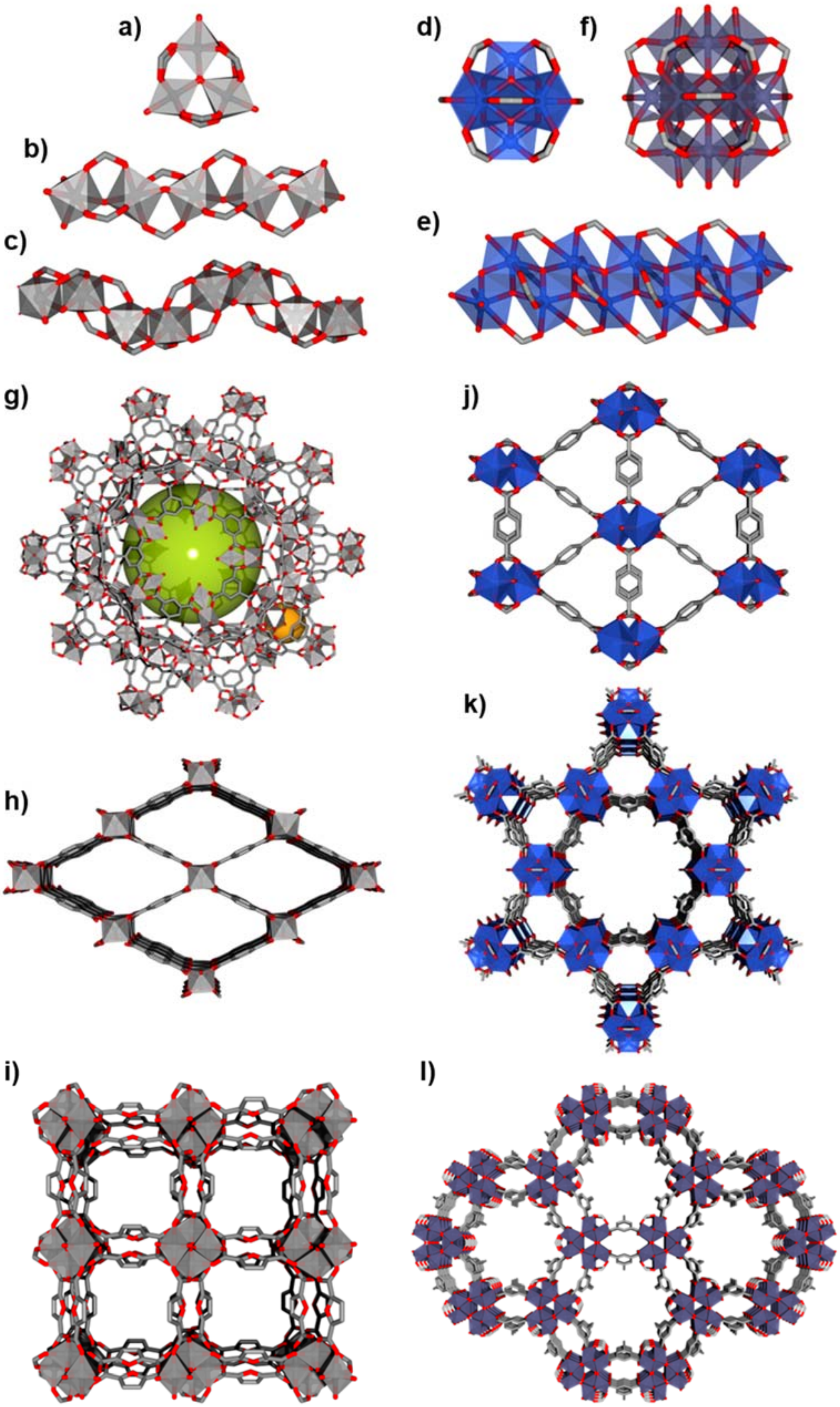

Figure 2. Selected M($^{\text{III-IV}}$)-carboxylate IBUs and MOFs: (a) $\mathrm{M^{III}}$-oxo-trimer, (b) MIL-53's $\mathrm{M^{III}}$-oxo-chains, (c) MIL-160 $\mathrm{M^{III}}$-oxo-chain, (d) $\mathrm{Zr^{IV}}$-hexanuclear oxo-cluster, (e) MIL-140's $\mathrm{Zr^{IV}}$-oxo-chain, and (f) $\mathrm{Ti^{IV}}$-dodecanuclear oxo-cluster. Crystalline structures of (g) MIL-100, (h) MIL-53 (i) MIL-160(Al), (j) MIL-140A, (k) MIP-200 and (l) MIP-177-LT. Color code: $\mathrm{M^{III}} = \mathrm{Fe^{3+}}$, $\mathrm{Al^{3+}}$, etc., dark gray; Zr, blue; Ti, blue-grey; C, gray; N, blue; O, red. Cages of MIL-100 are represented by colored spheres. Hydrogen atoms are not represented for the sake of clarity.

Moreover, involving high-valence cations (hard Lewis acids) and hard Lewis bases linkers bearing highly complexing functional groups has also proven to be very successful strategy for the synthesis of highly chemically stable MOFs. However, one should highlight here that the even more pronounced difficulties in controlling the crystallization process of these materials. In this category, one can recall the examples of MOFs obtained through the association of Zr^{IV} and highly complexing galates (or deprotonated trihydroxyphenyl) groups have been recently described [68–71] and show excellent chemical stability. For instance, MIL-163 (Figure 3), [71] constructed from Zr-oxo-chains connected by means of TzGal (5,5′-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2,3-triolate), can resist to boiling water for days. More interestingly, its crystalline structure can stand in presence of phosphate buffer solution for days, in contrast with Zr-carboxylate MOFs, where even the highly chemically stable MIL-140 can't resist even for 1 day. The chain-like IBU free of oxo/hydroxo bridges together with the high chelate effect of the ligand and the high strength of Zr–O bonds can be some of the elements to rationalize this exceptional chemical stability.

