



Review

Structural stability of metal organic frameworks in aqueous media – Controlling factors and methods to improve hydrostability and hydrothermal cyclic stability



Najam ul Qadir*, Syed A.M. Said, Haitham M. Bahaidarah

Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

Metal organic frameworks (MOFs) have recently emerged as a center of attention among the class of more traditional porous materials including zeolites, activated carbons, and silica gels, due to their significantly larger pore volumes and tunability of pore geometry. A large amount of literature exists incorporating the gas adsorption and separation characteristics of MOFs; however, only a limited portion has been dedicated to the water adsorption properties of these novel materials. Water adsorption capacities of MOFs are known to substantially exceed those of traditional porous materials, due to which they are continuously gaining increasing attention for potential applications in water desalination and purification, dehumidification, and adsorption cooling technologies. However, a vast majority of these materials is characterized by structural degradation on either immediate or prolonged exposure to moist environments, resulting in partial or complete deterioration of water adsorption characteristics of the framework. This article reviews the various structural parameters which control the dimensional stability of MOFs in aqueous media, as well as different strategies which have been reported in literature for improving the hydrothermal resistance of these materials for potential applications in the industrial sector.

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Contents

1. Introduction	62
2. Factors controlling structural stability of MOFs in aqueous media	64
2.1. Metal–ligand bond strength	64
2.2. Basicity of the ligand	65
2.3. Coordination number and type of metal center	66
2.4. Oxidation state of the metal center	67
2.5. Chemical functionality of the linker	68
2.6. Framework dimensionality	70
3. Methods to improve hydrostability of MOFs	71
3.1. In-situ functionalization of organic linker	71
3.2. Post-synthetic modification of organic linker and/or metal center	75
3.3. Ligand pillaring	77
3.4. Catenation	79
3.5. Plasma enhanced chemical vapor deposition of perfluoroalkanes	80
3.6. Thermal treatment	81
3.7. Metal ion doping	82

* Corresponding author.
 E-mail address: najam_980110@yahoo.com (N.ul Qadir).

3.8. In-situ synthesis of MOF nanocomposites	82
4. Hydrothermal cyclic stability	86
5. Summary and conclusions	87
Acknowledgements	88
References	88

1. Introduction

Metal organic frameworks (MOFs) are categorized as unique functional materials with exceptional features such as extremely large surface area to volume ratio, and a tremendous structural flexibility, which leads to the degree of geometric and chemical variability not exhibited by any other porous material. The structure of MOFs primarily consists of two major components – metal centers acting as joints in the structure, and organic linkers which act as struts and bridge the neighboring joints. The vast proportion of research based on the development of different types of MOF architectures has been devoted to the potential usefulness of these materials in applications like storage of light gases [1–4], gas separation [5–10], catalysis [11–15], optics [16–18], magnetism [19–21], and others [2,22–24]. A relatively negligible amount of research effort has been dedicated so far concerning the water adsorption characteristics of these materials, and the relevant applications where this unique attribute of MOFs is of fruitful importance. However, a majority of MOFs have been known to lose structural integrity in an aqueous medium (ambient moisture/water vapor, room temperature water, boiling water, steam, aqueous acidic/basic solutions, etc.), which has been considered as a major constraint regarding the potential usefulness of these materials in applications like adsorption cooling [25–27], and water desalination [28–30]. This is particularly true for MOFs based on divalent metal cations combined with organocarboxylate bridging ligands [31], which can be subject to hydrolysis and thermal decomposition on exposure to an aqueous medium [39,52]. On exposure to an aqueous medium, water molecules have been reported to attack the metal connectors within MOFs, displacing ligands and causing phase changes, loss in crystallinity, and/or structural decomposition resulting in significant loss in specific surface area and hence total pore volume of the materials [52,58]. For example, the $[Zn_4O]^{6+}$ clusters present in MOF-5 are easily hydrolyzed by water vapor, forming a non-porous product containing zinc(II) hydroxide chains commonly referred to as MOF-69C [31,38,40]. Hence a water-stable or a hydrostable MOF can be characterized by a structure which can successfully block the intrusion of water molecules into the framework, thereby effectively shielding the metal centers and ligands in order to avoid any potential phase changes, and associated losses in crystallinity and overall pore volume of the structure.

