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Citation	Rieth, Adam J. et al. "Kinetic stability of metal–organic frameworks for corrosive and coordinating gas capture." Nature Reviews Materials 4, 11 (September 2019): 708–725 © 2019 Springer Nature Limited
As Published	http://dx.doi.org/10.1038/s41578-019-0140-1
Publisher	Springer Science and Business Media LLC
Version	Author's final manuscript
Citable link	https://hdl.handle.net/1721.1/128201
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Kinetic Stability of Metal-Organic Frameworks: Consequences for Corrosive and Coordinating Gas Capture

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Abstract

Metal-organic frameworks (MOFs) have demonstrated their utility for a variety of applications involving the storage, separation, and sensing of weakly interacting gases of high purity. Exposure to more realistic, impure gas streams and interactions with corrosive and coordinating gases raises the question of chemical robustness, which remains a paramount concern for practical applications of MOFs. However, factors that determine the stability of MOFs remain incompletely understood. Although past researchers attempted to categorize framework materials as either thermodynamically stable or kinetically stable, recent work has elucidated an energetic penalty for porosity for all materials in this class with respect to a dense material. The metastability of porous phases has important implications for the design of materials for gas storage, heterogeneous catalysts, and electronic materials. Here, we focus on two main strategies for stabilization of the porous phase, either by using inert metal ions, or by increasing the heterolytic metal-ligand bond strength, both of which increase the activation barrier for framework collapse. These two strategies have led to exceptionally robust materials for the capture of coordinating and corrosive gases such as water vapor, ammonia, H₂S, SO₂, NO_x, and even elemental halogens, and we review the progress in designing stable materials for these gases. Looking forward, we envision that the continued pursuit of strategies for kinetic stabilization in the synthesis of new MOFs will provide increasing numbers of robust frameworks suited to harsh conditions, and that short-term stability towards these challenging gases will be predictive of long-term stability for applications in less demanding environments.

Introduction

Porosity is a useful and versatile material property for a range of current and future applications, including gas storage,¹⁻⁴ chemical separations,⁵⁻⁷ catalysis,⁸⁻¹⁰ and electronic devices.^{11,12} Yet, much like a cavern's susceptibility toward cave-in, the empty voids of porous materials also imply the possibility of collapse. Therefore, in order to be applicable, the stability of porous materials is of eminent importance. Metal-organic frameworks (MOFs) are materials consisting of regular arrays of metal ions or clusters linked by organic ligands, and they can exhibit record internal surface areas.¹³ Research into MOFs, and concomitantly the number of possible applications for these materials, has increased exponentially over the past several years. However, they are not yet widely applied in industry, and in many cases the deployment of MOFs is held back by a lack of long-term stability under environmental or application-specific conditions. Here, we focus on framework chemical stability toward coordinating and corrosive gases and vapors, such as water vapor, NH₃, H₂S, Cl₂, Br₂, NO_x and SO_x, which may be present in the atmosphere, or as components in applications for which MOFs find utility.

The Energetic Penalty for Porosity

Horror Vacui, a phrase attributed to Aristotle roughly translated as *nature abhors a vacuum*, was, until recently, thought to apply to the crystallization of permanently porous solids. Porous solids were believed to be unstable due to the relative lack of bonding or dispersive interactions within or between the voids.¹⁴ Of course, materials such as zeolites and MOFs are now commonly synthesized, normally by including solvent, surfactant, or structure-directing agents within the voids during crystallization, although the degree of kinetic or thermodynamic control responsible for their formation is still under debate.¹⁵ After the porous material is synthesized, the components within the pores are commonly removed by evacuation or annealing, leaving behind accessible voids. However, an increasing body of work suggests that crystalline porous materials with empty pores are metastable with respect to their dense phases (**Figure 1**).^{16–21} The dense phase is a hypothetical assemblage of the same constituent atoms, ions, or ligands, but carries negligible porosity. For an all-silica zeolite, the dense phase is easily envisaged as nonporous amorphous silica, which can be accessed via simple heating. For a MOF, the dense phase can be more difficult to conceptualize due to the directionality of the ligands, but denser, amorphous phases of some MOFs, achieved thermally, are known,^{22–25} and other structures transition to denser amorphous phases with the application of pressure.^{26–28}

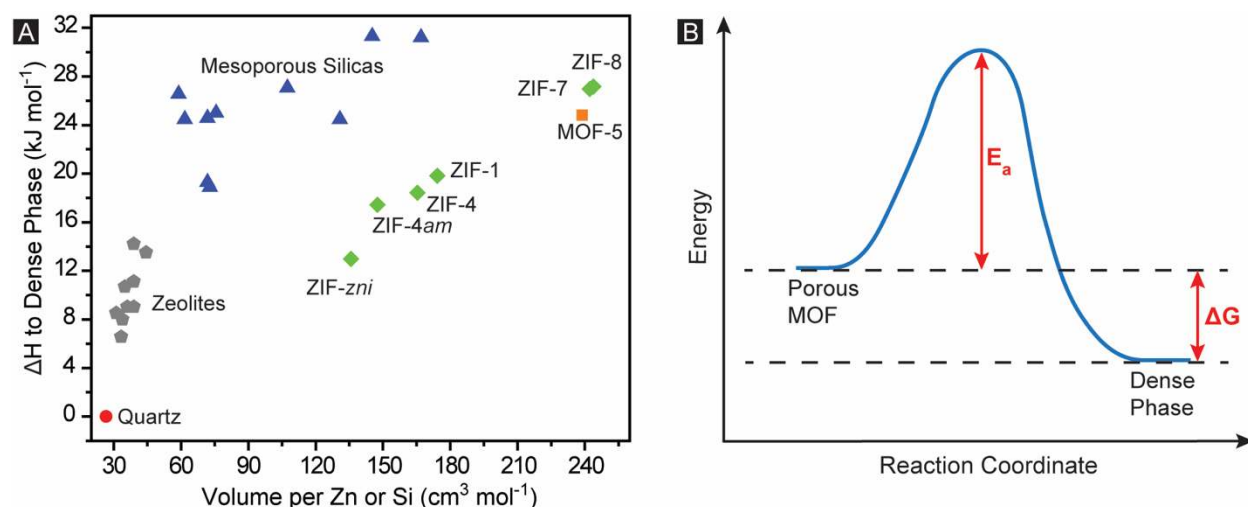


Figure 1: **Metastability of Porous Materials.** A) Enthalpic penalty relative to a dense phase versus molar unit cell volume per Zn or Si for porous materials including zeolites, mesoporous silicas, ZIFs, and MOF-5.^{16,17,20} B) Conceptualization of the energy penalty for porosity in a reaction coordinate diagram.

The metastability of solvent-free porous materials has been experimentally demonstrated for many zeolites,¹⁹ zeolitic imidazolate frameworks (ZIFs),¹⁷ as well as the prototypical MOFs $\text{Zn}_4\text{O}(\text{BDC})_3$ (MOF-5, BDC = 1,4-benzenedicarboxylate)¹⁶ and $\text{Cu}_3(\text{BTC})_2$ (HKUST-1, BTC = 1,3,5-benzenetricarboxylate).¹⁸ Inclusion of solvent in the thermodynamic equations can result in a thermodynamically stable porous phase (with respect to the dense phase) in the case of HKUST-1,¹⁸ whereas inclusion of solvent for MOF-5, though highly exothermic,²¹ is insufficient to result in net stabilization.¹⁶ Regardless of the thermodynamics of the solvent-inclusive phase, for the majority of applications the evacuated phase is desired. It has been argued that the increased vibrational entropy of porous phases of MOFs could represent enough energetic

stabilization to account for a net negative free energy with respect to dense phases at slightly elevated temperatures.¹⁵ However, the available calorimetric data indicate a trend of increasing energy penalty for increasingly porous structures, and a dense, amorphous phase should be entropically favored over a crystalline porous phase given that the driving force for crystallization is commonly enthalpic.²⁰

Kinetically Stabilizing the Porous MOF Phase

Conceptualizing MOFs with empty pores as metastable, kinetically-trapped phases has important implications for the development of design principles for chemically stable frameworks. Stabilization of the porous phase can only be kinetic and must increase the energy barrier for transitioning to the dense phase by 1) increasing the transition state energy or 2) decreasing the energy of the porous phase with respect to the transition state (**Figure 2**).