In addition, successful examples encompass also Zr-phosphonates MOFs such as UPG-1 [72, 73] and SZ-1-2-3 [74] that present remarkable stability in extremely harsh conditions (such as highly concentrated nitric acid or aqua regia in the case of SZ-3). This includes also Ti-phosphonates MOFs, reported in late 90's or early 2000's, that are also highly chemically stable. For instance, MIL-91(Ti) (Figure 3), obtained through the association or Ti^{IV}-oxo-chains bridged by highly complexing ligands, *N,N*-piperazinebismethylphosphonates, exhibits an outstanding hydrothermal stability. [75, 76]

Finally, scarce examples combining low valent cations (soft Lewis acid) and highly complexing ligands have been reported, attesting, as expected, an enhanced chemical stability. Here, it should be highlighted that this is mainly the case of linkers based on soft ligands (more suitable to react with soft Lewis acids). Among them, one can cite MOFs based on divalent metal-ions and azolate derivatives such as imidazolates -including zeolitic imidazolate frameworks (ZIFs) [77] and zeolite-like MOFs [78] that on the whole exhibit moderate to high tolerance to humidity and/or water- [79–81] and triazolates [82, 83] that sometimes show relatively good chemical stability even in presence of halogens or highly corrosive NH_3.

Besides, metal pyrazolates based MOFs [23, 84–89] are also a clear demonstration for remarkable stabilities not only in water but also in extremely basic conditions. This is for instance the case of MOFs built of 12-connected octanuclear Ni^{II}-oxo-cluster and linear di-pyrazolate ligands, such as *fcu*-Ni(DP) (Figure 3), capable to withstand to water, harmful organic compounds or SO_2. [23, 89] More recently, PCN-601, built of the same oxo-cluster assembled with square-shaped porphyrine-tetrapyrazolate ligands (Figure 3) and its extended isoreticular analogue (PCN-602) have also been reported to be remarkably stable in aqueous media, at basic pH and in presence of highly complexing species such as phosphates. [85, 90]