Isorecticular MOFs (IRMOFs) incorporate oxide-centered Zn_4O tetrahedral clusters as metal centers connected by dicarboxylate organic linkers, forming a three-dimensional (3-D) connected porous framework. IRMOF-1, also known as MOF-5 (Zn -BDC, BDC = 1,4-benzenedicarboxylate), was the first known member of this family and is an archetypal MOF which is characterized by the highest degree of instability in an aqueous medium of all the MOFs known to date. IRMOFs in general, and MOF-5 in particular, are known to be highly sensitive to moisture because it is believed that the weak zinc-oxygen coordination allows for an attack by water molecules [31,40]. The water molecules cause the framework to decompose, resulting in lower specific surface area and thus poor adsorption properties. A variety of research approaches have been adopted in a number of recent publications in order to increase the structural stability of MOF-5 framework in an aqueous

environment. These mainly include the functionalization of the BDC linker used in the MOF-5 framework with one or more hydrophobic functionalities during in-situ MOF synthesis [42], post-synthetic modification of the BDC linker with hydrophobic moieties like alkyl chains [43], coating the MOF-5 structure with a more hydrophobic material [171], incorporation of second-phase hydrophobic nanoparticles inside the MOF-5 framework [173], partial exchange of $Zn_{(II)}$ ions in the MOF-5 framework with other transition metal ions such as $Ni_{(II)}$ [177], and confinement of MOF-5 particles in a water-resistant matrix [180]. Table 1 summarizes all these different approaches adopted so far for improving the structural stability of MOF-5 in an aqueous medium, and the type(s) of aqueous medium/media (room temperature water, boiling water, ambient moisture, steam, aqueous acidic solutions, aqueous basic solutions) for which they have been proven practically successful. It can be easily seen in Table 1 that the approaches utilized so far in improving the stability of MOF-5 in aqueous media have only been successful either for ambient moisture or water at room temperature. Hence, there exists a need to modify these approaches or design better ones in order to stabilize the MOF-5 structure in more harsh humidity conditions like boiling water, steam, and aqueous acidic and basic solutions.

MOFs containing carboxylate–metal bonds have been reported in literature to exhibit varying degrees of hydrothermal stability. Huang et al. [32] reported that MOF-5 exhibits a decrease in its BET surface area from 900 to $45\text{ m}^2\text{ g}^{-1}$ upon water exposure, eventually reducing to a new crystal structure. They suggested that Zn_4O clusters in the framework undergo hydrolysis, on interaction with water molecules, to form the Zn ion and the corresponding organic linker acid (benzenedicarboxylic acid for MOF-5, and 1,3,5-benzenetribenzoate (BTB) for MOF-177) [32]. However, they proposed that the hydrolysis reaction might also occur favorably on framework exposure to an acidic medium. Furthermore, DMOFs have been experimented to prove that water stability in MOFs can also be improved through the incorporation of pendant functional

Table 1

Approaches adopted to improve the hydrostability of MOF-5 in various aqueous media (RTW = room temperature water, BW = boiling water, AM = ambient moisture, S = steam, AAS = aqueous acidic solutions, ABS = aqueous basic solutions).

Approach to improve hydrostability of MOF-5	Media in which modified MOF-5 is hydrostable (AM, RTW, BW, S, AAS, ABS)	Refs.
Functionalization of the BDC linker with one or more hydrophobic functionalities	AM	[42]
Post-synthetic modification of the BDC linker with hydrophobic moieties like alkyl chains	RTW and AM	[43]
Coating the MOF-5 structure with a more hydrophobic material	RTW and AM	[171]
Incorporation of second-phase hydrophobic nanoparticles	AM	[173]
Partial exchange of $Zn_{(II)}$ ions in the MOF-5 framework with other transition metal ions	AM	[177]
Confinement of MOF-5 particles in a water-resistant matrix	AM	[180]

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