1) Metal Ion Substitution Kinetics: increasing the transition state energy

Transitioning from a porous MOF phase to a dense phase must require ligand exchange or geometric reorganization around the metal ion. A major component in the energy barrier for reorganization towards a dense phase is contained in the inherent kinetics of ligand exchange of the metal ion. As a consequence of electronic configuration and of ionic radius, transition metal ions can exhibit vastly disparate ligand exchange kinetics, which are most often quantified by the homoleptic aquo complex self-exchange rate. The rate of ligand exchange in octahedral aquo complexes spans nearly twenty orders of magnitude from the labile Cu^{2+} and Cr^{2+} at $5.9 \times 10^9 \text{ s}^{-1}$ to the highly inert Ir^{3+} at $1.1 \times 10^{-10} \text{ s}^{-1}$.²⁹ MOFs formed with kinetically inert metals can be exceptionally robust. For instance, the most widely employed metal ion in MOF synthesis with a metal-aquo self-exchange rate slower than 1 s^{-1} is Cr^{3+} , which forms carboxylate frameworks stable to water, steam, and even high pressures of H_2S .³⁰⁻³² Cation inertness can be a better predictor of stability than metal-ligand bond strength, as was demonstrated in the MIL-53 and -47 family of isostructural frameworks where chemical stability decreases in the order $\text{Cr}^{3+} > \text{Al}^{3+} > \text{V}^{4+}$, as expected based on the water substitution rates of the metal-aquo complexes, but not in line with the thermodynamic metal-oxygen bond strength.³³ An additional example of the effects of inert metal ion substitution can be found in the M_2DOBDC (MOF-74 or CPO-27, DOBDC = dioxidobenzenedicarboxylate)^{34,35} family of frameworks, where partial replacement of Mg^{2+} with more inert Ni^{2+} can enhance the stability toward water.³⁶ Replacement of the native Zn^{2+} with Ni^{2+} in MOF-5 also grants increased water stability for the resulting Ni-MOF-5.³⁷ Further, in a family of MOFs formed from linear bistriazolate linkers, $\text{M}_2\text{Cl}_2\text{BBTA}$ (BBTA = bibenzotriazolate)^{38,39} and $\text{M}_2\text{Cl}_2\text{BTDD}$ (BTDD = bistriazolodibenzodioxin),^{40,41} stability towards water and ammonia decreases in the order $\text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+}$, in agreement with the trend in metal-aquo substitution rates.^{42,43} Based on these examples, the metal ion ligand substitution rate is a systematic descriptor of MOF stability that nevertheless is less recognized in the literature.

The trend in stability for MOFs based on ligand exchange rate is distinct from the stability trends for divalent metal complexes observed by Irving and Williams,^{44,45} with the most notable divergence being many Cu^{2+} materials. Due to the d^9 electronic configuration of Cu^{2+} , resulting in a Jahn-Teller distortion, its complexes exhibit relatively short, strong bonds to four equatorial ligands, accounting for the high measured stability constants for ligand complexes, but also exhibit extremely rapid ligand exchange at axial positions, resulting in lower observed stability for many Cu^{2+} MOFs than what would be expected from the Irving-Williams series.

2) Bond Strength: stabilizing the porous phase relative to the transition state

The weakest link in a MOF is commonly the metal-ligand bond. Substantial previous literature has demonstrated that stability towards polar analytes can be augmented by increasing the heterolytic metal-ligand bond strength,⁴⁶⁻⁴⁹ a result of lowering the energy of the porous framework relative to the heterolytic bond-breaking transition state.⁵⁰ For example, MOFs formed using pyrazolate or imidazolate ligands in combination with late transition metals often exhibit superlative chemical stability, which can be attributed to the stronger donating ability of these ligands versus carboxylates, and can be quantified by the ligand basicity. Metal-binding groups that are more donating will increase the heterolytic metal-ligand bond strength, particularly for late transition metals, and enhance MOF stability, up to a point. Ligands with greater donating ability than pyrazolates have not been widely explored in MOF chemistry, due largely to synthetic difficulties in either accessing the ligand or crystallizing the framework. Yet increasing the donating ability significantly more may not result in increased stability towards water because of the concomitant increase in driving force for metal-ligand bond hydrolysis.

An additional strategy for increasing the metal-ligand bond strength for carboxylate frameworks is to increase the valency of the metal ion. Although augmenting the ligand donation strength is successful for late transition metals because it results in a stronger, more covalent bonds, increasing the ionic bond strength is also possible when employing carboxylate ligands by simply increasing the charge density on the metal ion. Higher-valent metals paired with carboxylates, such as Ti^{4+} , Zr^{4+} , Cr^{3+} , and Al^{3+} will form stronger metal-ligand bonds than those constructed with divalent metal ions.

Although increasing the metal-ligand bond strength is often thought of as a route towards the thermodynamic stabilization of the porous phase, there may be no net change in the driving force towards the dense phase because the dense phase with the same metal-ligand bond is equally stabilized. For instance, moving from carboxylate ($pK_a(\text{DMSO}) = 11.1$)⁵¹ to imidazolate ($pK_a(\text{DMSO}) = 18.6$)⁵² in Zn^{2+} frameworks results in nearly identical energy penalties for the porous MOFs, MOF-5 and Zn-methylimidazolate (ZIF-8), with respect to the corresponding dense phases.¹⁷ Nonetheless, the increased metal-ligand bond strength of ZIF-8 does result in greater kinetic stability relative to MOF-5, especially towards coordinating species, due to an increased energy barrier for heterolytic metal-ligand bond breaking.⁵⁰

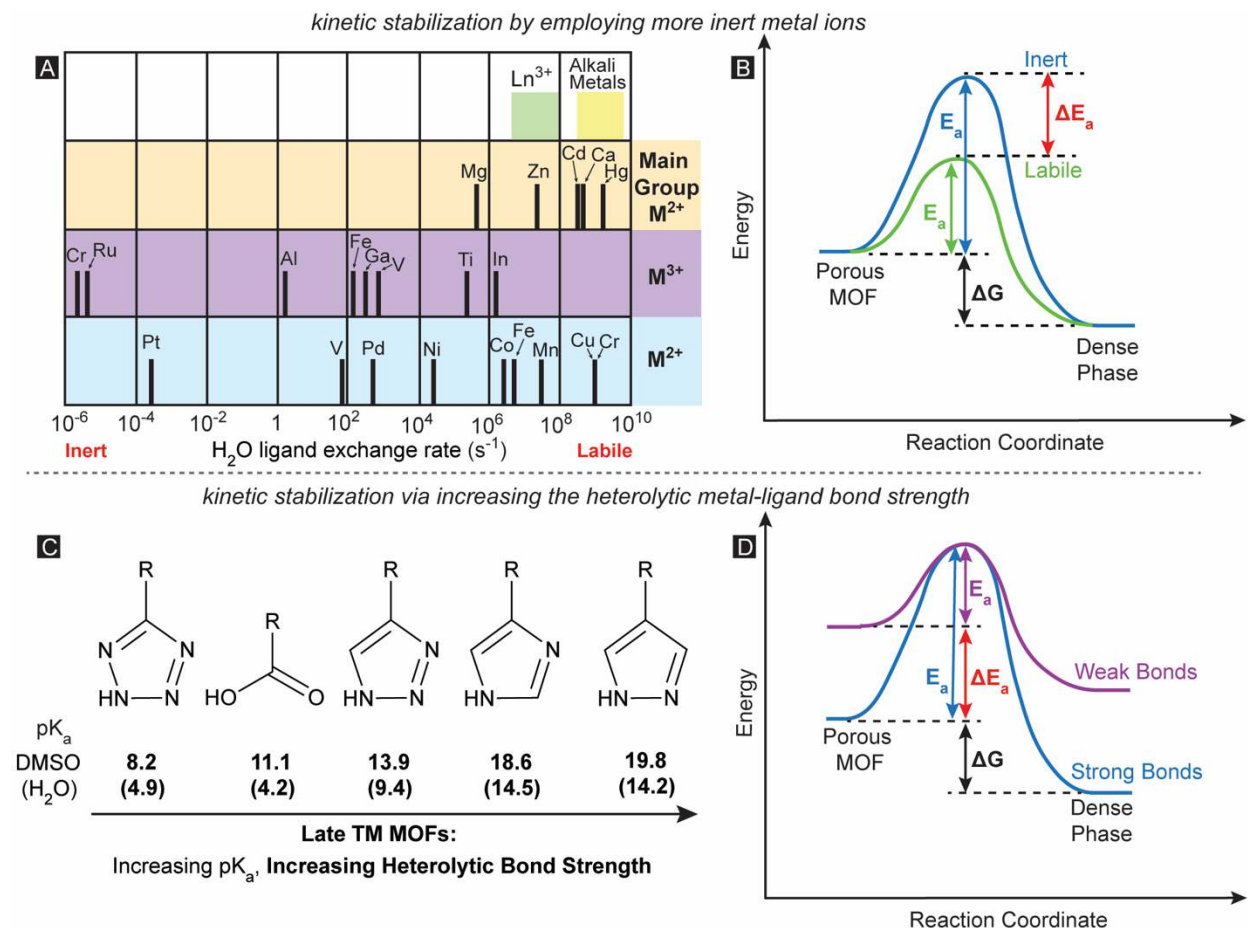


Figure 2: Routes towards kinetic stabilization of MOFs. Methods towards stabilization of the porous phase with respect to the dense phase must involve increasing the activation energy barrier.^{29,53,54} B) Metal ion inertness increases the activation energy barrier for rearrangement to the dense phase. C) The use of more strongly donating azolate ligands, as measured by pK_a,^{51,52,55} in combination with late transition metals, results in stronger metal-ligand bonds. D) Increasing the heterolytic metal-ligand bond strength results in a greater activation energy barrier for a bond-breaking transition state, while not affecting the net driving force towards the dense phase.