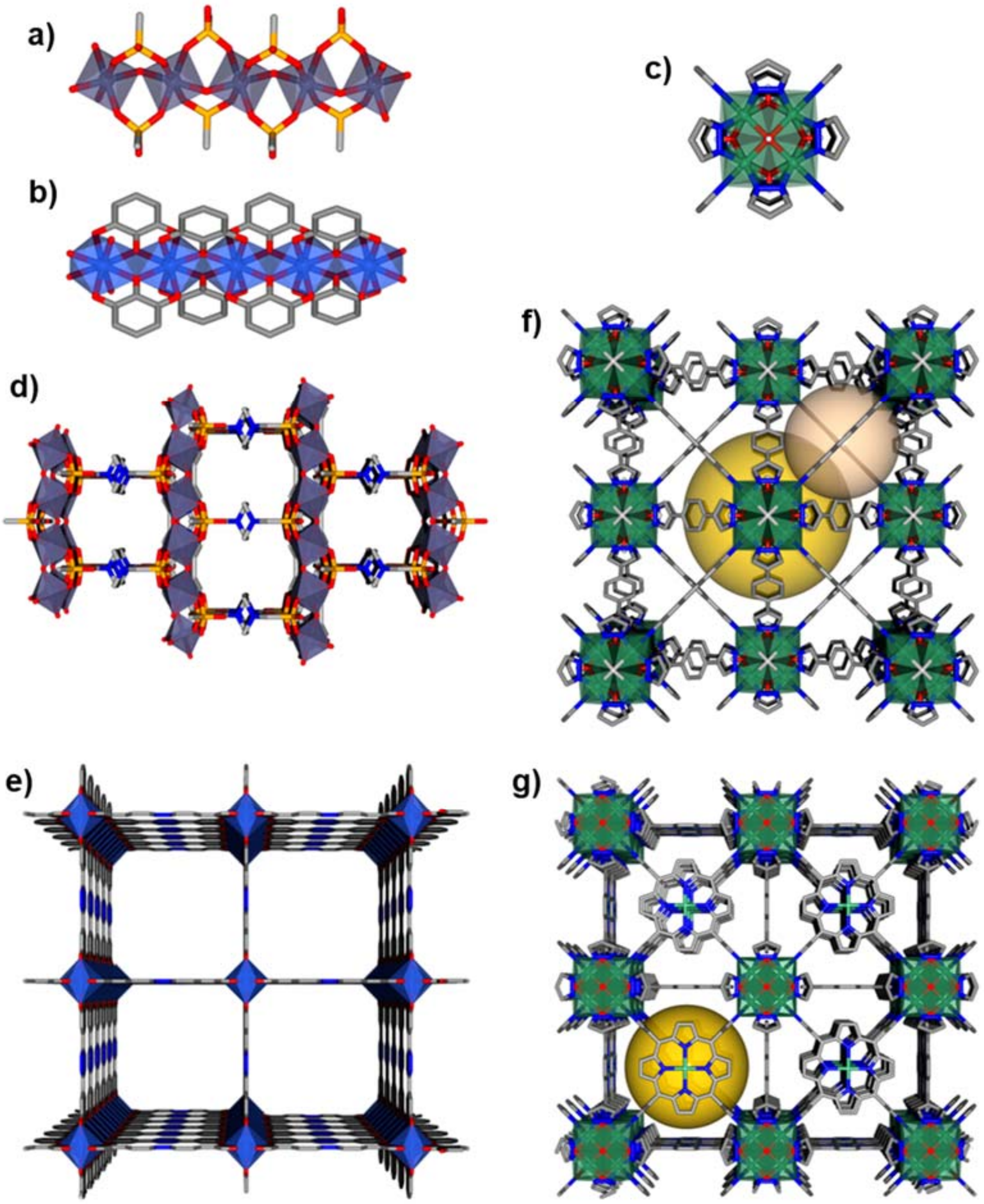

Figure 3. Selected IBUs and MOFs based on highly complexing ligands: (a) Ti^{IV}-oxo-phosphonate chain, (b) Z^{IV}-galates-chain, (c) octanuclear Ni^{II}-oxo-pyrazolate cluster, (d) MIL-91 and (e) MIL-163, (f) *fcu*-Ni(DP), (g) PCN-601. Color code: Ni^{II}, green; Zr, blue; Ti, blue-grey; C, gray; N, blue; O, red. Cages are represented by colored spheres. Hydrogen atoms are not represented for the sake of clarity.

2.1.2. Preserving the coordination bond

Besides the strengthening of the coordination bond between the IBU and the organic linker, there are other strategies in order to improve the chemical stability of MOFs. This relies on the use of a protective "shield" near the metal-ligand bond in order to limit the effect of a competitive reaction. This strategy can be helpful for instance when a given MOF shows high potential for a given particular application, but presents a limited chemical stability. Beyond the chemical stability, embedding MOFs in a (flexible) polymeric matrix can also provide additional mechanical stability (see section 2.3). In both cases, the inherent stability of the MOF is not changing but the degradation kinetics are sufficiently slowed down for the application in play because the MOF is more protected. This approach has been proven to be relevant to enhance the chemical resistance of MOF in presence of water/humidity. It mainly consists in increasing the hydrophobicity of the MOF, therefore limiting the hydrolysis of the framework.

In this regard, two main approaches can be considered:

i. The introduction of bulky groups within the crystalline framework (such as hydrophobic groups to limit the diffusion of water molecules); and
ii. The incorporation of the MOF into a protecting matrix (such as coating the crystallites or simply embedding it into a (polymeric) support).

The introduction of hydrophobic functional groups can be done at the beginning of the synthesis of the MOF (during its crystallization) by choosing the correct organic precursor, or in a subsequent step, as part of a post-synthetic modification. In both cases, the result of the modification should be the same: the presence of linkers with hydrophobic groups that can limit the access of water molecules into the framework. Fluorinated groups such as $–CF_3$ or alkyl groups are the most common options. Note that in any case, the resulting material are necessarily (much) more expensive and less scalable compared with the starting bare MOF due to the (often) high cost of the hydrophobic functional groups and/or the need of a post-synthetic treatment.

Walton et al. studied the influence of the addition of different functional groups on the hydrothermal stability of a MOF. For this, $[Zn(BDC)(DABCO)_{0.5}]$ was chosen as a model case, where BDC corresponds to 1,4-benzenedicarboxylic acid and DABCO to 1,4-diazabicyclo[2.2.2]octane. Different functionalized BDC linkers were tested, arriving to the conclusion that polar functional groups such as nitro, bromo, and hydroxy groups would have a negative effect on the MOF stability in comparison to the parent MOF, while non-polar (hydrophobic) groups like methyl groups, enhance the stability of the MOF in presence of humidity. This systematic study in which the topology and the porosity where maintained constant, allowed to see the beneficial shielding effect that non-polar functional groups have on the Zn-O coordination bond stability. [91] Similarly, MIL-88B(Fe)-$(CF_3)_2$ or UiO-66-$(CF_3)_2$ have shown an enhancement in hydrothermal stability compared with their bare analogs due to the presence of the hydrophobic fluorinated groups. [92, 93]

Another interesting example is the case of phosphonate monoester-based MOFs where the presence of one ester group allows phosphonates play a double role: providing to phosphonates a carboxylate-like coordination mode (only two over three oxo-groups will coordinate but with stronger interaction), and in the same time providing a shielding effect (due the presence of alkyl-groups on the third O-atom) enhancing the stability to moisture. [94, 95]

Following a different approach, Farha *et al.* used the solvent-assisted ligand incorporation (SALI) method to attach perfluoroalkane carboxylates, as well as some other hydrophobic groups, into the channels of NU-1000. It was observed that the presence of the different functional carboxylates increased the hydrophobicity of the material, maintaining their crystallinity and surface area even after 20 cycles of water vapor adsorption-desorption. The main drawback of this method is the significant reduction of the pore size of the material due to the presence of functional groups that occupy the channels of the MOF. However, this reduction in pore size means also a reduction in the size of water clusters that can be formed inside the pores, therefore, limiting the accessibility of water. [96]

A post-synthetic functionalization approach was also used to exchange the monocarboxylic ligands coordinated to the metal oxo-clusters of DUT-67 by a series of different fluorinated monocarboxylates. All the prepared materials presented an increase in their hydrophobic character, evidenced by higher values of contact angles, especially when functionalized with perfluorooctanoic acid (≥110°). At the same time, it was observed that only one type of pore was able to be functionalized, causing a change in the water adsorption mechanism when compared to the pristine material. [97]

A very recent study has demonstrated the improvement of chemical stability thanks to electrostatic interactions. It was demonstrated on isoreticular Ni^{II}-azolate based MOFs that, PCF-8, built up with 1,4-bis(4H-1,2,4-triazol-4-yl)benzene and showing a cationic skeleton (in comparison with a neutral analogue PFC-9, built using the deprotonated form of 1,4-di(1H-pyrazol-4-yl)benzene) is resistant to extremely acidic, oxidative, reductive, and high ionic strength conditions such as 12 M HCl, aqua regia, H_2O_2, and seawater (30 days). This has been explained by the presence of repulsive interaction and steric hindrance toward the positively charged species, thus protecting the vulnerable dative bonds in structure. [98]

