engineering proceedings

Proceeding Paper

Stability of Metal–Organic Frameworks: Recent Advances and Future Trends [†]

Lance Phillip L. Mosca [1], Andrew B. Gapan [1], Rica Angela Angeles [1] and Edgar Clyde R. Lopez [2,3,*]

[1] Chemical Engineering Department, College of Engineering, Adamson University, Ermita, Manila 1000, Philippines; lance.phillip.mosca@adamson.edu.ph (L.P.L.M.); andrew.gapan@adamson.edu.ph (A.B.G.); rica.angela.angeles@adamson.edu.ph (R.A.A.)
[2] Nanotechnology Research Laboratory, Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines
[3] Department of Chemical Engineering, University of Santo Tomas, España Blvd., Sampaloc, Manila 1015, Philippines
* Correspondence: edgarclydelopez09@gmail.com

† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

Abstract: In recent years, metal–organic frameworks (MOFs) have gained a lot of attention from researchers because of their potential applications in gas separation, storage, catalysis, as well as sensing. In spite of this, further development for the actual utilization of this material is hindered mainly by its lack of ability to withstand harsh conditions. Advances over the past few years have made it possible to create MOFs with greater variability and structural properties that are more robust in nature. This paper focuses on the development of synthesis and design of MOFs so as to attain robust frameworks that are relevant for various applications. Finally, this paper also discusses the possible future directions of study for synthesizing highly durable MOFs.

Keywords: metal–organic frameworks; stability

check for updates

Citation: Mosca, L.P.L.; Gapan, A.B.; Angeles, R.A.; Lopez, E.C.R. Stability of Metal–Organic Frameworks: Recent Advances and Future Trends. *Eng. Proc.* **2023**, *56*, 146. https://doi.org/10.3390/ASEC2023-16280

Academic Editor: Manoj Gupta

Published: 15 November 2023

1. Introduction

Metal–organic frameworks (MOFs) are a type of porous materials that are mainly made out of two components: metals and organic compounds. The organic compounds are usually responsible for linking the basic components together. MOFs are crystalline in nature and initially possess simple building blocks that later on build into sophisticated structures. These structures, upon closer inspection, form uniform cavities that are cage-like in nature. MOFs can be made from different materials and can be synthesized in various ways, such as electrochemical processing, ultrasonic processing, microwave processing, etc. Because of this, they offer structural diversity and can be customized for specific applications. Overall, MOFs make for an ideal material for separation as well as storing compounds [1].

Aside from research regarding the synthesis of MOFs over the years, researchers have studied the thermal and chemical stability of these materials for various reasons. Firstly, they have been characterized for their durability. For instance, a MOF sample may show signs of decomposition if it is subjected to X-ray diffraction testing, thus making the MOF's crystal structure unable to be assessed. Secondly, a MOF's gas absorption and surface area cannot be determined if it easily collapses upon being subject to solvent removal. Furthermore, a MOF's utility might be overlooked if the produced samples are not stable in ambient conditions as it will prove to be uneconomical to produce materials that may offer less performance but are more robust in nature. In general, metal–organic frameworks can be potentially used for a number of applications because of their customizable characteristics, but their stability must also be taken into consideration for them to be a viable solution in the industry [2].

2. Fundamentals of Frameworks Stability

Chemical stability refers to the ability of MOFs to withstand various chemical treatments while maintaining their structural stability and porosity. One key attribute that can contribute to a MOF's stability is its coordination bonds' strength and protective groups surrounding those bonds. By bolstering these aspects of a MOF's structure, it becomes more resistant to the harmful effects of harsh environmental conditions that may degrade the material. Various factors can influence the strength of metal–ligand bonds. These factors include the coordination chemistry, structural context, and environmental factors [3].

Efforts to improve MOFs' chemical stability have predominantly centered on mitigating the effects of water (acid, alkali, and salt aqueous solutions) and water vapor [4]. The practical application of MOFs is contingent upon their ability to withstand exposure to aqueous or humid environments. Therefore, it is imperative to ensure the resilience of these materials under such conditions. The degradation of MOFs upon prolonged subjection to water is a critical issue that must be addressed. This phenomenon is deemed unacceptable as it significantly limits the practical applications of MOFs in numerous industries. The instability of MOFs in aqueous environments has been the subject of extensive research, and several strategies have been proposed to mitigate this problem. Developing MOFs with enhanced water stability remains a crucial challenge that requires further investigation. Metal–organic frameworks (MOFs) have come a long way since their early days of being highly sensitive to water. With advancements in their development, MOFs have become increasingly stable and can now be developed to withstand even the harshest environmental conditions [5].

Bonds created from the coordination of metal ion linkers are easily broken down upon exposure to water, which causes structural decomposition and phase changes. For a MOF structure to be considered water stable, it must possess a robust framework that can resist the corrosive effects of water molecules on its coordination bonds. Water cannot rupture the coordination bonds between the metal ions and linkers if the metal ions are inert, the linkers are hydrophobic and robust, the secondary building units are firmly connected, and the frameworks are interpenetrated [5].

Metal–organic frameworks (MOFs) composed of carboxylate-based linkers and high-valent metal ions have been found to possess remarkable robustness in acidic water. However, their resistance in alkaline environments is only moderate. Despite their stability in normal water, MOFs degrade under acidic conditions. Such odd behavior may be explained by interactions between metal ions and protons in their coordination with the linkers. The exceptional stability of MOFs in acidic solutions can be attributed to carboxylic acids' low pKa. The vulnerability of MOFs of this nature to degradation in basic solutions results from the high degree of attraction of OH^- and high-valency metal ions [6]. The trivalent metal–organic frameworks (MOFs) composed of chromium (Cr), aluminum (Al), and iron (Fe) in conjunction with carboxylate groups have demonstrated the ability to withstand acid solutions of usual strength. In a more acidic solution, MIL-101(Cr) crystallinity was unaffected [7]. The structural integrity of BUT-8A(Cr) remained unchanged after undergoing a one-day treatment in concentrated acid [8]. The hydrophobic nature of the framework may account for the observed stability of trivalent and carboxylate MOFs in acidic environments [9–12].