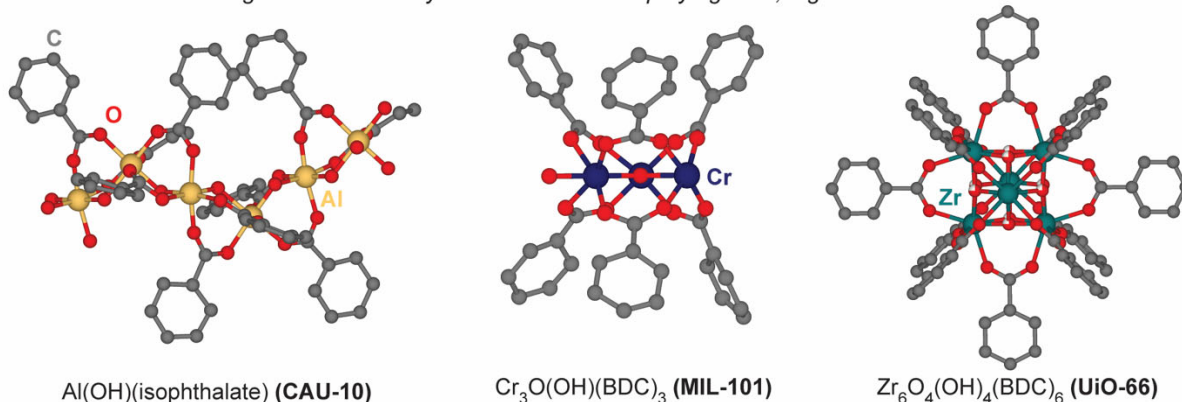
Linker and node connectivity

The transition state energy can additionally be boosted by increasing the connectivity of framework components, improving stability in a manner similar to the chelate effect. The stabilization comes as a result of increasing the number of metal-ligand bonds which must dissociate or rearrange simultaneously in order for a phase transition to occur or a pore to collapse. For instance, the barrier to linker removal or reorganization will be greater for a tetratopic carboxylate, such as the linker of NU-1000 (Zr₆O₄(OH)₄(HCOO)₄(TBAPy)₂, TBAPy = pyrene tetra-*p*-benzoic acid),⁵⁶ than a ditopic carboxylate, such as the biphenyl dicarboxylate (BPDC) linker of UiO-67 (Zr₆O₄(OH)₄(BPDC)₆).⁵⁷ Similarly, frameworks made up of secondary building units (SBUs) with greater connectivity exhibit enhanced stability, exemplified by MOFs constructed from Zr⁴⁺ oxo-hydroxo nodes which may be linked by 6, 8, 10, or 12 carboxylate groups, whose stability generally covaries with node connectivity.^{58–60}

Sterics and Hydrophobicity:

Steric shielding of metal-ligand bonds can impede the access of water and other coordinating vapors to delicate metal-ligand linkages.^{60–64} However, this strategy also may decrease overall porosity as well as inhibit the access of desirable sorbates to the framework sites, which often exhibit the strongest guest binding interactions.

fragments of carboxylate frameworks employing inert, high-valent metal ions



fragments of late transition metal-azolate frameworks

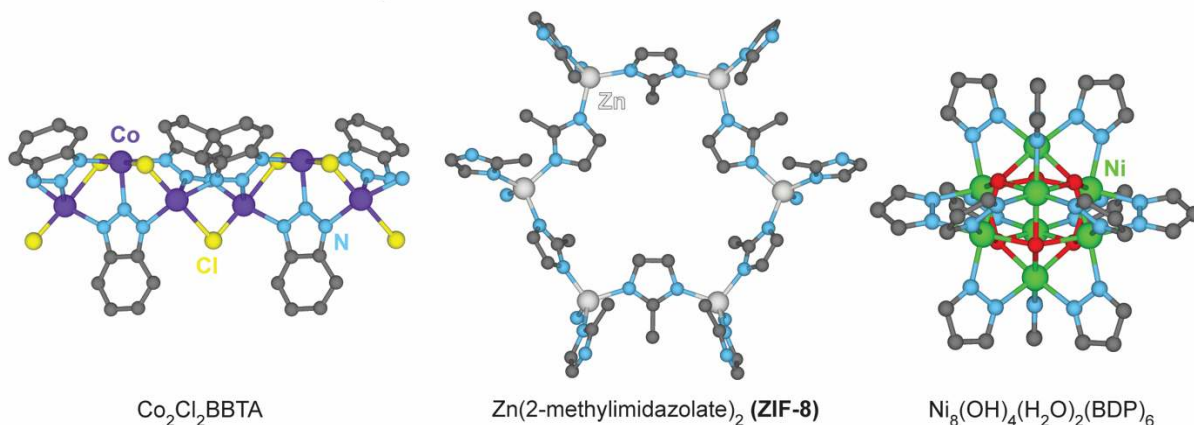


Figure 3: **MOF building blocks with high kinetic stability.**^{30,38,57,65–67} BDP = 1,4-benzene-dipyrzolate. H atoms omitted for clarity.

Effects of Gases and Vapors on Framework Stability

Coordinating Gases and Vapors: H₂O, NH₃, H₂S

Perturbations in the bonding and connectivity of a MOF frequently result in decreases in the useful surface area and porosity. Framework exposure to coordinating gases and vapors are one cause of such perturbations. The ability of a MOF to withstand exposure is directly related to the energy barrier towards ligand rearrangement or substitution. Several reaction pathways can be operative, including ligand substitution,⁵⁰ metal-ligand bond hydrolysis,^{68–70} coordination-induced ligand rearrangement,^{71,72} or pore collapse due to capillary forces.^{73,74} Common to all mechanisms is a requirement for ligand rearrangement around the SBU, as well as some degree of heterolytic metal-ligand bond breaking. These factors directly relate the stability of a MOF towards coordinating gases and vapors to the kinetics of ligand exchange at the metal center, as well as the heterolytic metal-ligand bond strength. For example, theoretical calculations for

metal-ligand hydrolysis and water substitution reactions reveal that hydrolysis to form the metal hydroxide and the protonated ligand is universally downhill for diverse frameworks including Zn-MOF-5, Cu-HKUST-1, Cr-MIL-101, and Zn-ZIF-8, but the activation energy barrier for ligand substitution is much larger for Cr-MIL-101 and Zn-ZIF-8, in line with the experimentally observed high steam stability for these two frameworks versus Zn-MOF-5 and Cu-HKUST-1.⁵⁰

The stability trends of MOFs towards polar gases is largely dependent on the gas' acidity as well as its nucleophilicity. The stability of MOFs towards NH₃ and H₂S trend with the stability for water. However, the greater nucleophilicity of NH₃ makes ligand substitution potentially more favorable. In combination with water, ammonia forms NH₄OH, which is highly corrosive and may result in metal ligand bond hydrolysis.⁷⁵ Moving to the more acidic H₂S, with a pK_a of 7.0 in water, seven orders of magnitude more acidic than H₂O, protonation of the ligand occurs more readily, resulting in a metal sulfhydryl or sulfide.³² Further, H₂S is strongly nucleophilic and coordinating to metal ions, therefore it can readily substitute for a framework ligand.

Acidic and Oxidizing Gases and Vapors: SO_x, NO_x, elemental halogen X₂

Designing materials that are stable to acidic and oxidizing gases such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), and halogens (X₂) present unique challenges. In particular, oxidation of the metal center by an oxidizing gas can drastically alter the kinetics of ligand substitution as well as the preferred ligand geometry around a metal center. Further, many materials are stable to corrosive gases in single component studies, but in the presence of humid air a variety of new challenges arise from potential side reactions that form strong acids.⁷⁶ For instance, in combination with water vapor, SO₂ forms sulfurous acid (H₂SO₃), and over time in the presence of oxygen it can form SO₃ and sulfuric acid (H₂SO₄).⁷⁷ Consequently, SO₂ adsorption in humid air, most relevant for industrial applications, is challenging, and linker protonation resulting in the formation of metal sulfites or sulfates can be extremely destructive.⁷⁸

The capture of NO_x presents additional challenges. Much the same as SO₂, both NO and NO₂ under humid conditions can form the strong acids HNO₂ and HNO₃, which may protonate linkers to cause framework degradation. NO and NO₂ can also undergo a variety of redox reactions, such as NO disproportionation ($3 \text{ NO} \rightarrow \text{NO}_2 + \text{N}_2\text{O}$), NO oxidation ($2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$), or NO₂ dimerization/disproportionation ($2 \text{ NO}_2 \rightarrow \text{N}_2\text{O}_4 \rightarrow \text{NO}^+ + \text{NO}_3^-$).⁷⁹

Formation of NO⁺ can be very destructive as it may react with aromatics, amino groups, or transition metals to cause irreversible framework damage. Therefore, in order to design frameworks for NO_x capture, it is important to either employ methods to mitigate the reactive chemistry of NO_x or to design materials that accommodate the daughter products.⁸⁰

Framework Design for Strongly Interacting Gas Capture

The modularity of MOFs allows for three main strategies towards increasing the interaction strength between the framework and polar gases. The first approach relies on MOFs containing metal ions with open coordination sites, typified by frameworks such as HKUST-1, MOF-74, and M₂Cl₂BBTA. These frameworks can exhibit strong affinities for Lewis basic gases as well as oxidizing gases. However, direct coordination by an analyte gas to a framework node can lead to ligand rearrangement or hydrolysis of the metal-ligand bond. Therefore, the deployment of this method requires robust stability. The second strategy focuses on the installation of functional groups, such as -NH₂, -OH, or -SO₃H moieties, on the organic ligands. This approach can effectively modulate framework polarity and hydrophilicity. However, the

functional groups occupy pore volume and reduce the surface area of the resulting frameworks. Thirdly, auxiliary ligands integral to the SBU can be leveraged as strongly interacting sites for polar gases. For instance, the μ -OH moieties in $Zr_6O_4(OH)_4^{12+}$ SBUs can serve as primary sorption sites for water as well as SO_2 .^{58,81} It should be noted that augmenting the surface area, although it may increase the overall capacity for gas uptake at high relative pressure, does not result in improved affinity for polar gases at low relative pressure. While the number of purely dispersive interaction sites increases with higher surface area, these weak binding sites are insufficient for selective polar gas capture.