The second approach for increasing water stability of MOFs is based on increasing the hydrophobicity of the material by the formation of a hydrophobic layer on the surface of the MOF. This coating, usually consisting of a polymeric material, is expected to protect the MOF from water without affecting the inner porosity (and the performance) of the pristine framework. In 2014, Zhang et al. worked on the external coating of MOF-5, HKUST-1, and ZnBT with a thin layer of hydrophobic polydimethysiloxane (PDMS) by using a thermal vapor deposition technique. This method improved the water resistance of the MOFs by increasing their hydrophobicity, passing from a water contact angle of almost 0° to angles of 130 ± 2°, while maintaining their porosity and surface area. [99] Since then, some other coating matrices have been tested as well as some other coating techniques. Park et al. reported the carbon-coating of IRMOF-1, [100] Maspoch et al. described the coating of HKUST-1 (Cu-BTC) with polystyrene using a spray-drying synthesis method [101], while, more recently, Xu et al. used the simple solution-immersion technique to deposit a hydrophobic layer of organosilicon on the surface of DUT-4. [102]

As an extension to this approach, the formation of a hybrid composite consisting of a mixture of a MOF and a second substrate which can result in a better and enhanced properties for both materials has been tested. Substrates such as carbon nanotubes (CNTs), silica, clays, [103] and graphite oxide (GO) have been tried for the formation of composites with metal organic-frameworks giving encouraging results. Park et al. prepared a hybrid composite by incorporating CNTs into MOF-5. The synthesis method consisted in the dispersion of the carbon nanotubes in a DMF solution containing the required precursor for the synthesis of MOF-5 followed by a heating step. The resulting MOF-composite showed to be stable after one week in air with a relative humidity of 33% while the pristine MOF-5 was almost completely decomposed. [104] Sun et al. reported that at the optimal incorporation of 8.7 wt % of graphite oxide in HKUST-1, both the hydrothermal stability of the material as well as the surface area were increased. The growth of the MOF was observed in-between the graphite layers, which enhanced the porosity. The hydrothermal stability of the sample was improved due the incorporation of the graphite oxide when exposed to water vapor at 363 K for 12 h. Nevertheless, at concentrations of graphite oxide higher than 34.3 wt %, the hydrothermal stability decreased again, due probably to the formation of distortions on the structure that create “easier targets” for the “attack” of water molecules. [105] On the other hand, Decoste et al. achieved the formation of a hydrophobic form of HKUST-1 by the chemical vapor deposition of perfluorohexane (PFH). Grand canonical Monte Carlo (GCMC) simulations showed that, even though the position of the PFH in the pores would not prevent the coordination of water molecules to the Cu atoms in the oxo-cluster, its hydrophobic nature could help preventing the formation of water clusters that are needed to break the Cu-BTC bond, ensuring the preservation of the sample in the presence of water. [106]

2.2. Thermal Stability

Industrial applications where MOFs are used at high temperatures (one should keep in mind that for MOFs, high temperature should not be exceeding ca. 400 °C) are typically catalysis or in some cases gas or vapor phase separation, or other energy-related applications. Besides, withstanding relatively high temperatures is, in some cases, important not only during the application itself, but also for the activation and/or the regeneration process of the material. In this regard, the thermal stability –the capacity of the framework to maintain its crystalline structure and porosity at high temperatures– is a significant parameter to consider.

The most common technique used to study the thermal stability of a given material is thermogravimetric analysis (TGA). Nevertheless, while the TGA of a sample can give important information directly related to its chemical composition (i.e., loss of guest molecules, dehydration of the oxo-cluster, loss of specific molecule) or even the temperature at which the calcination of the organic linker occurs, this technique finds some limitations by not being able to show the precise temperature at which the amorphization of the crystalline structure begins. In this case, a more extensive study of the thermal stability of a MOF can be achieved by using variable temperature X-ray diffraction (VT-XRD) as well as other typical characterization techniques (IR, NMR, porosimetry, SEM…).

VT-XRD is a powerful tool that can give important information about the structural changes that MOFs undergo at variable temperature, even though the conditions at which the measurement takes place may not faithfully represent the real working conditions. Various measurement conditions can be chosen, such as the temperature sweep rate, the scanning time, the atmosphere (sealed conditions or under gas flux), not taking into account, though, that the MOF particle size (and the defect content) can also play an important role in the kinetics of thermal degradation... All these factors make rather difficult the comparison of thermal results among different reported studies, which means that the information obtained by this technique must be analyzed with caution.

Compared to the chemical stability of a MOF, the thermal properties of a framework are even more difficult to predict. However, some common rules can be found, giving an idea of the different aspects that may influence the robustness of the structure at relatively high temperatures. In summary, a higher stability is directly related to a stronger coordination bond between the Lewis acid and the Lewis base, which means that a stronger metal-ligand interaction is translated into a higher thermal stability. A dense packing will also produce the desired effect, whereas the presence of defects in framework usually results in a decrease of the thermal stability of the material. In fact, Lillerud et al. showed that by increasing the synthesis temperature, the number of missing-linker defects (sites of weakness) in UiO-66 can be decreased. Consequently, as shown in Figure 4, the most “ideal” UiO-66 obtained, presented the highest thermal stability by retaining its crystallinity until 450 °C. [107, 108]