The wide range of possible uses for MOFs has led to a surge in interest in this class of materials. One of the notable areas where MOFs are being explored is desalination. As the world's population grows and water sources become increasingly contaminated, the demand for freshwater is steadily rising globally. In a recent study, it is discovered that metal–organic frameworks (MOFs) effectively remove salt ions from seawater [13]. However, it is important to note that MOFs must withstand saline conditions to be effective. In an aqueous salt solution, the building units of MOFs can be exchanged for ions with a higher affinity; hence, the building units should develop stronger coordinated relationships than any opposing species. Stronger coordinating bonds ensure the MOFs' stability and longevity, making them more effective for their intended purposes. In alkaline waters, the long-term stability of MOFs made of azolate links and ions with low valency stands out, whereas, in acidic conditions, their resistance is only moderate. Due to low-valency metal's intense connection to azolate and hydroxyl's poor interaction with low-valency metals, MOFs are stable in alkaline environments. The hydrophobicity of the framework may also contribute to this condition. The strong binding affinity between azolate linkers and protons is indicated by azoles with high-degree pKa values, resulting in the reactivity of the comparable MOFs to acidic solutions [6]. The metal–organic frameworks (MOFs) containing Zn, Co, and Ni in a bivalent state are notable examples of materials that demonstrate exceptional stability in solutions with high alkalinity. Lu and colleagues have also documented that MAF-X27-Cl (Co) can maintain its crystalline structure after exposure to a 1.0 M KOH solution for seven days [14]. In addition, the structural integrity and porosity of PCN-601(Ni) remained unaltered even upon immersion in solutions with pH∼14 and saturated NaOH [15].

In recent years, several metal–organic frameworks (MOFs) have been studied for their stability under saline conditions; among these MOFs are MIL-121 (Al) [16], UiO-66 (Zr) [17], and PCN-602 (Ni) [18]. UiO-66(Zr) maintained both its crystalline structure and porosity even after being immersed in various saline (0.2 weight percent of different salt solutions) solutions for three months. In a review article, they attributed this preservation to tetravalent Zr's strong affinity with carboxylate linkers, which is stronger than the affinity of low-valency metal ions [5]. The PCN-602 (Ni) showed remarkable stability. The affinity between soft metal ions Ni and soft azolate linkers is notably stronger compared with hard linkers. The inertness of ion Ni [19] and the high framework connectivity [18] further strengthen the structure.

3. Design Strategies for Enhancing Chemical Stability

There have been significant developments in the field of MOFs, particularly in hydrophobicity tuning. These advancements have been aimed at broadening the range of applications of MOFs in diverse fields such as absorption and separation, purification, detection, and other related areas. Water-sensitive MOFs possess remarkable properties; however, their usage in industrial or large-scale applications has yet to be prevalent. Water-sensitive MOFs have shown great potential in various applications, but some challenges still need to be addressed for their successful implementation in real-world scenarios. Some of these challenges, including the need for robustness in acidic and basic solutions, improved reusability and enhanced performance in complex environments [20]. These issues must be resolved to realize the benefits of water-sensitive MOFs in practical applications fully. A promising approach to enhancing the water stability of MOFs is to identify an existing MOF and improve its water stability [21]. This strategy is often deemed more practical and advantageous than creating a new MOF from the ground up. The challenges to MOFs' performance on certain solutions have been highlighted by Liu et al. [5]. It is a requirement for resilience in alkaline and acidic water for more effective recycling and performance improvement in harsh environments. These issues must be resolved to fully realize the benefits of water-sensitive MOFs in practical applications. MOFs' chemical stability and kinetic behavior are subject to many factors, including the framework's connectivity, size, strength of ligand and metal nodes, coordination number, hydrophobicity of ligands, and interpenetrated framework.

3.1. De Novo Synthesis

The degradation of metal–organic frameworks (MOFs) can be ascribed to two primary factors: the weakening of coordination bonds and the creation of byproducts that are comparatively more stable than the original MOFs [22]. Their intrinsic structures primarily determine metal–organic frameworks' resilience to harsh conditions. These structures include the charge density, the coordination numbers, the configuration, and the hydrophobicity of ligands. Combining carboxylate as ligands and high-valency ions forms highly stable metal–organic frameworks [23]. Phosphonate and phenolate are also promising ligand candidates for forming stable frameworks with high-valency ions. These ligands are anticipated to exhibit excellent performance, offering a reliable and effective means of achieving stable metal–ligand complexes. Stable frameworks may be built by low-valency metal ions using soft ligands like those containing nitrogen. Considering the bond's strength and the framework's rigidity is essential when assessing the overall stability. Structures that are dense and rigid tend to exhibit higher stability.

3.2. Connective Building Unit and Rigid Ligand

The kinetics study has revealed that metal clusters and ligands with strong connectivity can hinder the pace at which new species are being replaced, leading to a slowdown in the framework decomposition process [6]. Its coordination bonds must be broken to fully substitute or exchange a coordination node. As the connectivity of the nodes increases, the MOF breakdown occurs at a slower rate. By incorporating highly connected building units, MOFs can be designed to withstand harsh conditions and maintain their structural integrity [1]. The activation energy will increase with increasing ligand stretching, preventing the framework from breaking down and allowing for exceptional inertness. Lv et al. designed and synthesized three distinct ligands with identical connectivity that exhibit varying degrees of flexibility [24]. MOFs composed of ligands with high structural rigidity exhibit greater stability and are less susceptible to degradation when exposed to aqueous solutions containing water, acid, or base. MOFs incorporating flexible ligands tend to be more labile and prone to degradation under similar conditions. Rigid ligands tend to maintain their conformation within metal–organic frameworks (MOFs) and have a greater deformation energy barrier. The adjacent connections typically constrain dissociation, facilitating a prompt restoration of structural integrity. The deformation of flexible ligands does not interfere with the functioning of other coordination sites; however, reforming ligand bonds is more difficult. The framework is destroyed due to the accumulation of defects throughout the reaction process. The kinetic stability of MOFs would improve if they had a short, stiff, and strongly linked ligand [1].