H₂O

Occurrence, Applications:

The stability of MOFs towards water has been extensively investigated^{58–60,82} because it is the most common coordinating and corrosive gas present in the atmosphere as well as in many applications like postcombustion gas streams,^{6,83} gas sensing,⁸⁴ or in fuel cells requiring proton conducting materials.⁸⁵ Additionally, the capture of water vapor has several desirable applications including dehumidification,^{73,86,87} heat transfer,^{88,89} and atmospheric water capture.^{41,90–94} These applications all rely on cycles in which water alternatively fills the pores, and then is desorbed, creating a requirement for extensive cycling stability. Water is unique among the gases and vapors considered herein because it is a liquid at STP and will thus completely fill the entire pore interior of a porous material above a suitable humidity. Strategies for the design of water sorbents have focused on optimizing the relative humidity (RH) of pore filling, such that it is favorable under the temperature and vapor pressure conditions of a given application. The partial pressure of pore filling is highly dependent on the pore size as well as the pore hydrophilicity. Smaller pores fill at lower RH and larger pores fill closer to 100% RH.^{58,82,95} Additionally, framework hydrophilicity may be modulated by appending polar groups to the organic ligands. As above, this strategy results in a reduction of total pore volume and it leads to broadening of the water uptake step, both of which equate to a lower usable capacity.^{48,96–98} Anion and cation exchange strategies at the node can control the partial pressure of pore filling without modifying pore size and shape, but may require careful consideration of the changes to framework stability inherent to SBU alterations.⁹⁹

MOF Sorbents for H₂O:

Water sorbents with extended cycling stability generally fall into two categories: 1) High-valent inert early transition metal-carboxylate frameworks, and 2) Late transition metal-azolate frameworks. The stability of MOFs towards water has been reviewed several times previously,^{60,82} and a comprehensive review of all MOFs investigated for water sorption is available.⁸⁹ Here we focus on the trends in stability for MOF building blocks and the superlative sorbents constructed from the more stable building blocks.

1) Inert, high-valent metal carboxylates

Zr^{4+} MOFs featuring $Zr_6O_4(OH)_4(RCOO)_{12}$ nodes, typified by the terephthalate-linked UiO-66⁵⁷ have been widely explored as stable water sorbents.¹⁰⁰ Varying the ditopic carboxylate linker from the smallest (fumarate, MOF-801)¹⁰¹ to the largest (4,4'-[(2,5-Dimethoxy-1,4-phenylene)bis(ethyne-2,1-diyl)]dibenzoic acid, PIZOF-2)¹⁰² results in the controlled modification of the pore size from 6 Å to 20 Å, enabling the tuning of the water uptake step from 9% RH to 75% RH.⁵⁸ Although Zr^{4+} carboxylate frameworks are generally thought of as stable to water, this is not the case for all members of the family. MOF-805, -806 and -808 were found

to degrade significantly with water sorption, whereas MOF-801, MOF-802, MOF-841, and UiO-66 were found to be stable to at least five cycles of water uptake and release.⁵⁸ Differences in the stability of hexanuclear zirconium frameworks are often attributed to the connectivity of the node, as well as the rich defect chemistry of zirconium MOFs,^{74,103–106} with more defective frameworks collapsing faster due to their lower connectivity. Recently, MIP-200 ($\text{Zr}_6\text{O}_4(\text{OH})_4(\text{HCOO})_4(\text{methylene diisophthalate})_2$) was reported to have a water capacity of nearly 40 percent by weight (wt%) achieved below 25% RH and further, the framework exhibits exceptional chemical and water cycling stability over 50 cycles, attributed to residual extra-framework anions bound to the nodes. MIP-200 withstands NH_4OH vapor, 6M H_3PO_4 , aqua regia, HNO_3 , and HCl at reflux.¹⁰⁷

Nodes consisting of inert Al^{3+} ions linked by carboxylates, commonly forming oxo-centered trinuclear SBUs found in $\text{Al}_3\text{O}(\text{OH})(\text{BTC})_2$ (Al-MIL-100),^{108,109} or infinite chains of Al^{3+} bridged by hydroxo groups, an SBU found in $\text{Al}(\text{OH})(\text{BDC})$ (Al-MIL-53),¹¹⁰ make up another family of exceptionally stable carboxylate MOFs. One of the most mass-produced MOFs, $\text{Al}(\text{OH})(\text{fumarate})$, isoreticular to MIL-53, has been tested on a full-scale heat exchanger for heat transfer processes. This MOF coating exhibited a 95% capacity retention for water after 360 cycles.¹¹¹ Aluminum MOFs formed with bent dicarboxylate linkers, typified by CAU-10 ($\text{Al}(\text{OH})(\text{isophthalate})$)^{65,112,113} exhibit exceptional water sorption characteristics for heat transfer processes. CAU-10 is extremely scalable¹¹⁴ and has a water isotherm step well positioned to be of use in adsorptive heat transfer processes. Extensive water cycling of a heat exchanger coated with a sample of CAU-10 in a binder resulted in a negligible loss in capacity after 10,000 cycles.¹¹² Moving to the lighter-weight 2,5-furandicarboxylate linker produces the isostructural MIL-160 framework,¹¹⁵ which has an increased water affinity as well as augmented gravimetric water capacity. Further, the recently reported Al-MOF-303 employs 2,5-pyrazole dicarboxylate as the linker, and retains its water capacity of 33 wt% after 150 cycles.⁹⁴

The most kinetically inert of the first-row transition metals, Cr^{3+} forms exceptionally robust frameworks with multitopic carboxylates. Cr^{3+} frequently forms SBUs similar to those formed by Al^{3+} . For instance, $\text{Cr}_3\text{O}(\text{OH})(\text{BTC})_2$ (Cr-MIL-100) and Cr-MIL-101³⁰ are made up of trinuclear oxo-centered clusters, and $\text{Cr}(\text{OH})(\text{BDC})$ (Cr-MIL-53)³¹ consists of infinite chains of metal ions bridged by hydroxo groups. Cr-MIL-101 has been widely explored for water sorption due to its exceptional overall water uptake of 1.6 g g^{-1} as well as its superlative cycling stability.^{97,116–118} As a consequence of its exceptional inertness, the synthesis of Cr^{3+} frameworks present substantial challenges due to the irreversibility of bond-forming on a reasonable timescale. In order to obtain water sorbents with both high capacity and exceptional stability, one strategy to overcome the difficulties of direct Cr^{3+} MOF synthesis is to first crystallize an Fe^{3+} carboxylate framework, and subsequently use cation exchange of Cr^{2+} for Fe^{3+} in order to incorporate chromium into the framework. The labile Cr^{2+} is able to rapidly enter the SBU, and once inserted, it is oxidized by Fe^{3+} to Cr^{3+} , which is thereby kinetically trapped. This strategy was pursued to synthesize the record-setting Cr-*soc*-MOF,^{73,119} which can uptake nearly 2 g g^{-1} water, as well as the Cr-*acs*-MOF termed NU-1500.¹²⁰ Testament to the fundamental analysis presented earlier, the Fe^{3+} analogs, as well as the Al^{3+} analog for the mesoporous *soc*-MOF, collapse due to capillary forces during pore filling or when activated from water, whereas the Cr^{3+} -exchanged frameworks withstand repeated water cycling.^{73,120}

Carboxylate frameworks incorporating other metal ions including Ti^{4+} and Fe^{3+} have also been investigated for water sorption applications. $\text{Ti}_8\text{O}_8(\text{OH})_4^{12+}$ nodes are among the more stable building blocks for MOFs. $\text{Ti}_8\text{O}_8(\text{OH})_4(\text{H}_2\text{N-BDC})_6$ (Ti-MIL-125-NH₂) absorbs more than

50 wt% water below 25% RH, with minimal loss of capacity over 10 cycles.¹²¹ Additionally, $\text{Fe}_3\text{O}(\text{OH})(\text{BTC})_2$ (Fe-MIL-100) was investigated for latent cooling load reduction dehumidifying climate control air streams, and a MOF coating on a heat exchanger could be cycled 2000 times, while losing only 4.5% of the original capacity.⁸⁶ Carboxylate MOFs employing transition metals later or lower-valent than Fe^{3+} are not candidates for water sorption applications due to stability concerns.