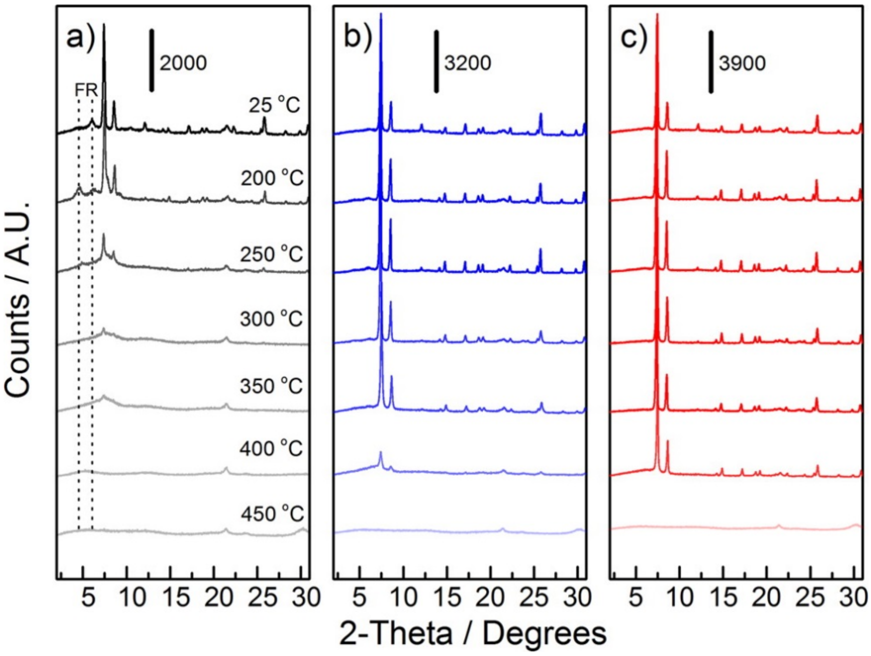

Figure 4. PXRD patterns (Cu-K*α* radiation 1.5418 Å) recorded after heating UiO-66 samples for 12 hours in air at various temperatures. The two reflections labelled "FR" are symmetry forbidden. The red curves correspond to a more "ideal" UiO-66, showing a higher thermal stability. Figure reproduced with permission from reference. [108] Copyright (2014) American Chemical Society.

Concerning the nature of the metal ions that build the MOF, it has been observed that a higher thermal stability can be obtained for materials containing metals at their most stable oxidation state. For example, MOFs containing Fe(III) and Cu(II) are more thermally stable than those based on Fe(II) [109, 110] and Cu(I). [111, 112]

Another important factor to be taken into consideration when analyzing the thermal stability is the nuclearity of the IBU. When comparing the thermal properties of a series of MIL-140, which consists of a long infinite zirconium oxide chains, against the thermal stability of a series of UiO-66 materials (Zr-oxo-cluster), it can be observed that the formers present a relatively higher stability, preserving their crystallinity up to 500 °C while the materials formed by the $Zr_6O_4(OH)_4$ oxo-clusters lose it around 450 °C. [58] A similar trend was observed for MIL-125 with a Ti_8-oxo-cluster against COK-69, consisting of Ti_3-oxo-clusetrs. This observation leads to the conclusion that MOFs with IBU of higher nuclearity, including infinite chains, will present higher thermal stabilities. Indirectly, this enhanced thermal stability can be also related to condition in which the metal oxide (or the IBU) can be formed. The more thermodynamically stable is the IBU, the more thermally stable will be the corresponding MOF.

Concerning the organic linkers that form the MOF, some tendencies have also been observed. When exposed to high temperatures in presence of oxygen, carboxylates and phenolates undergo decarboxylation and oxidation reactions, respectively, which makes these two kinds of linkers less suitable for the synthesis of a highly thermally stable MOF, although to a much lower extent for the carboxylates. In comparison, phosphonates and sulfates linkers present a certain chemical inertness that will be favorable their thermal stability. [113–115] It can lead to sensitively high thermal stabilities such as the one of the Zr methylene bisphosphonate MIL-57 that is thermally stable up to 700°C under air atmosphere. Finally, when choosing the organic linker for a thermally stable MOF, short aromatic molecules are usually favored due to their rigidity and robustness in comparison to flexible aliphatic linkers. Indeed, it has been observed that the thermal stability is usually lower for these systems. [116]

2.3. Mechanical Stability

The number of studies focusing on the mechanical stability of MOFs is considerably lower when compared to those aiming to enhance their chemical or thermal stability. Nevertheless, this type of stability becomes of great importance when a certain material needs to pass through a process associated to a mechanical stress such as compacting and shaping. This step is usually imperative before the material can be used in an industrial process and commercialized.

The mechanical stability of MOFs refers also to the resistance of the material to collapse under vacuum or when in presence of a certain external pressure. Most of the first MOFs synthesized presented a relatively low mechanical stability, resulting in the collapse of the porous structure once the guest molecules were removed. [117] However, with time and after the development of more chemically stable MOFs, the mechanical properties of these materials have also seen great improvement.

Even now, the activation step or the removal of guest molecules in the pores is still an important step to take into consideration. The collapse of the structure during the activation of a sample is due to the capillary forces created by the presence of solvent molecules trapped in the pores. Some values are summarized in Figure 5. In order to prevent this problem, the molecules in the pores might be ideally exchanged with another solvent that presents a lower surface tension, or in an ideal situation, supercritical CO_2 activation can be used to guaranty almost zero-capillary force. [118, 119]

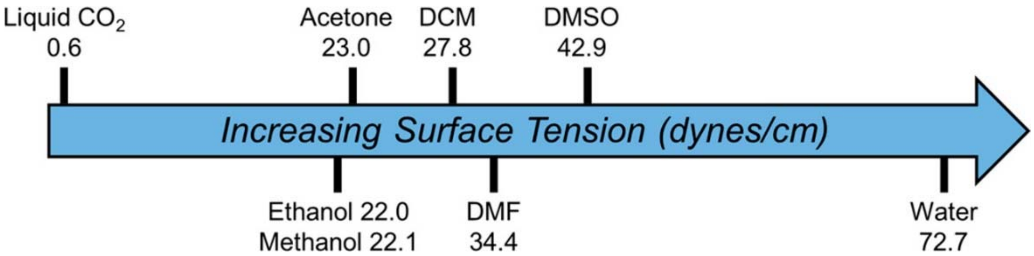

Figure 5. Surface tension of different organic solvents (DCM: dichloromethane; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide) compared to liquid CO_2. Figure reproduced with permission from reference. [118] Copyright (2017) American Chemical Society.