3.3. Introduction of Functional Groups

By modifying the ligands, researchers enhanced the MOFs' ability to withstand exposure to water [21,25]. Incorporating functionalized ligands in the synthesis or post-synthetic modification is an effective method for achieving specific functionalities. Post-synthetic modification is useful when functionalized ligands may hinder MOF crystallization. The functionalization of ligands can significantly impact the external surface of MOFs, altering their steric properties and hydrophobicity [25]. Catenation, a widely recognized structural process, is a successful method for enhancing the stability of pillared frameworks. A recent study evaluated the robustness of JCM-1, a pyrazolate-imidazolium framework [26]. The study's results revealed that even after being soaked in water for two months, the structure of JCM-1 remained intact. This finding highlights the potential of JCM-1 as a promising material for various applications that require stability in aqueous environments.

3.4. Stabilizing Pillars and an Interpenetrated Framework

Another factor that can significantly impact the stability properties is the presence of free spaces within the framework. MOFs with a high degree of porosity in their structures or large surface areas may demonstrate a certain level of instability. The durability of metal–organic frameworks (MOFs) can be improved by incorporating size-matching ligands within the channels of the MOFs. Stabilizing pillars corresponding to the channel's dimensions divide the larger area into smaller segments. The segmented pore space enhances the overall stability of the MOFs [27]. Excessive spaces can contribute to the high energy and instability of the MOF. To address this issue, interpenetration (framework catenation) provides another approach to improving MOF stability. Independent frameworks become interwoven or entangled in interpenetration. The process has been observed to provide numerous advantages in enhancing stability. It has been observed that interpenetration can lead to increased wall thickness and decreased pore size. This reduction in the pore size restricts the movement and displacement of ligands, thus enhancing the overall structural stability. This characteristic has been observed because of its unique structural composition. Incorporating interpenetration in MOF design offers a promising approach to mitigating large porous frameworks' inherent energy and instability [3].

3.5. Hydrophobicity of Ligands or Frameworks

Hydrophobic groups modified in MOFs' ligands can improve their chemical stability by creating a hydrophobic framework or local environment. Methyl functionalization on ligands may cause BUT-12 and -13's superior water stability [28]. BUT-13 as well as BUT-1 isotherms show signs of apparent hysteresis and possess areas of large contact with water, indicating the hydrophobicity of its surfaces. This property may increase MOF stability by preventing water from reaching coordination bonds. Modified ligands with hydrophobic groups have increased MOF stability, as shown by BUT-18 and BUT-19 [29]. Hydrophobic MOFs are assembled by inputting moieties with hydrophobic properties to the linkers to generate moieties in the nodes that can be seen in the metals. This vicinity helps to mitigate moisture attraction. The functional groups surrounding the metal clusters exhibit a significant ability to safeguard the weak coordination bonds, offering hydrophobic protection. Chen et al. conducted a study to demonstrate the efficacy of hydrophobic ligands [30]. To achieve this, they created an octatopic carboxylic ligand, specifically 3,30,5,50-tetrakis (3,5-di carboxy phenyl) -2,20,4,40,6,60-hexamethyl biphenyl, which was utilized to synthesize a copper (II)-paddle wheel MOF known as BUT-155. The compound BUT-155 demonstrates remarkable water stability, maintaining its structural integrity even when subjected to boiling water and aqueous solutions with acidic or basic pH levels ranging from 4 to 10. The ligand with functional groups induces hydrophobicity in MOF and imposes a rigid tetrahedral geometry on the ligand. The exceptional chemical stability of BUT-155 has been attributed to the combined effects of ligand connectivity and geometry, pore hydrophobicity, and electron donation [30].

3.6. Hydrophobic Surface Modification

Ding et al. noted that some types of modification processes might possibly reduce MOFs' absorption and porosity characteristics [3]. Surface hydrophobic modification represents a possible method to mitigate this concern. The porosity of MOFs can be maintained by improving the hydrophobicity of their exterior framework, which protects them from water [25]. Encapsulation structures, in which a water-stable MOF or material shields the MOF water-sensitive structure, increasing MOFs' surface hydrophobicity. The water or chemical stability of MOFs can be increased by coating the MOF surface with polymers [31,32]. A recent study introduced a novel method for coating MOF surfaces with a thin hydrophobic polymer overlayer [33]. This approach involves a one-step surface polymerization process. The resulting coated MOF surfaces exhibit enhanced hydrophobicity, which can benefit various applications. This approach serves as a protective shield, preventing the bond from weakening due to water exposure. The effectiveness of this technique has been demonstrated in various studies, highlighting its potential for use in a range of applications. The MOFs with a polymer overlayer have been found to possess remarkable catalytic activity and recyclability for water-mediated organic reactions, attributed to their high-water stability and hydrophobicity, which are superior to the parent MOFs. These findings suggest that the polymer overlayer is a promising strategy for enhancing the performance of MOFs in various applications.

Drug MOF nanocarriers have gained significant attention due to their potential in drug delivery applications. One unique approach to enhancing these nanocarriers' stability is using polyethylene glycol (PEG) coatings. This technique has been extensively studied and has been shown to improve the nanocarriers' chemical and colloidal stability [34]. In a recent study, UiO-66 nanoparticles were coated with PEG550 and PEG2000 [35]. Applying a polymer coating could significantly improve the stability of nanoparticles in phosphatebuffered saline, which could be significantly improved by applying a polymer coating. In a study conducted by Hidalgo et al., the stability of MIL-100 (Fe) was investigated, and researchers demonstrated that the degradation of MOFs can be effectively slowed down by coating them with chitosan [36]. The study highlights the potential of chitosan as a promising coating material for enhancing the stability and performance of MOFs.

4. Applications of Stable Metal–Organic Frameworks

4.1. Sensing and Detection

Modified MOFs can achieve selective detection of a given pollutant molecule through elaborate design and specific tailoring of their structure and function. BUT-12 and -13, two Zr-based metal–organic frameworks (MOFs) exhibiting high water stability, demonstrate remarkable responses in detecting antibiotics and explosives in aqueous environments [28]. The ability to detect at the parts per billion level places fluorescent MOF-based sensors in high-performing sensors. Stable MOFs have significant potential in environmental monitoring and food and water safety.