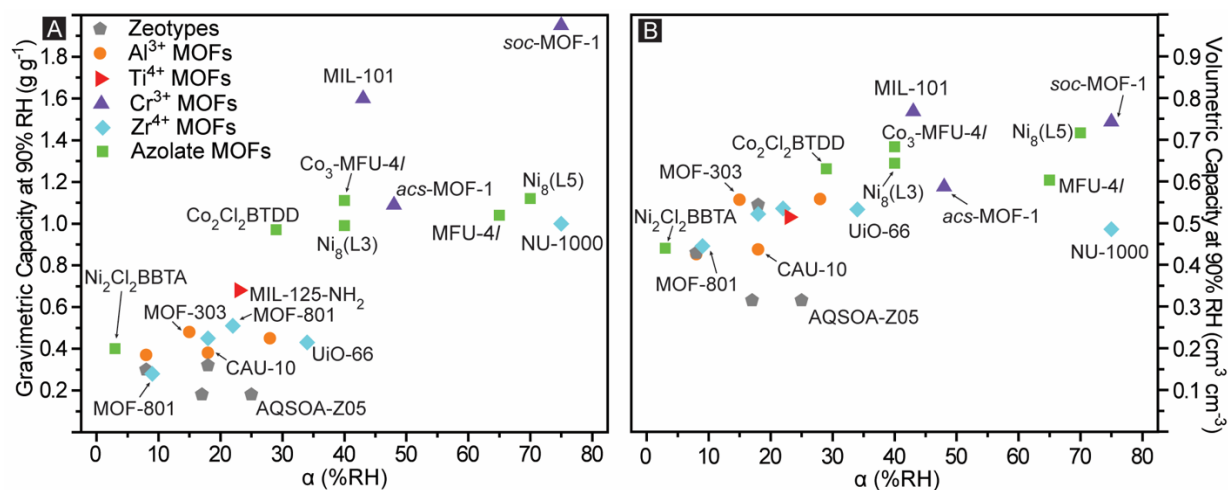


Figure 4: **Water Capacities of Porous Solids.** A) Gravimetric uptake capacity versus α , the RH value at which half the total capacity is reached. Materials with larger pores can achieve higher gravimetric capacities with concomitant reduction in hydrophilicity. B) Plotting the capacity in volumetric units highlights the significantly reduced variation in total capacity as a function of hydrophilicity. Values and references listed in **Table 1**.

2) Late transition metal azolate frameworks

Moving from the hard, weakly donating carboxylate ligands to the comparatively soft, strongly donating azolate ligands such as triazolate, pyrazolate and imidazolate engenders heterolytically stronger metal-ligand bonds with late transition metals. This strategy has been effective in creating robust Zn^{2+} MOFs with imidazolates and pyrazolates, even though Zn^{2+} is quite labile. The ZIFs have been widely explored as water sorbents and exhibit exceptional stability, yet their general hydrophobicity as well as their limited total pore volume, which governs the total deliverable capacity, restricts the utility of ZIFs in applications such as heat transfer and water harvesting.^{89,116} Pyrazolate frameworks have been explored as water sorbents for heat transfer, however, the topologies heretofore synthesized with these linkers lack open coordination sites and the frameworks are typically hydrophobic. Linear bispyrazolate⁶⁷ and square tetrapyrazolate¹²² linkers paired with $\text{Ni}_8(\text{OH})_4(\text{H}_2\text{O})_2$ SBUs can result in exceptionally stable MOFs that are also highly hydrophobic, absorbing water only above 80% RH in one case.¹²³ The hydrophilicity of pyrazolate frameworks can be modulated via organic linker modification, though these modifications can reduce the overall water capacity, as they occupy space in the pore, and can also result in broadening of the water uptake step (see also above).⁴⁸

MOFs constructed from linear bistriazolate frameworks contain a high density of open coordination sites, making them very hydrophilic. $\text{M}_2\text{Cl}_2\text{BTDD}$ has a topology similar to that of MOF-74, including hexagonal pores lined with infinite one-dimensional (1D) chains of metal ions exhibiting open coordination sites, and the Co^{2+} and Ni^{2+} analogs are stable to repeated

water uptake.⁴¹ Although the size of its mesopores exceed the critical diameter for water capillary condensation, Co₂Cl₂BTDD reversibly sorbs water without hysteresis due to water coordination at the open metal sites prior to the pore filling step. The smaller pore analog M₂Cl₂BBTA also has been explored for water uptake, and by virtue of its smaller pore size, it is significantly more hydrophilic, capturing water near 0% RH.⁴³ Among the metal ions tested, Ni₂Cl₂BBTA was found to be most stable, and the stability trend is in line with the metal-aquo substitution rates. Although they form hexagonal structures with the majority of late transition metals, linear bistriazolate linkers form a cubic structure when treated with Zn²⁺. The resulting framework, Zn₅Cl₄(BTDD)₃ (MFU-4l),^{124,125} has a very large water uptake capacity greater than 1 g g⁻¹. Cation exchange of the native Zn²⁺ material for Co²⁺ enables the modulation of the RH of water uptake over a range of nearly 30%, without decreasing the overall capacity, due to the greater propensity for a tetrahedral Co²⁺ to accept a fifth ligand.⁹⁹ However, the cubic BTDD-based frameworks exhibit significantly decreased stability relative to the hexagonal frameworks, with the fully exchanged Co²⁺ material collapsing in the presence of water vapor.⁹⁹

Table 1: Water Capacities for Selected Porous Materials

	α^a (% RH)	Uptake (g g ⁻¹)	Crystal ρ (g cm ⁻³)	Uptake (cm ³ cm ⁻³)
Co ₂ Cl ₂ BTDD ⁴¹	29	0.97	0.65	0.6305
Cr- <i>soc</i> -MOF ⁷³	75	1.95	0.381	0.74295
Cr-MIL-101 ⁹⁷	43	1.6	0.48	0.768
MOF-841 ⁵⁸	22	0.51	1.05	0.5355
MOF-801 ⁵⁸	9	0.28	1.59	0.4452
Ni ₂ Cl ₂ BBTA ⁴³	3	0.4	1.1	0.44
Cr- <i>acs</i> -MOF ¹²⁰	48	1.09	0.539	0.58751
CAU-10 ¹¹²	18	0.38	1.15	0.437
MIL-160 ¹¹⁵	8	0.37	1.15	0.4255
MOF-303 ⁹⁴	15	0.48	1.159	0.55632
Ti-MIL-125-NH ₂ ¹²¹	23	0.68	0.757	0.51476
Al fumarate ⁸⁹	28	0.45	1.24	0.558
MIP-200 ¹⁰⁷	18	0.45	1.16	0.522
UiO-66 ⁸⁹	34	0.43	1.24	0.5332
Ni ₈ (L3) ¹²³	40	0.99	0.69	0.6831
Ni ₈ (L5) ¹²³	70	1.12	0.64	0.7168
Zn-MFU4l ⁹⁹	65	1.04	0.58	0.6032
Zn ₂ Co ₃ -MFU4l ⁹⁹	40	1.11	0.58	0.6438
NU-1000 ⁸⁹	75	1	0.486	0.486
ALPO-78 ¹²⁶	18	0.32	1.7	0.544
AQSOA Z02 ⁸⁹	8	0.3	1.43	0.429
AQSOA Z01 ⁸⁹	17	0.18	1.75	0.315
AQSOA Z05 ⁸⁹	25	0.18	1.75	0.315

^a α is the %RH at which half of the total uptake is reached

NH₃

Occurrence, Applications:

Ammonia is an industrial gas produced on a massive scale, whose toxicity has prompted significant research focused on its detection and sensing^{127–129} as well as personal protection and mitigation.^{130–133} To reduce the ammonia concentration below the NIOSH immediate danger threshold (300 ppm)¹³⁴ or below the odor threshold of 5 ppm,¹³⁵ sorbents must have a high affinity for ammonia at low relative pressure. Research in materials for personal protection has not focused substantially on framework stability because single-use sorbents that could collapse on contact with ammonia are acceptable under certain conditions. However, stability remains somewhat important as pore collapse during use can substantially impact the performance of a protective sorbent. Other applications may require extensive NH₃ cycling stability. For instance, ammonia is a common impurity in feed gas streams which may poison catalysts and membranes, necessitating the use of sorbents to capture NH₃ prior to the desired chemical process. Finally, on a thermodynamic basis NH₃ is an excellent working fluid for heat transfer in adsorption heat pumps, which require many thousands of adsorption cycles and materials with extreme stability to this corrosive gas.⁸⁹

MOF sorbents for NH₃:

In order to capture NH₃ at low relative pressure, one commonly employed strategy is the use of MOFs exhibiting Lewis acidic open metal sites, including HKUST-1, MOF-74, and M₂Cl₂BBTA frameworks. For example, HKUST-1 exhibits a high capacity for ammonia of 12.1 mmol g⁻¹ at 1 bar¹³⁶ but loses crystallinity upon ammonia exposure in under two hours.¹³⁷ According to NMR data, the reaction of HKUST-1 with anhydrous ammonia produces a diamine copper complex with a pendant anionic trimesate ligand. In the presence of water, the product is Cu(OH)₂ and (NH₄)₃BTC.⁷⁵ A polyvinylidene difluoride (PVDF) coating was found to protect HKUST-1 from ammonia; the composite maintained crystallinity as well as a constant NH₃ capacity over 28 days.¹³⁸ Analogs of MOF-74 have high capacities for ammonia based on breakthrough measurements, with the champion Mg²⁺ material able to capture 7.6 mmol g⁻¹ NH₃ before breakthrough, although the presence of water substantially decreased the uptake.¹³⁹ In a separate study, Cu-MOF-74 was found to take up more ammonia with water vapor present, though the material was unstable to ammonia.¹⁴⁰

Employing more donating triazolate linkers, M₂Cl₂BTDD materials were the first examples of MOFs exhibiting a high density of open metal sites stable to repeated sorption and desorption of ammonia.⁴⁰ The Ni²⁺ analog is stable to complete pore filling with ammonia, which occurs in a stepwise fashion near 0.8 bar of pure NH₃ at 263 K.⁴² Due to their greater density of open coordination sites, the smaller-pore M₂Cl₂BBTA materials capture significantly more ammonia, particularly at low pressures. The Cu²⁺ analog has the greatest static capacity at 1 bar and 298 K of any MOF, but it is unstable to even low concentrations of NH₃, which compromises its dynamic breakthrough performance. The cobalt material, though it loses crystallinity at 1 bar of ammonia, is stable to 1 mbar NH₃, the conditions of a typical breakthrough test. This enables M₂Cl₂BBTA to capture the greatest quantity of ammonia of any material under dry breakthrough conditions. The nickel material is significantly more stable, and the stability trend based on the NH₃ pressure required to effect loss of crystallinity and porosity in this family of triazolate MOFs is once again in line with that expected based on the substitution kinetics of the metal ion hexaaquo complexes.⁴²