The mechanical properties of a solid material can be evaluated using different parameters. The Young's modulus corresponds to the capacity of a solid to undergo compression in one direction, the shear modulus corresponds to the withstand to deformation when applying a force parallel to one face of a solid, the Poisson's ratio is the ratio of transverse strain to longitudinal strain in the direction of the applied force, while the bulk modulus represents the deformation of the material in all directions when a uniform pressure is applied. One or several of these parameters can be reported as a measurement for the mechanical stability of the MOFs.

While it may be difficult to determine exactly what makes one MOF more mechanically stable than another, several studies along the years have provided some general tendencies. For this purpose, structural and topological factors must be considered. For example, the computational study performed by Coudert *et al.* showed that the presence of missing linkers in UiO-66 results in the decrease of its shear and bulk moduli, demonstrating the negative effect of defects in the mechanical stability of the material. [120]

In general, MOFs with higher porosity tend to have a lower mechanical stability. It means that denser materials can present better mechanical properties. Numerous factors can influence the mechanical stability of a MOF. The coordination number, the functionalization [121] and structure of the organic ligand, the presence of guest molecules in the pores, [122] the strength of the chemical bonds, and the topology [122] of the framework are some of the parameters that must be taken into account when studying the mechanical stability of a MOF.

Zhou et al. predicted by the use of density functional theory (DFT) calculations that MOFs with higher connectivity between organic−inorganic nodes present a higher mechanical stability. In this light, UiO-66, a MOF based on 12-connected Zr_6-oxo-clusters will present a higher bulk and shear moduli in comparison to other Zr_6-oxo-clusters based MOFs with lower network connections. [123] In the same study, the influence of the linker's length was evaluated by comparing the same mechanical parameters calculated for isoreticular structures. Again, UiO-66 (linker with one phenyl ring) presented a much higher mechanical stability compared to UiO-67 (linker with two phenyl ring) and UiO-68 (linker with three phenyl ring), evidencing the negative effect that longer organic linkers have in the mechanical properties of a MOF.

As mentioned before, frameworks with larger pore sizes can be quite unstable. Subsequently, the insertion of bridging ligands that can split the bigger channels into smaller segments can be a plausible solution to enhance the rigidity of the MOF and its mechanical stability. Indeed, it is very rational that minimizing the tension of the porous framework by installing molecular struts which help better holding the walls. [124, 125] For instance, Yaghi et al. achieved the improvement of the mechanical stability of MOF-520 $[(Al_8(\mu\text{-}OH)_8(HCOO)_4(BTB)_4)]_n$ by what they call the "molecular retrofitting" of the material. In this method, an additional linker is incorporated into the framework in order to reinforce its structure. As shown for MOF-520 in Figure 6, a molecule of 4,4′-biphenyldicarboxylate (BPDC) was integrated between two IBUs. This molecule acts as a "rafter" to further support the structure. The reinforced MOF-520-BPDC was stable to a pressure up to 5.5 GPa, while its pristine counterpart (MOF-520) was destroyed at 2.8 GPa. [126] Similarly, self-catenated or interpenetrated structures are also expected to show enhanced mechanical stability. [127]

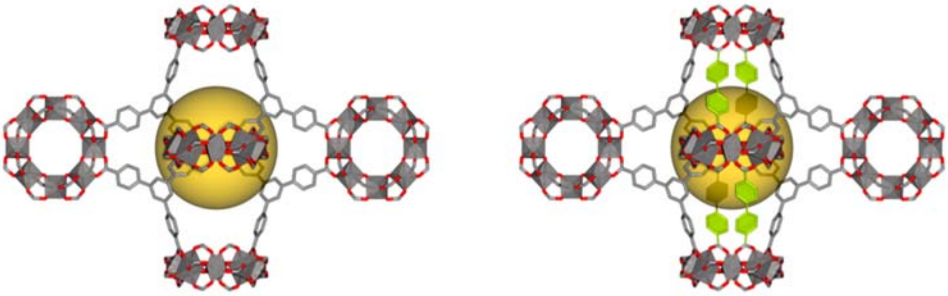

Figure 6. Left: structure of pristine MOF-520. Right: retrofitted MOF-520-BPDC. BPDC girders are shown in green. [126]

In summary, a MOF will more likely exhibit a better mechanical stability when it possesses smaller pores, short linkers, strong linker-metal interactions, defect-free, and dense structures. Moreover, the flexibility (either of the linker and/or of the MOF framework and inducing structural phase transition without bond breakage) [128] is a non-trivial parameter that one should also keep in mind. Indeed, it is expected that the flexibility helps the material to support better the external stimuli (such as pressure). However, this complex aspect has not been discussed in this section focusing only on rigid structures (without phase transition).