4.2. Adsorption and Separation

MOFs' adjustable porosity architectures and considerable surface areas make their molecule sorption and separation abilities appealing. Energy-related gases, including hydrogen, carbon dioxide, and methane, are the main study subjects on the sorption and separation of metal–organic frameworks (MOFs) [3]. To come into contact with adverse conditions in many practical sorption and separation procedures is expected, including but not limited to water- or moisture-laden surroundings. For instance, when CO_2 is extracted from the gas generated by coal-fired power plants, the mixture often contains low levels of SO_x, NO_x, and other trace gases along with around 15–16% CO_2, 73–77% N_2, 5–7% H_2O, and 3–4% O_2. High prices often complicate removing H_2O, NH_3, H_2S, SO_x, and NO_x from the ambient or feed gas streams. MOFs that remove CO_2 from flue gas must thus be stable over time against corrosive and linking species. Exploring the limitations of sorbent durability and improving our knowledge of the underlying kinetics and thermodynamics of MOF stability is necessary to create frameworks for capturing these complex gases [37,38].

BUT-66, a promising material for capturing trace amounts of benzene, has been the subject of recent studies. Various adsorbents were tested to determine their effectiveness in absorbing benzene; BUT-66 stood out, absorbing benzene at a value of 1.65 mmol/g at 0.12 kPa and 80 °C [19]. This impressive performance surpassed all of the other adsorbents examined in the study. These studies have demonstrated that BUT-66 has a benzene absorption of 0.27 mmol/g and that this absorption value remains stable even under humid conditions. BUT-66 has been found to possess exceptional benzene capture ability at low concentrations, owing to its hydrophobicity and local flexibility. This observation highlights the significant role played by the structure–function relationship in determining the performance of this material. Tailored MOFs have shown great potential for various applications in pollution management, especially in real-world settings, thanks to their remarkable water stability.

Strong water adsorption functions at low H_2O partial pressures indicate that the potential of metal–organic frameworks (MOFs) is a promising alternative to solid desiccants. Selective removal of low amounts of water vapor from natural gas at a pressure ratio of 0.05 has been shown by Cadiau et al. using two water-stable fluorinated metal–organic frameworks [39]. Heating a typical desiccant, zeolites 4A, to about 250 °C [40] utilizes nearly twice as much energy as is required to remove the adsorbed water molecules altogether. However, this process may be accomplished at a much lower temperature, around 105 °C. Mohideen et al. showed that tetrazolate linkers and zinc cations may create fcu-MOFs, kag-MOF-1 [41]. This MOF's sharp water vapor adsorption isotherm suggests it might be utilized to dehumidify gas streams. In another study, in the context of 2-dimethyl amino ethyl azide dehydration, the water absorption of MIL-101(Cr) was found to be 7–8.5 times greater than that of commercial 3A and 4A zeolites [42]. MIL-101 was more hydrothermally stable than zeolite, with a regeneration temperature of just 343 K compared to the 573 K regeneration temperature.

Water scarcity is challenging in areas with restricted water resources and insufficient infrastructure. Conventional water purification methods, such as reverse osmosis and multistage flash purification, may need to be more practical in these regions. To tackle this concern, researchers have suggested the utilization of atmospheric water harvesting (AWH) as a substitute approach instead of depending on energy sources such as solar or wind power [43]. Present-day atmospheric water harvesting (AWH) systems employ a direct cooling mechanism for water collection. Attaining a dew point of water above 273 K presents a challenge, significantly increasing energy usage as the humidity levels decrease. Adsorption-based atmospheric water harvesting (AAWH) has garnered attention as a prospective revival of AWH technology [44,45]. The AAWH system captures and enriches water vapor from a dry atmosphere through an adsorbent material and subsequent desorption and condensation processes. Although hygroscopic salts have been frequently utilized for water sorption, the problem of solution leakage has been a concern. Hence, the exploration of metal–organic frameworks (MOFs) for this purpose was inevitable owing to their advantageous water adsorption–desorption properties.

Hanikel et al. conducted a thorough experimental assessment of adsorption kinetics, wherein various adsorbents such as MOF-303(Al), Al-fumarate, zeolite SAPO-34, and zeolite 13X were examined [46]. The study's findings indicate that Zeolite 13X displayed the most rapid water absorption at a relative humidity (RH) of 20%, whereas MOF-303(Al) exhibited superior kinetics at elevated RH levels. Al-fumarate exhibited a faster desorption response time than MOF-303(Al). Nonetheless, the kinetics of both zeolites were slow. The study results suggest that MOF-303(Al) and Al-fumarate exhibit superior adsorption properties compared to zeolites, thus warranting their recommendation as more effective adsorbents. The significance of adsorption kinetics was emphasized by the Pdv (grams of water adsorbed per gram of adsorbent per day) measurements, revealing that MOF-303(Al) exhibited a Pdv value exceeding that of Al-fumarate by a factor of two. The present study conducted a practical viability assessment of the MOF-303(Al) harvester in the arid Mojave Desert. During the three-day testing period, the Pdv value measured 0.8 g mL-1d-1. It is noteworthy that the MOFs MOF-801(Zr) and MOF-303(Al) have been subjected to practical experimentation for atmospheric water harvesting (AAWH) exclusively, suggesting that the investigation of MOF-based AAWH is still in its nascent phase.

Using metal–organic framework (MOF) adsorbents has demonstrated significant potential in regulating humidity levels [5]. Implementing an adsorptive humidity control mechanism can be more energy-efficient by avoiding the traditional cooling, dew point determination, and reheating processes. This mechanism effectively controls humidity levels and can be a great alternative to conventional methods. Vivekh et al. have highlighted the potential benefits of using alternative MOFs with lower inflection points in various applications, such as air-conditioning and drying, for dehumidification [47]. This process optimization can reduce energy consumption compared to traditional dew-pointing methods. The coadsorption of moisture and volatile organic compounds (VOCs) in open systems has been found to offer potential benefits for enhancing indoor air quality. The release of hazardous VOCs is a matter of concern. In recent years, integrating catalytic functions into MOFs has been explored as a potential solution to address the issue of volatile organic compounds (VOCs). Several studies have stated the effectiveness of this approach in enabling the controlled release and degradation of VOCs into non-toxic substances [48–50]. A zeolitic material has recently been used in a household dishwashing appliance, significantly reducing energy consumption by almost 1 kilowatt-hour. The material has also proven highly effective in achieving optimal drying performance, showing the potential of metal–organic frameworks (MOFs) as alternative sorbents. MOFs' low regeneration temperature makes them a highly intriguing option for various humidity regulation applications.