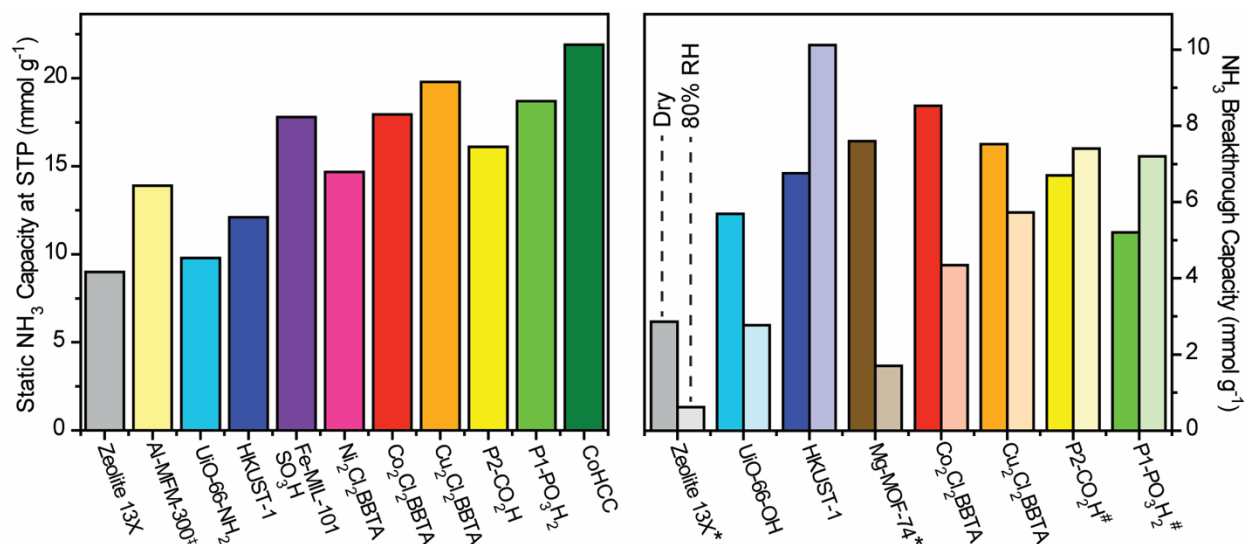


Figure 5: **Ammonia Capacities of Porous Solids.** Left: NH₃ capacity at 1 bar, 298 K based on equilibrium isotherm data. [†]Tested at 293 K. Right: NH₃ capacity under dynamic breakthrough conditions at 1000 ppm, 298 K in both dry and humid conditions. Tested at ^{*}1440, [#]2880 ppm. Values and references listed in **Tables 2** and **3**.

MOFs without open coordination sites have also been investigated for ammonia capture. In order to enhance the affinity for NH₃, ligand functionalization with polar or acidic groups is commonly employed. For instance, amino-functionalized MOF-5 has a high capacity for ammonia, sorbing 6.2 mmol g⁻¹ in breakthrough testing in a stream 1% NH₃, exceeding the capacity of Zn-MOF-74.¹⁴¹ Composites of graphene oxide with MOF-5 can also enhance ammonia uptake, though the framework collapses rapidly in the presence of NH₃.¹⁴² Zn²⁺ frameworks isorecticular to MOF-5 featuring ligands with free -OH groups can capture up to 16.4 mmol g⁻¹ NH₃ in static measurements at STP, though with loss of surface area and crystallinity.¹⁴³

The Zr⁴⁺ carboxylate framework UiO-66 has been extensively investigated for ammonia capture, and a diverse array of organic functional groups have been explored to enhance the affinity for NH₃.⁸⁴ Amino-functionalized UiO-66 outperforms derivatives with more acidic but bulkier functional groups such as -COOH and -SO₃H in breakthrough measurements, presumably due to pore clogging effects with larger moieties.¹⁴⁴ Similarly, the addition of copper sites to pendant free carboxylates can enhance equilibrium NH₃ uptake at the expense of diffusion.¹⁴⁵ Further investigation of UiO-66-NH₂ revealed that a portion of the amino groups may be protonated -NH₃Cl groups under typical acidic synthesis conditions, and that further functionalization to the hemiaminal or aziridine can enhance NH₃ capacity.¹⁴⁶ Although stable to short exposure times,¹³⁷ repeated cycling of ammonia uptake in UiO-66-NH₂ revealed a loss of capacity, surface area and crystallinity.⁴⁰

Trivalent Cr³⁺, Al³⁺, and Fe³⁺ carboxylate frameworks can exhibit increased stability toward ammonia,¹³⁷ though they have not been widely explored as sorbents. A framework comprised of Al³⁺ and a biphenyl tetracarboxylate linker, termed Al-MFM-300, was stable for 50 cycles of ammonia uptake with a high static capacity of 13.9 mmol g⁻¹ at 1 bar.¹⁴⁷ Additionally, a highly stable Al³⁺ porphyrin MOF can be loaded with HCl or formic acid to achieve up to 7.9 wt% breakthrough capacity.¹⁴⁸ Further, Fe³⁺-MIL-101 functionalized with sulfonic acid groups captures 17.8 mmol g⁻¹ NH₃ at STP, and has a high affinity for ammonia at low pressure.¹⁴⁹

Other families of porous materials have recently been investigated for ammonia capture. All-inorganic Prussian blue analogs, by virtue of their exceptional density of Lewis acidic metal sites, have particularly high static capacities for NH₃ of over 20 mmol g⁻¹ and can be regenerated.¹⁵⁰ Further, more recent covalent organic frameworks (COFs) with more robust linkages may find utility in ammonia sorption. Thus, although boronate ester-linked COF-10 can capture 15 mmol g⁻¹ NH₃ at STP, slow degradation was observed with cycling as the linkages remain susceptible to nucleophilic attack.¹⁵¹ On the other hand, porous polymers with all-carbon backbones such as diamondoid structures densely functionalized with acidic groups can exhibit superlative capacity and stability for NH₃, with uptake of 18.7 mmol g⁻¹ NH₃ at STP for the phosphonic acid functionalized material, although diffusion is compromised due to their interpenetrated nature.^{149,152}

Table 2: Equilibrium Ammonia Capacities at 1 bar, 298 K for Selected Porous Materials

	NH₃ Capacity (mmol g⁻¹)
Zeolite 13X ¹⁴⁷	9
Amberlyst 15 ¹⁴⁷	11
MCM-41 ¹⁴⁷	7.9
UiO-66-NH₂ ⁴⁰	10.6
HKUST-1 ¹³⁶	12.1
DUT-6 ¹⁴³	12
DUT-6-(OH)₂ ¹⁴³	16.4
Fe-MIL-101-SO₃H ¹⁴⁹	17.8
Al-MFM-300 ¹⁴⁷	13.9
P1-PO₃H₂ ¹⁵²	18.7
P2-CO₂H ¹⁵²	16.1
Mn₂Cl₂(BTDD) ⁴⁰	15.47
Co₂Cl₂(BTDD) ⁴⁰	12
Ni₂Cl₂(BTDD) ⁴⁰	12.02
Cu₂Cl₂(BTDD) ⁴²	16.74
Co₂Cl₂(BBTA) ⁴²	17.95
Ni₂Cl₂(BBTA) ⁴²	14.68
Cu₂Cl₂(BBTA) ⁴²	19.79
Al-MFM-300 ¹⁴⁷	13.9
Prussian blue ¹⁵⁰	12.5
CoHCC ¹⁵⁰	21.9
CuHCF ¹⁵⁰	20.2
MgCl₂ ¹⁵³	54.8

Table 3: Breakthrough NH₃ Capacities for Selected Porous Materials

	ppm NH₃	Dry (mmol g⁻¹)	Humid (80% RH) (mmol g⁻¹)
UiO-66-OH ¹⁴⁴	2880	5.69	2.77
Zeolite 13X ¹³⁹	1440	2.86	0.62

P1-PO₃H₂ ¹⁵²	2880	5.2	7.2
P2-CO₂H ¹⁵²	2880	6.7	7.4
HKUST-1 ¹⁵⁴	1000	6.76	10.12
Mg-MOF-74 ¹³⁹	1440	7.6	1.7
Co₂Cl₂BTDD ⁴²	1000	4.75	3.37
Co₂Cl₂BBTA ⁴²	1000	8.53	4.34
Cu₂Cl₂BTDD ⁴²	1000	7.52	5.73

H₂S

Occurrence, Applications:

Hydrogen sulfide is a major contaminant in flue gas streams as well as in many sources of natural gas, termed sour gas. When present in process streams it can poison catalysts, corrode components, and if not removed, combust into SO_x, a major air pollutant. Additionally, H₂S is highly toxic and heavier than air, making personal protection and mitigation vital to reduce the concentration below the OSHA exposure limit of 10 ppm, or the odor threshold of 1.5 ppm.^{135,155} The detection^{156–158} and removal of H₂S is therefore of great interest, and limited research in the MOF community has focused on these applications.