3. Environmentally friendly MOFs

Making a flawlessly environmentally friendly MOF is not an easy endeavor. Indeed, one of the most important targets should be to help driving MOF properties into real applications. In fact, when trying to lower the impact to the environment, several interconnected parameters are at play, all of which closely related to economic necessary compromises. The production of MOFs requires, as for other chemicals, various important aspects such as safety, health, environment impacts, synthesis and engineering processes (e.g., product recovery, purification, etc.). [129] Moreover, it is important to consider different production scales for a given material i.e., i) *lab scale*: This is generally around the 100 mg to a few g scale. Here not much efforts are dedicated to optimizations in terms of energy used, chemicals toxicity, processes, etc. The goal is to obtain a pure and performant product and efforts on fundamental science and understanding are the most important; ii) *kilo scale*: This scale from a few hundred g up to a few kg, is crucial and the target is here to optimize the fabrication for large scale purposes, prior to further industrial manufacture end targets. The goal is to reduce the cost of fabrication using chemicals that are safe, non-toxic and with minimal impacts to the environment but also in most cases to produce enough MOF to integrate them into various process demonstration tests at the laboratory pilot scale; it often involves the shaping of the MOF powder to avoid any diffusion issues. Most of the improvement of the synthesis and the material recovery and purification are done in this step; iii) *pilot scale*: this scale (from a few dozen kg to a few hundred kg) precedes the industrial scale where further improvement is made in the process engineering (e.g., solvent and unreacted precursor recirculation) and produce in all cases shaped MOFs; and iv) *industrial scale*: Normally most of the possible synthesis and engineering processes improvements are validated and the production exceeds the ton scale; at this stage note that industry shall overcome important regulation issues such as those associated with REACH or other economical perquisites, etc.

3.1. Chemicals

Lowering the impact to the environment requires a careful choice of the types and quantities of chemicals to be employed during the whole process of fabrication of the final material. [130] The common synthetic methods involve the use of various metal-ions precursors, organic linkers, solvents and sometimes additives. [131] An environmentally friendly MOF should be built of components that have as low as possible impact on the ecological system during its utilization and/or after (recycling of the material).

Metal-ion precursors

Some metal-ions that have been thoroughly used for the synthesis of MOFs and that can be accepted as safe for the environment are aluminum, iron, zirconium, titanium, copper, zinc, etc. [132] However, these metals are mostly incorporated in the material via a reaction involving metal salts and linkers. Therefore, the choice of the metal source is crucial in the fabrication of the materials as the counter ions are not part of the materials. Sulfates and oxides metal sources are preferred. However, they are usually not so trivial to use generally because of the lower solubility of the reactants. [131] Chlorides and nitrates are more frequently employed as for instance their reactivity toward carboxylates or phosphonates is favorable. Nevertheless, they have to be avoided for safety and corrosion reasons and as a result are not favorable for large scale production. [131]

Linkers

If one analyses the final cost of a MOF material, the part related to the linker is usually prominent. The fabrication process of these linkers is typically well established as in most cases commercially available ligands are already considered for other industrial applications. These molecules are often produced at large scale and their price is in some cases rather attractive. In addition, it is better if their fabrication process exhibits a minimal environmental impact. Thus, bio-sourced ligands or bio-mass derived linkers are usually preferred due to their lower environmental impact. [40,131,133] In addition, these latter are usually more soluble in water and thus the related MOF synthesis is greener, which leads to a reduced final cost of the material. Larger and often costly ligands with poor solubilities in water or alcohols have therefore to be discarded as in most cases the corresponding MOF synthesis requires the use of toxic solvents and/or larger amounts of solvents (dilution) that negatively impact their production (cost, low space time yields, etc.). [55]

Solvent

The choice of the best solvent for a given MOF synthesis is not trivial. The optimal solvent should be safe, non-toxic, environmentally friendly, recyclable and cheap. Although finding a solvent fulfilling these requirements is ideal, when one deal with lab scale synthesis, the choice is more driven by other considerations such as i) maximal solubilization of the precursors to enable an appropriate and successful metal-ligand reaction and ii) a possible template effect to favor certain topological arrangements. Other solvents are also typically required during purification processes such as the washing and the so-called activation steps of the material. Unfortunately, lab scale activation often requires larger solvent quantities than the synthesis itself. Reducing the volume of solvent is therefore of utmost importance to minimize safety, health, environmental and cost issues. [131,134] Solvent waste can indeed be a source of pollution itself via VOC emissions or as liquid during the various phases of the manufacture processes. Therefore, water is the best economic and environmental choice while having no negative impact on health and safety. Other preferred solvents are alcohols and esters. However, one shall take into account that the use of high boiling point solvents can have a negative impact on the environment because of the energy demand to recycle.

Additives

Additives are often used as inhibitors during the synthesis reactions since they have an effect on the metal-ligand reactions, acting as competitors for the MOF linker and therefore allowing a more controlled material synthesis. However, they are usually used in large excess which raises economic issues even if greener ones are selected. [40,133,135] Additives are also used to improve the solubility of the linkers by promoting the formation of linkers salts. Many reports on MOF synthesis involve the use of inorganic or organic bases however in a stoichiometric amount. Typical bases are inorganic ones such as NaOH or KOH that have a minimized negative environmental impact. However, when using organic solvents, organic bases are considered and, therefore, attention should be given to select bases (e.g. amines, etc.) that possess a minimum effect on safety, health and environment. Thus, as general rule, it is preferable to use water, alcohols or esters with inorganic bases to promote the solubility than using a toxic solvent with higher solubilizing capabilities.

3.2. Synthesis and purification processes

The preparation of MOFs involves mostly two steps i.e., the fabrication of the material in its raw form so called as-synthesized form and a purification process in which the material is cleaned of any unreacted precursors and the pore content is exchanged with a clean, preferably low boiling point and as green as possible solvent.