4.3. Catalysis

Stable MOFs as catalysts in diverse reactions are ascribed to the existence of Brønsted acid sites, Lewis acid/basic sites, and redox-active sites. MOF catalysts exhibit stability and resilience in aqueous or acidic/basic environments, where numerous reactions occur [50]. BUT-8(Cr)A MOF exhibits a high-density and uniform distribution of -SO_3H groups within its pores, which serve as efficient Brønsted acid sites for catalyzing esterification reactions. The BUT-8(Cr)A catalyst exhibits remarkable efficacy in diverse esterification reactions, exhibiting a wide spectrum of substrates, significant size selectivity, elevated ester yield, and exceptional recyclability. The MOF BUT-8(Cr)A exhibits substantial Brønsted acid sites and notable acid stability, rendering it a promising candidate for catalyzing esterification reactions [8,51].

4.4. Biomedical Applications

Metal–organic frameworks (MOFs) are widely used in various medical fields due to their adaptable physical and chemical properties, tunable pore sizes, and large surface area [3]. Nevertheless, MOFS must demonstrate a notable degree of chemical stability to employ biomedical applications effectively. The significance of this lies in the fact that MOFs are anticipated to operate in physiologically relevant settings, encompassing the acidic milieu of the stomach, the alkaline conditions in the intestines, and the mechanical perturbations of the esophagus, stomach, and intestines. Hence, MOFS must exhibit substantial resistance to hydrolysis and collapse to uphold their structural integrity and efficacy.

4.5. Electrochemical Storage

The field of proton conductivity, particularly in metal–organic frameworks (MOFs), has garnered increasing attention in recent years due to the highly adaptable architectures of MOFs [52,53]. The manipulation of the surface hydrophilicity and acidity represents a viable strategy for regulating proton conduction in MOFs, distinguishing them from alternative porous materials. Wu et al. have noted that despite the extensive research on proton conduction in MOFs, only a select few MOFs have demonstrated notable stability and high conductivity [54]. The endurance of metal–organic frameworks (MOFs) as proton conductors are paramount, as it governs their capacity to endure diverse environmental circumstances for a prolonged duration. Hydrogen-bonded water networks inside the cavities of MOFs are necessary for the Grotthuss process, also known as proton hopping [52,55]. Investigating the proton-conducting properties of metal–organic frameworks (MOFs) present a substantial potential for advancing, manufacturing, and customizing MOFs that exhibit remarkable chemical stability, conferring significant benefits in this domain.

5. Research Gaps

The comprehensive investigation of MOF frameworks should extend beyond pH range tests to examine decomposition mechanisms [1]. The optimization of stability is crucial throughout the design and synthesis process, taking into account the specific conditions that MOFs will encounter in their applications. Optimization of stability entails exploring the potential to enhance the resilience of MOFs by tailoring stabilizing techniques to particular materials or incorporating multiple strategies within a single framework [1]. The emergence of nanocarrier drug delivery systems presents a new challenge for MOFs [23], necessitating careful consideration and the resolution of various open questions. Merely conducting drug release studies and attributing different release rates at different pH values to material degradation without examining material stability is inadequate, as factors beyond stability can affect pH-triggered drug release. Therefore, it is recommended to conduct stability studies under conditions that closely resemble in vivo environments, carefully selecting appropriate operational parameters such as concentration, temperature, and surface properties. Although there are reports of stability tests for MOF nanoparticles conducted under conditions mimicking the human body, further research is needed to establish connections and translate these findings into in vivo studies. While MOFs have predominantly been explored for oral drug administration, it is essential to investigate their stability and performance for other modes of administration through diverse experimental setups. In addition to applications in desiccation and water harvesting, MOFs' water adsorption/desorption characteristics can also be beneficial for antimicrobial purposes in food moisture absorption [5]. The overall stability of MOFs enables their utilization in diverse contexts and enhances their potential usefulness. The progress in MOF chemistry warrants continued research funding, focusing on improving stability and studying MOFs that can reliably operate on short cycle times [1,5]. A comprehensive assessment of MOFs' mechanical and thermal stability, which is crucial for their industrial applications, still needs to be completed. The routine synthesis of MOFs with diverse topologies and chemistries that can withstand extended exposure to corrosive acidic gasses, elevated temperatures, and humid conditions poses a notable challenge [3]. Thoroughly investigating and resolving the stability issue would represent a significant advancement toward commercializing MOFs. Subsequent research studies should address availability issues, manufacturing optimization, and cost reduction, as the production and dissemination of stable MOFs will become the next critical research focus [3]. Moreover, the safety and toxicity of the utilized MOF studies must be developed to ensure public acceptance [5]. By optimizing manufacturing processes, it would be possible to fabricate robust and adaptable MOFs on a larger scale, thereby enabling their industrial application and opening a new era for the field of MOFs.

6. Future Outlook

Chemical stability in metal–organic frameworks (MOFs) has a bright future. The design and synthesis of novel MOFs with greatly increased chemical stability have been made possible by recent advancements in MOF design and synthesis. These novel MOFs are less susceptible to chemical deterioration from water, acids, bases, and other substances. They are more suited for usage in a variety of applications as a result, including gas storage, catalysis, and sensing. Gas storage is one of the most promising fields for the use of novel MOFs with enhanced chemical stability. MOFs are perfect for storing gases since they are very porous and have a huge surface area. However, a lot of MOFs lack the necessary chemical stability to be employed for gas storage under extreme conditions like those present in fuel cells and other devices. In these extreme settings, new MOFs with enhanced chemical stability could be employed to store gases, making them more effective and dependable.

Catalysis is another attractive field for the use of novel MOFs with better chemical stability. A wide variety of chemical processes, including the synthesis of drugs and fuels, can be catalyzed by MOFs. However, the necessary chemical stability is lacking for MOFs to be employed for sensing in abrasive conditions, like those seen in industrial settings. In these severe settings, new MOFs with enhanced chemical stability could be employed to detect substances, making them more dependable and practical [56].