MOF sorbents for H₂S:

MOFs with open metal sites have been explored to capture H₂S, including HKUST-1, which exhibits a high capacity, though as with NH₃, the framework is unstable to H₂S. Partial protonation of the trimesate ligand by H₂S is proposed to result in framework collapse, although formation of CuS may also drive decomposition in this case. Similar to their performance with NH₃, HKUST composites with graphene oxide capture more H₂S than the parent materials, but suffer from similar stability issues.^{159,160} The use of non-structural metal ions with open coordination sites can provide strong binding sites for H₂S while also maintaining framework stability. Employing UiO-67-bipyridine grafted with Cu²⁺ gives a high capacity for H₂S of up to 7.8 wt%, on par with the 8 wt% in the comparatively unstable HKUST-1.¹⁶¹

High-valent metal terephthalates including Zr-UiO-66, Cr-MIL-101 and Ti-MIL-125 as well as their amino-functionalized derivatives were investigated for H₂S capture from natural gas. Of the materials tested, amino-functionalized derivatives performed better, and Ti-MIL-125-NH₂ was the top performer. H₂S was preferentially absorbed over CO₂, though the addition of CO₂ did decrease capacities for H₂S. Cr-MIL-101 performed best with CO₂ present.¹⁶² Additionally, V-MIL-47 and Cr-MIL-53 were investigated for H₂S capture at high pressures. Both V and Cr materials appear to be stable up to 15 bar H₂S, whereas Fe-MIL-53 decomposes under similar conditions to what is likely iron sulfide and H₂BDC.³²

Select pyridinic MOFs with relatively inert divalent metal ions can withstand H₂S exposure. For example, Mg₃(OH)₂(2,4-pyridine dicarboxylate)₂ (Mg-CUK-1), captures more than 3 mmol H₂S g⁻¹ when exposed to 15% H₂S in nitrogen, and the material remained stable over five cycles.¹⁶³ Additionally, Ni²⁺-pyrazine (py) frameworks employing anionic inorganic pillars can absorb both CO₂ and H₂S from natural gas streams,¹⁶⁴ and were investigated for H₂S separations using mixed-matrix membranes. The Ni²⁺-based NbOF₅²⁻ and AlF₅²⁻-pillared materials¹⁶⁵ significantly increase both the selectivity and the permeability of the host polymer membrane for H₂S, and both materials remain stable by PXRD after exposure to 14 bar H₂S.¹⁶⁶

The Ni²⁺ materials are more stable to H₂S, as well as to water, than analogous Cu²⁺ frameworks employing SiF₆²⁻ as the pillar, with Ni(py)(AlF₅) stable to 15 cycles of water uptake.^{167,168}

MOFs employing more strongly donating azolate ligands have not been widely explored for H₂S capture. Notwithstanding, Zn(tetrazolate) (*kag*-MOF-1), which is stable to water and low concentrations of H₂S, selectively absorbs H₂S over higher hydrocarbons due to its small pore diameter.¹⁶⁹

SO₂

Occurrence, Applications

Sulfur dioxide is a major air pollutant generated by combustion of sulfur-containing materials including coal, sour natural gas, or metal sulfide ores. SO₂ is a significant contributor to the formation of acid rain and fine particulate matter (PM_{2.5}), making the capture of SO₂ from exhaust gases vital. In North America, SO₂ emissions have decreased by 90% over the past 20 years¹⁷⁰ because of the implementation of SO₂ removal technologies, including dry limestone scrubbing and the wet sulfuric acid process,¹⁷¹ yet these processes are not 100% efficient. As a result, coal-fired power plants continue to emit 1.2 million tons yr⁻¹ of SO₂ in the USA alone.¹⁷² In addition to the environmental benefits of reducing SO₂ emissions, the complete removal of SO₂ is often critical prior to contact with downstream catalysts or adsorbent materials intended for other gases.^{173,174} Consequently, new adsorbent materials that remove SO₂ at low partial pressure are attractive targets in post-combustion exhaust capture, an application which would require extensive cycling stability under humid conditions. Here, we cover standout examples of MOF stability towards SO₂, as recent reviews provide detailed coverage.¹⁷⁵

MOFs for SO₂ Adsorption

Metal-carboxylate MOFs

Tetravalent metal carboxylate frameworks can exhibit high uptake capacities for SO₂. For instance, the eight-connected Zr⁴⁺ material MFM-601, [Zr₆(μ³-O)₄(μ³-OH)₄(OH)₄(H₂O)₄(L)₂] (L = 4,4',4'',4'''-(1,4-Phenylenebis(pyridine-4,2,6-triyl))tetrabenzoate), adsorbs 12.3 mmol g⁻¹ SO₂ at STP. In-situ powder X-ray diffraction revealed six binding sites, the strongest of which is adjacent to a terminal hydroxyl group at the node. Adsorption properties under humid conditions have not been reported. Moving to Ti⁴⁺ frameworks, Ti-MIL-125 has a high uptake capacity under anhydrous conditions of 10.9 mmol g⁻¹ at 2.6 bar, but decomposes under humid SO₂.¹⁷⁶ By contrast, the addition of an -NH₂ group to the linker stabilizes the framework under humid conditions, and Ti-MIL-125-NH₂ retains a comparable SO₂ adsorption capacity of 10.3 mmol g⁻¹ at 2.6 bar. Decomposition in Ti-MIL-125 was proposed to result from hydrolysis of the metal ligand bond, followed by reaction with SO₂ to form bisulfite (HSO₃⁻) and a dangling linker. Calculations reveal that in Ti-MIL-125-NH₂, the activation energy barrier for hydrolysis of the Ti-O bond is augmented by ~5 kcal mol⁻¹ which engenders enough additional stabilization to sufficiently slow the decomposition pathway.¹⁷⁶

Initial results show that trivalent Al³⁺ and In³⁺ carboxylate frameworks reversibly bind dry SO₂ in static adsorption experiments.¹⁷⁷⁻¹⁷⁹ The Al³⁺ carboxylate MOFs, MFM-305-CH₃, MFM-305, and MFM-300 (née NOTT-300) all reversibly adsorb SO₂ with high capacities above 5 mmol g⁻¹.^{178,179} In situ powder X-ray diffraction analysis on MFM-300 revealed that SO₂ strongly interacts with the bridging hydroxyl groups of the SBU.¹⁷⁸ Moving to the more labile In³⁺, NOTT-202a [In(O₂CR)₄] (O₂CR = biphenyl-3,3',5,5'-tetra-(phenyl-4-carboxylate)) reversibly binds SO₂ with an adsorption capacity of 10 mmol g⁻¹ at 1 bar and temperatures between 293–

303 K.¹⁷⁷ However, low temperature (268–283 K) SO₂ adsorption isotherms feature hysteretic adsorption of an additional 2-6 mmol SO₂ g⁻¹ as a consequence of an irreversible phase change to form a denser crystalline polymorph. Despite the phase change, SO₂ is completely removed from NOTT-202b at zero pressure, suggesting that SO₂ does not react directly with the framework. It was suggested that the phase change in NOTT-202a occurs due to ordering of SO₂ within the pore at adsorption capacities greater than 7 mmol g⁻¹ SO₂, similar to a pore condensation phenomenon, and the internal pressure thus created provides enough energy to overcome the activation barrier to transform to the denser NOTT-202b, which is 20 kJ mol⁻¹ downhill in energy due to increased ligand pi-stacking.

Late transition metal-carboxylate frameworks exhibit poorer stability towards SO₂. Dynamic breakthrough measurements of MOF-5, IRMOF-3, Zn-MOF-74, MOF-177, and MOF-199, all Zn²⁺-based, revealed uptake capacities of less than 0.5 mmol g⁻¹ for all materials except MOF-74, which adsorbs 3.0 mmol g⁻¹ presumably due to its open metal sites.¹⁸⁰ Increased stability towards dry SO₂ in pillared Zn²⁺ carboxylate MOFs can be achieved by either increasing the steric bulk on the linker, or by replacing Zn²⁺ with the more inert Ni²⁺.^{76,181}

Pyridinic coordination networks SIFSIX-1-Cu and SIFSIX-2-Cu-i can exhibit high and stable uptakes to dry SO₂. Consisting of square grids of Cu²⁺ and 4,4'-bipyridine or 4,4'-dipyridylacetylene pillared by SiF₆²⁻ anions, these frameworks exhibit dry SO₂ adsorption capacities of 11.01 and 6.90 mmol g⁻¹, respectively. Replacing Cu²⁺ with Zn²⁺ or Ni²⁺ results in lower capacities of 2.10 and 2.74 mmol g⁻¹, respectively. The materials were stable to dry breakthrough testing over 4-6 cycles with mild reactivation parameters of 313 K and He flow, though humid stability above 1000 ppm H₂O was not evaluated.¹⁸² Additionally, the pyridinic frameworks Ni(py)₂(NbOF₅) and Ni(py)₂(AlF₅) both exhibit dry uptakes of 2.2 mmol g⁻¹ when exposed to 7% SO₂ in N₂.¹⁸³ Moreover, these materials exhibit stability towards SO₂ under humid environments.