3.2.1. Synthesis process

In a typical MOF reaction preparation, precursors are mixed together in order to promote metal-ligand bond formation. Batch and flow type synthesis can be distinguished. However, the great majority of the reported material syntheses use batch type methods. This class of preparation involves a closed vessel in which precursors are mixed together using a single solvent or a mixture. The reaction takes place in an auto-generated pressure environment i.e., at temperatures exceeding the boiling point of the solvent or at ambient pressure at temperatures below the boiling point. For economical and safety reasons, ambient pressure synthesis is clearly advantageous and is therefore a method of choice for large scale production. [131] As of today, this is the only reported method for an industrial batch ton scale production of an Al based MOF (Basolite A520) synthesized in water, with environmentally friendly and economically favorable precursors and a space time yield as high as 3600 $kg/m^3/day$. [131] Among these types of processes (batch and flow), some methods can also be of great economic and environmental interest. For instance, microwave (hydro/solvo-thermal) synthesis is a very attractive method and is often used to produce small particle size with a minimum polydispersity. The heating process is rapid and very efficient in terms of thermal energy loss and is therefore environmentally and economically favorable. This mode of synthesis is beneficial for fast and efficient heating. It enables the uniform formation of crystallization nuclei in the whole reaction mixture. Crystal growth is therefore controlled, and the entire MOF formation process involves very short time. However, the safety and the high cost of the instrumentation is limiting a possible industrial scale production. One interesting though less used method is the electrochemical synthesis. Even if it often requires organic solvents, this type of synthesis can be very advantageous as it is a metal salt free synthesis. The materials can also be obtained in shorter times and a continuous synthesis mode can be envisaged. [136, 137]

In contrasts to batch type syntheses, flow type process is very attractive method to scale-up MOFs as associated to a continuous production together with a very high space time yield and a minimal solvent use. It can therefore be of a high economic and environmental value and thus promising for MOF industrialization. Numerous reports have devoted to date efforts to produce various MOFs following this route. [138] One can consider extrusion as a successful method to produce through thermo-mechanical effect the large scale production of MOFs associated with high space time yields. [139] However, as this method involves short reaction contact times as well as low mixing efficiency, precursors poor solubilities can be an issue. Therefore, this method still needs further optimization to be applied to a larger variety of MOFs. Another attractive method is spray drying; this allows the synthesis and shaping of small objects at the same time. [140, 141] This is therefore an environmentally and economically attractive method. High space time yields may be obtained using as green as possible precursors and solvent, making this process a method of choice for the industrial preparation of shaped MOFs. As for the extrusion method, one cannot however produce any type of MOFs using this technique. More generally, solvent free types syntheses (or minimal solvent amount) are indeed very favorable in terms of environmental impact and cost of production. [142] However, these methods still need further developments to include more industrially relevant materials as well as purification of the crude materials that often requires the use of solvent.

3.2.2. Purification processes

Purification processes in MOF synthesis have not, to date, been well addressed. These should however not be neglected because of the time allocated, the expensive necessary materials such as the important quantities of solvent required to perform all the necessary steps. Therefore, the final space time yield of the entire processes (synthesis and purification) can be greatly reduced. Typical purification steps comprise filtration or centrifugation when the MOF particle size is small associated with clogging effects. The impact on the environment is therefore not negligible and could even be worse than the synthesis process itself. Reducing or eliminating these steps when possible can be a remarkable step toward a greener and cheaper manufacturing cost. Purification processes include recuperation of the material as a powder and elimination of any impurities from the as-synthesized material (i.e., unreacted precursors, solvent or additives). For mostly economic but also environmental reasons, a chemical recirculation process shall be in place when addressing scale up of materials. An ideal system would be a flow type water based and ambient pressure synthesis process with highly soluble and green precursors along with a maximized yield and minimum unreacted precursors that require little to no extra purification steps. When dealing with a typical batch synthesis process, one shall however consider the use of a precursor recirculation process to avoid any chemical loss.

4. Concluding remarks

It is now clear that the era of MOFs has substantially evolved over the last decade demonstrating the great potential of this new family of materials in addressing serious societal and industrial challenges.

If achieving chemically stable MOFs seems to follow clear guidelines, thermal and mechanical stabilities are still less rationalized. Though, whatever is the required stability for each application, the robustness of MOFs is governed by a complex interplay between chemical and/or structural parameters that one can tune to achieve a satisfying compromise. Moreover, it is worth mentioning here that stability assessment is now needed to be more widened and not be limited to only one or two parameters. Indeed, it is essential now to look into a more global picture and take into consideration the overall operating conditions including the time scale of the targeted process. In this regard, serious efforts are still needed. To our opinion, this task cannot be achieved without a cooperation between industrial partners and academic researcher from different horizons, to first identify the process "real" needs and then evaluate the MOF stability at the micro- and macroscopic levels.

Besides, novel routes towards greener, more sustainable and/or more economically viable synthesis have also started to emerge. Rising startups are also contributing to pave the way of MOFs to reach the doors of industrialization production. If routes to achieve more environmentally friendly MOFs can be successfully developed, the cost (mainly, of the organic raw materials) remains still one of the most challenging parameters that can be very probably overcame only when a real commercialization strategy for a wide potential market will be defined.

To conclude, it is obvious that the achieved progress in terms of robustness and respect of environmentally friendly syntheses is promoting MOFs closer to real-world applications. Though, one should also highlight that in order to be considered as socio-economically viable for a given application, the superiority in terms of performances of these relatively new materials is expected to be significantly higher (i.e. by at least one order of magnitude) compared to existing solutions. This being said, addressing novel challenges (such new fields of application, niche applications, new criteria of updated regulations, etc.) can be also a wise alternative.

Acknowledgments

RDA, GM and CS would like to acknowledge CONACYT (grant number 2018-000003-01EXTF-00075) for the financial support.

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