The creation of novel MOF structures is a viable strategy for enhancing MOF stability. By including elements like metal–metal bonds, big ligands, and rigid frameworks, new MOF structures can be created that have better thermal and chemical stability. For instance, it has been demonstrated that MOFs having metal–metal bonds are more thermally stable than MOFs without these interactions. Adding additional ligands is another strategy for enhancing MOF stability. The molecules that attach to the metal centers in MOFs are known as ligands. The MOF's stability may be significantly impacted by the choice of ligands. The stability of the MOF can be increased, for instance, by using ligands that are larger or have stronger connections to the metal centers.

Finally, to increase the stability of already existing MOFs, modifications might be used. MOFs can be altered using several techniques, including the inclusion of stabilizing groups or the addition of protective coatings. For instance, silica can be used to coat MOFs to shield them from moisture and other environmental elements. The stability of MOFs has recently improved, which is encouraging for the development of this technology. These developments may increase the number of applications where MOFs can be used [57].

Author Contributions: Conceptualization, E.C.R.L.; resources, E.C.R.L.; writing—original draft preparation, L.P.L.M., A.B.G. and R.A.A.; writing—review and editing, E.C.R.L.; visualization, E.C.R.L.; supervision, E.C.R.L.; project administration, E.C.R.L.; funding acquisition, E.C.R.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. He, T.; Kong, X.-J.; Li, J.-R. Chemically Stable Metal–Organic Frameworks: Rational Construction and Application Expansion. *Acc. Chem. Res.* **2021**, *54*, 3083–3094. [CrossRef] [PubMed]
2. Li, G.; Xia, L.; Dong, J.; Chen, Y.; Li, Y. Metal-organic frameworks, Solid-Phase Extraction. In *Solid-Phase Extraction*; Handbooks in Separation Science; Elsevier: Amsterdam, The Netherlands, 2020; pp. 285–309. [CrossRef]
3. Ding, M.; Cai, X.; Jiang, H.-L. Improving MOF stability: Approaches and applications. *Chem. Sci.* **2019**, *10*, 10209–10230. [CrossRef]
4. Howarth, A.J.; Liu, Y.; Li, P.; Li, Z.; Wang, T.C.; Hupp, J.T.; Farha, O.K. Chemical, thermal and mechanical stabilities of metal–organic frameworks. *Nat. Rev. Mater.* **2016**, *1*, 15018. [CrossRef]
5. Liu, X.; Wang, X.; Kapteijn, F. Water and Metal–Organic Frameworks: From Interaction toward Utilization. *Chem. Rev.* **2020**, *120*, 8303–8377. [CrossRef] [PubMed]
6. Yuan, S.; Feng, L.; Wang, K.; Pang, J.; Bosch, M.; Lollar, C.; Sun, Y.; Qin, J.; Yang, X.; Zhang, P.; et al. Stable Metal–Organic Frameworks: Design, Synthesis, and Applications. *Adv. Mater.* **2018**, *30*, e1704303. [CrossRef] [PubMed]
7. Leus, K.; Bogaerts, T.; De Decker, J.; Depauw, H.; Hendrickx, K.; Vrielinck, H.; Van Speybroeck, V.; Van Der Voort, P. Systematic study of the chemical and hydrothermal stability of selected "stable" Metal Organic Frameworks. *Microporous Mesoporous Mater.* **2016**, *226*, 110–116. [CrossRef]
8. Yang, F.; Xu, G.; Dou, Y.; Wang, B.; Zhang, H.; Wu, H.; Zhou, W.; Li, J.-R.; Chen, B. A flexible metal–organic framework with a high density of sulfonic acid sites for proton conduction. *Nat. Energy* **2017**, *2*, 877–883. [CrossRef]
9. Atallah, H.; Mahmoud, M.E.; Ali, F.M.; Lough, A.; Hmadeh, M. A highly stable indium based metal organic framework for efficient arsenic removal from water. *Dalton Trans.* **2017**, *47*, 799–806. [CrossRef]
10. Ugale, B.; Dhankhar, S.S.; Nagaraja, C.M. Exceptionally Stable and 20-Connected Lanthanide Metal–Organic Frameworks for Selective CO_2 Capture and Conversion at Atmospheric Pressure. *Cryst. Growth Des.* **2018**, *18*, 2432–2440. [CrossRef]
11. Yang, C.; Cheng, J.; Chen, Y.; Hu, Y. Experimental investigation on the water stability of amino-modified indium metal–organic frameworks. *RSC Adv.* **2016**, *6*, 61703–61706. [CrossRef]
12. Guo, Z.-J.; Yu, J.; Zhang, Y.-Z.; Zhang, J.; Chen, Y.; Wu, Y.; Xie, L.-H.; Li, J.-R. Water-Stable In(III)-Based Metal–Organic Frameworks with Rod-Shaped Secondary Building Units: Single-Crystal to Single-Crystal Transformation and Selective Sorption of C_2H_2 over CO_2 and CH_4. *Inorg. Chem.* **2017**, *56*, 2188–2197. [CrossRef] [PubMed]
13. Lee, S.J.; Hann, T.; Park, S.H. Seawater Desalination Using MOF-Incorporated Cu-Based Alginate Beads without Energy Consumption. *ACS Appl. Mater. Interfaces* **2020**, *12*, 16319–16326. [CrossRef]
14. Lu, X.-F.; Liao, P.-Q.; Wang, J.-W.; Wu, J.-X.; Chen, X.-W.; He, C.-T.; Zhang, J.-P.; Li, G.-R.; Chen, X.-M. An Alkaline-Stable, Metal Hydroxide Mimicking Metal–Organic Framework for Efficient Electrocatalytic Oxygen Evolution. *J. Am. Chem. Soc.* **2016**, *138*, 8336–8339. [CrossRef] [PubMed]
15. Wang, K.; Lv, X.-L.; Feng, D.; Chen, S.; Sun, J.; Song, L.; Xie, Y.; Li, J.-R.; Zhou, H.-C. Pyrazolate-Based Porphyrinic Metal–Organic Framework with Extraordinary Base-Resistance. *J. Am. Chem. Soc.* **2016**, *138*, 914–919. [CrossRef] [PubMed]
16. Ou, R.; Zhang, H.; Wei, J.; Kim, S.; Wan, L.; Nguyen, N.S.; Hu, Y.; Zhang, X.; Simon, G.P.; Wang, H. Thermoresponsive Amphoteric Metal–Organic Frameworks for Efficient and Reversible Adsorption of Multiple Salts from Water. *Adv. Mater.* **2018**, *30*, e1802767. [CrossRef]
17. Liu, X.; Demir, N.K.; Wu, Z.; Li, K. Highly Water-Stable Zirconium Metal–Organic Framework UiO-66 Membranes Supported on Alumina Hollow Fibers for Desalination. *J. Am. Chem. Soc.* **2015**, *137*, 6999–7002. [CrossRef]
18. Lv, X.-L.; Wang, K.; Wang, B.; Su, J.; Zou, X.; Xie, Y.; Li, J.-R.; Zhou, H.-C. A Base-Resistant Metalloporphyrin Metal–Organic Framework for C–H Bond Halogenation. *J. Am. Chem. Soc.* **2016**, *139*, 211–217. [CrossRef]
19. Rieth, A.J.; Wright, A.M.; Dincă, M. Kinetic stability of metal–organic frameworks for corrosive and coordinating gas capture. *Nat. Rev. Mater.* **2019**, *4*, 708–725. [CrossRef]

20. Liu, B.; Vikrant, K.; Kim, K.-H.; Kumar, V.; Kailasa, S.K. Critical role of water stability in metal–organic frameworks and advanced modification strategies for the extension of their applicability. *Environ. Sci. Nano* **2020**, *7*, 1319–1347. [CrossRef]
21. Wang, C.; Liu, X.; Demir, N.K.; Chen, J.P.; Li, K. Applications of water stable metal–organic frameworks. *Chem. Soc. Rev.* **2016**, *45*, 5107–5134. [CrossRef]
22. Antwi-Baah, R.; Liu, H. Recent Hydrophobic Metal-Organic Frameworks and Their Applications. *Materials* **2018**, *11*, 2250. [CrossRef] [PubMed]
23. Bunzen, H. Chemical Stability of Metal-organic Frameworks for Applications in Drug Delivery. *Chemnanomat* **2021**, *7*, 998–1007. [CrossRef]
24. Lv, X.-L.; Yuan, S.; Xie, L.-H.; Darke, H.F.; Chen, Y.; He, T.; Dong, C.; Wang, B.; Zhang, Y.-Z.; Li, J.-R.; et al. Ligand Rigidification for Enhancing the Stability of Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2019**, *141*, 10283–10293. [CrossRef]
25. Feng, M.; Zhang, P.; Zhou, H.-C.; Sharma, V.K. Water-stable metal-organic frameworks for aqueous removal of heavy metals and radionuclides: A review. *Chemosphere* **2018**, *209*, 783–800. [CrossRef] [PubMed]
26. Lee, J.; Chuah, C.Y.; Kim, J.; Kim, Y.; Ko, N.; Seo, Y.; Kim, K.; Bae, T.H.; Lee, E. Separation of Acetylene from Carbon Dioxide and Ethylene by a Water-Stable Microporous Metal-Organic Framework with Aligned Imidazolium Groups inside the Channels. *Angew. Chem. Int. Ed.* **2018**, *57*, 7869–7873. [CrossRef]
27. Zhai, Q.-G.; Bu, X.; Zhao, X.; Li, D.-S.; Feng, P. Pore Space Partition in Metal–Organic Frameworks. *Acc. Chem. Res.* **2017**, *50*, 407–417. [CrossRef] [PubMed]
28. Wang, B.; Lv, X.-L.; Feng, D.; Xie, L.-H.; Zhang, J.; Li, M.; Xie, Y.; Li, J.-R.; Zhou, H.-C. Highly Stable Zr(IV)-Based Metal–Organic Frameworks for the Detection and Removal of Antibiotics and Organic Explosives in Water. *J. Am. Chem. Soc.* **2016**, *138*, 6204–6216. [CrossRef] [PubMed]
29. Lv, J.; Wang, B.; Xie, Y.; Wang, P.; Shu, L.; Su, X.; Li, J.-R. Selective detection of two representative organic arsenic compounds in aqueous medium with metal–organic frameworks. *Environ. Sci. Nano* **2019**, *6*, 2759–2766. [CrossRef]
30. Chen, Y.; Wang, B.; Wang, X.; Xie, L.-H.; Li, J.; Xie, Y.; Li, J.-R. A Copper(II)-Paddlewheel Metal–Organic Framework with Exceptional Hydrolytic Stability and Selective Adsorption and Detection Ability of Aniline in Water. *ACS Appl. Mater. Interfaces* **2017**, *9*, 27027–27035. [CrossRef]
31. McGuire, C.V.; Forgan, R.S. The surface chemistry of metal–organic frameworks. *Chem. Commun.* **2014**, *51*, 5199–5217. [CrossRef]
32. Forgan, R.S. The surface chemistry of metal–organic frameworks and their applications. *Dalton Trans.* **2019**, *48*, 9037–9042. [CrossRef] [PubMed]
33. Ding, M.; Jiang, H.-L. Improving Water Stability of Metal–Organic Frameworks by a General Surface Hydrophobic Polymerization. *CCS Chem.* **2021**, *3*, 2740–2748. [CrossRef]
34. Van Witteloostuijn, S.B.; Pedersen, S.L.; Jensen, K.J. Half-Life Extension of Biopharmaceuticals using Chemical Methods: Alternatives to PEGylation. *ChemMedChem* **2016**, *11*, 2474–2495. [CrossRef] [PubMed]
35. Lázaro, I.A.; Haddad, S.; Sacca, S.; Orellana-Tavra, C.; Fairen-Jimenez, D.; Forgan, R.S. Selective Surface PEGylation of UiO-66 Nanoparticles for Enhanced Stability, Cell Uptake, and pH-Responsive Drug Delivery. *Chem* **2017**, *2*, 561–578. [CrossRef] [PubMed]
36. Hidalgo, T.; Giménez-Marqués, M.; Bellido, E.; Avila, J.; Asensio, M.C.; Salles, F.; Lozano, M.V.; Guillevic, M.; Simón-Vázquez, R.; González-Fernández, A.; et al. Chitosan-coated mesoporous MIL-100(Fe) nanoparticles as improved bio-compatible oral nanocarriers. *Sci. Rep.* **2017**, *7*, 43099. [CrossRef]
37. Xie, L.-H.; Liu, X.-M.; He, T.; Li, J.-R. Metal-Organic Frameworks for the Capture of Trace Aromatic Volatile Organic Compounds. *Chem* **2018**, *4*, 1911–1927. [CrossRef]
38. Liang, L.; Liu, C.; Jiang, F.; Chen, Q.; Zhang, L.; Xue, H.; Jiang, H.-L.; Qian, J.; Yuan, D.; Hong, M. Carbon dioxide capture and conversion by an acid-base resistant metal-organic framework. *Nat. Commun.* **2017**, *8*, 1233. [CrossRef]
39. Cadiau, A.; Belmabkhout, Y.; Adil, K.; Bhatt, P.M.; Pillai, R.S.; Shkurenko, A.; Martineau-Corcos, C.; Maurin, G.; Eddaoudi, M. Hydrolytically stable fluorinated metal-organic frameworks for energy-efficient dehydration. *Science* **2017**, *356*, 731–735. [CrossRef]
40. Ciahotný, K.; Hlinčík, T.; Vagenknechtová, A.; Prokeš, O. Adsorbents for the natural gas drying at CNG stations. *Acta Montan. Slovaca* **2016**, *21*, 306–313.
41. Mohideen, M.I.H.; Pillai, R.S.; Adil, K.; Bhatt, P.M.; Belmabkhout, Y.; Shkurenko, A.; Maurin, G.; Eddaoudi, M. A Fine-Tuned MOF for Gas and Vapor Separation: A Multipurpose Adsorbent for Acid Gas Removal, Dehydration, and BTX Sieving. *Chem* **2017**, *3*, 822–833. [CrossRef]
42. Noorpoor, Z.; Pakdehi, S.G.; Rashidi, A. High capacity and energy-efficient dehydration of liquid fuel 2-dimethyl amino ethyl azide (DMAZ) over chromium terephthalic (MIL-101) nanoadsorbent. *Adsorption* **2017**, *23*, 743–752. [CrossRef]
43. Tu, Y.; Wang, R.; Zhang, Y.; Wang, J. Progress and Expectation of Atmospheric Water Harvesting. *Joule* **2018**, *2*, 1452–1475. [CrossRef]
44. Kalmutzki, M.J.; Diercks, C.S.; Yaghi, O.M. Metal–Organic Frameworks for Water Harvesting from Air. *Adv. Mater.* **2018**, *30*, e1704304. [CrossRef] [PubMed]
45. LaPotin, A.; Kim, H.; Rao, S.R.; Wang, E.N. Adsorption-Based Atmospheric Water Harvesting: Impact of Material and Component Properties on System-Level Performance. *Acc. Chem. Res.* **2019**, *52*, 1588–1597. [CrossRef] [PubMed]

46. Hanikel, N.; Prévot, M.S.; Fathieh, F.; Kapustin, E.A.; Lyu, H.; Wang, H.; Diercks, N.J.; Glover, T.G.; Yaghi, O.M. Rapid Cycling and Exceptional Yield in a Metal-Organic Framework Water Harvester. *ACS Cent. Sci.* **2019**, *5*, 1699–1706. [CrossRef] [PubMed]
47. Vivekh, P.; Kumja, M.; Bui, D.; Chua, K. Recent developments in solid desiccant coated heat exchangers—A review. *Appl. Energy* **2018**, *229*, 778–803. [CrossRef]
48. Wang, H.; Lustig, W.P.; Li, J. Sensing and capture of toxic and hazardous gases and vapors by metal–organic frameworks. *Chem. Soc. Rev.* **2018**, *47*, 4729–4756. [CrossRef] [PubMed]
49. Bobbitt, N.S.; Mendonca, M.L.; Howarth, A.J.; Islamoglu, T.; Hupp, J.T.; Farha, O.K.; Snurr, R.Q. Metal–organic frameworks for the removal of toxic industrial chemicals and chemical warfare agents. *Chem. Soc. Rev.* **2017**, *46*, 3357–3385. [CrossRef]
50. Bavykina, A.; Kolobov, N.; Khan, I.S.; Bau, J.A.; Ramirez, A.; Gascon, J. Metal–Organic Frameworks in Heterogeneous Catalysis: Recent Progress, New Trends, and Future Perspectives. *Chem. Rev.* **2020**, *120*, 8468–8535. [CrossRef]
51. Dou, Y.; Zhang, H.; Zhou, A.; Yang, F.; Shu, L.; She, Y.; Li, J.-R. Highly Efficient Catalytic Esterification in an $-SO_3H$-Functionalized Cr(III)-MOF. *Ind. Eng. Chem. Res.* **2018**, *57*, 8388–8395. [CrossRef]
52. Meng, X.; Wang, H.-N.; Song, S.-Y.; Zhang, H.-J. Proton-conducting crystalline porous materials. *Chem. Soc. Rev.* **2016**, *46*, 464–480. [CrossRef] [PubMed]
53. Li, A.-L.; Gao, Q.; Xu, J.; Bu, X.-H. Proton-conductive metal-organic frameworks: Recent advances and perspectives. *Coord. Chem. Rev.* **2017**, *344*, 54–82. [CrossRef]
54. Wu, H.; Yang, F.; Lv, X.-L.; Wang, B.; Zhang, Y.-Z.; Zhao, M.-J.; Li, J.-R. A stable porphyrinic metal–organic framework pore-functionalized by high-density carboxylic groups for proton conduction. *J. Mater. Chem. A* **2017**, *5*, 14525–14529. [CrossRef]
55. Borges, D.D.; Devautour-Vinot, S.; Jobic, H.; Ollivier, J.; Nouar, F.; Semino, R.; Devic, T.; Serre, C.; Paesani, F.; Maurin, G. Proton Transport in a Highly Conductive Porous Zirconium-Based Metal–Organic Framework: Molecular Insight. *Angew. Chem. Int. Ed.* **2016**, *55*, 3919–3924. [CrossRef] [PubMed]
56. Li, Y.; Zhang, X.; Wang, Y.; Li, Z. Metal-Organic Frameworks: Recent Advances and Future Perspectives. *Adv. Mater.* **2019**, *30*, 1806135.
57. Lin, Y.; Huang, Y.; Chen, X. Recent Advances in Metal-Organic Frameworks for Biomacromolecule Sensing. *Chemosensors* **2022**, *10*, 412. [CrossRef]