Metal-Azolate MOFs

To date, few metal azolate frameworks have been explored for SO₂ sorption. One exception is a series of nickel pyrazolate MOFs based on (Ni₈(OH)₄(H₂O)₂(BDP)₆), which show good stability towards SO₂.¹⁸⁴ Dynamic adsorption experiments revealed that the unfunctionalized framework has an SO₂ adsorption capacity of 2.0 mmol g⁻¹ under 2.5% SO₂ in N₂. The addition of amino or hydroxyl functional groups to the BDP ligand, as well as treatment with Bronsted bases to augment the defect concentration, both result in enhanced SO₂ capacity (**Table 4**). Within this family of Ni²⁺ pyrazolate MOFs, SO₂ binding was not completely reversible: cycling experiments revealed a decrease of 26-37% capacity after the first cycle. However, the decay appeared to stop after the first cycle, and the remaining SO₂ capacity in the second cycle appeared to be reversible. The initial decrease in capacity was attributed to the irreversible formation of bisulfite (M-SO₃H) or sulfite (M-SO₃(H₂O)) at the node.

Although no sorption was reported, the stability of several ZIFs under dry and humid SO₂ conditions has been explored.¹⁸⁵ A negligible ~4% decrease in the surface area of ZIF-8 was observed after exposure to dry SO₂, however, the surface area decreases by ~70% after exposure to 20 ppm SO₂ at 85% RH over 10 days. Similar loss of porosity was observed for other ZIFs, except for ZIF-71 (Zn(4,5-dichloroimidazolate)₂), which retained its full pore volume, though curiously, it transitions to a dense polymorph in liquid water. Analysis by X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy revealed formation of bisulfite and bisulfate, presumably resulting from metal-ligand bond hydrolysis, within the ZIFs which lost porosity.¹⁸⁵

Table 4: Static SO₂ Capacities at 1 bar, 298 K for select MOFs.

	SO ₂ Capacity (mmol g ⁻¹)
MFM-601 ¹⁸⁶	12.3
MFM-600 ¹⁸⁶	5.0
MFM-202a ¹⁷⁷	10
Ni(bdc)(ted) _{0.5} ¹⁸¹	9.97
Zn(bdc)(ted) _{0.5} ¹⁸¹	4.41
MOF-74(Mg) ¹⁸¹	8.60
MFM-300(Al) ¹⁷⁸⁺ (NOTT-300)	8.1
MFM-300(In) ¹⁸⁷	8.3
Zn-DMOF-TM ^{a76}	~4.5 (dry)
Zn-DMOF-DM ^{b76}	degrades
Zn-DMOF-NDC ^{c76}	~4 (dry)
Zn-DMOF-ADC ^{d76}	~5.5 (dry)
Cu-DMOF-TM ^{a76}	~2.8 (dry)
Ni-DMOF-TM ^{a76}	~5 (dry)
Co-DMOF-TM ^{a76}	~3.8 (dry)
FMOF-2 ¹⁸⁸	1.8
MFM-305-CH ₃ ¹⁷⁹	5.16
MFM-305 ¹⁷⁹	6.99
SIFSIX-1-Cu ¹⁸²	11.01
SIFSIX-2-Cu-i ¹⁸²	6.9
MIL-125 ¹⁷⁶	~9.5
MIL-125-NH ₂ ¹⁷⁶	~9.5

^aTM – tetramethylterephthalic acid, ^bDM – 2,5-dimethyl terephthalic acid, ^cNDC – 1,4-naphthalenedicarboxylic acid, ^dADC – 9,10-anthracenedicarboxylic acid. ^e250 ppm with days long exposure to SO₂. ⁺Measured at 273 K

Table 5: Dynamic SO₂ Capacities for select MOFs.

	ppm SO ₂	SO ₂ Capacity (mmol g ⁻¹)
MOF-5 ¹⁸⁰	pure	<0.02

IRMOF-3 ¹⁸⁰	pure	0.94
Zn-MOF-74 ¹⁸⁰	pure	3.03
MOF-177 ¹⁸⁰	pure	<0.02
MOF-199 ¹⁸⁰	pure	0.50
IRMOF-62 ¹⁸⁰	pure	<0.02
Co-MOF-74 ¹³⁹	382	0.63 (dry) 0.03 (humid)
Mg-MOF-74 ¹³⁹	382	1.60 (dry) 0.72 (humid)
Ni-MOF-74 ¹³⁹	382	0.04 (dry) 0.02 (humid)
Zn-MOF-74 ¹³⁹	382	0.26 (dry) 0.04 (humid)
[Ni₈(OH)₄(H₂O)₂(BPD_H)₆] ¹⁸⁴	25000	2.02
[Ni₈(OH)₄(H₂O)₂(BPD_OH)₆] ¹⁸⁴	25000	2.11
[Ni₈(OH)₄(H₂O)₂(BPD_NH₂)₆] ¹⁸⁴	25000	3.35
K[Ni₈(OH)₃(EtO)₃(BDP_H)_{5.5}] ¹⁸⁴	25000	3.26
K₃[Ni₈(OH)₃(EtO)(BDP_O)₅] ¹⁸⁴	25000	2.54
K[Ni₈(OH)₃(EtO)₃(BDP_NH₂)_{5.5}] ¹⁸⁴	25000	4.38
Ba_{0.5}[Ni₈(OH)₃(EtO)₃(BDP_H)_{5.5}] ¹⁸⁴	25000	4.0
Ba_{1.5}[Ni₈(OH)₃(EtO)(BDP_O)₅] ¹⁸⁴	25000	3.65
Ba_{0.5}[Ni₈(OH)₃(EtO)₃(BDP_NH₂)_{5.5}] ¹⁸⁴	25000	5.61
Ni^{II}₂{Ni^{II}₄[Cu^{II}₂-(Me₃mpba)₂]₃} ¹⁸⁹	25000	2.0
Ba^{II}₂(H₂O)₉{Ni^{II}₄[Cu^{II}₂-(Me₃mpba)₂]₃} ¹⁸⁹	25000	2.5

NO_x

Occurrence, Applications

The major components of nitrogen oxides (NO_x) are nitrogen monoxide (NO) and nitrogen dioxide (NO₂). These highly toxic species are damaging to respiratory health and contribute to environmental pollution in the troposphere (photochemical smog) and stratosphere (ozone depletion). Anthropogenic NO_x sources are approximately split between agriculture and combustion processes in power plants and automobiles.¹⁹⁰ Given their detrimental effects to health and the environment, NO_x emissions are highly regulated, and recently, more stringent regulations are further incentivizing capture or mitigation of NO_x prior to release.¹⁹¹ Current exhaust systems use catalytic converters to reduce NO_x to N₂ and H₂O, and some MOFs have been investigated for this application,^{192–195} but to achieve further reductions, for instance, during cold engine starting, the exhaust systems of combustion engines require added technologies that can adsorb NO or convert NO_x into environmentally benign species. The composition of NO_x

from an exhaust engine varies depending on the fuel source, yet the majority of NO_x is initially composed of NO.¹⁹⁶

Somewhat counterintuitively given its toxicity, NO plays a signaling role in many critical physiological processes, such as vasodilation, immune defense, and neuronal signal transduction.¹⁹⁷ The therapeutic properties of NO have motivated efforts to design materials which release NO under specific biologically-relevant conditions.^{198,199}

MOFs for NO Adsorption

Adsorption of NO predominantly occurs in MOFs exhibiting open metal sites. For instance, HKUST-1 adsorbs 9 mmol NO g⁻¹ MOF at 1 bar and 196 K.²⁰⁰ NO interacts directly with the metal, as evidenced by the ν(NO) band at 1887 cm⁻¹, comparable to IR bands of Cu²⁺-NO in molecular complexes²⁰¹ and zeolites.²⁰² Exposure of NO-loaded HKUST-1 to a flow of humid air resulted in minor release of NO (2 μmol g⁻¹), and the material lost crystallinity after NO release. The incorporation of amino-functionalized trimesic acid linkers into HKUST-1 improved the quantity of NO released, but the stability remained poor.²⁰³

Fe₃O(OH)(BDC)₃ (Fe-MIL-88) and a series of functionalized derivatives adsorb between 1 and 2.5 mmol NO g⁻¹ MOF with no loss of crystallinity.²⁰⁴ For therapeutic applications, only 5-14% of NO was released upon exposure to humid conditions, and it was noted that most of the NO was likely released prior to the measurement run, suggesting that these materials do not bind NO tightly enough to be stable for long term storage.²⁰⁴

The high density of open metal sites in the MOF-74 series make them attractive for NO sorption studies. The Co²⁺ and Ni²⁺ derivatives each adsorb ~7 mmol NO g⁻¹, and can be stored with NO bound for several months under inert conditions, making them attractive for medical therapies. Flowing humid air through the MOFs results in complete recovery of the starting material.^{205,206} The biocompatible Mg²⁺ and Zn²⁺ MOF-74 analogs have also been investigated for NO adsorption/desorption. Mg-MOF-74 binds NO too strongly and does not release NO under 11% RH conditions, whereas Zn-MOF-74 loses NO too readily under preparatory conditions. However, by doping Mg-MOF-74 with up to 40% Ni²⁺, the quantity and rate of deliverable NO can be tuned.²⁰⁷ Moving to NO-loaded Fe-MOF-74, gradual release of NO occurs under a flow of 11% RH.²⁰⁸ Additionally, the Fe material adsorbs 6.21 mmol NO g⁻¹ MOF at 7 mbar, corresponding to 95% occupation of the Fe²⁺ open metals sites by NO.²⁰⁸

MOFs for NO₂ Adsorption

There are only limited reports of NO₂ adsorption in MOFs. The Zr⁴⁺ carboxylate frameworks UiO-66 and UiO-67 capture 7.3 wt% and 7.9 wt% NO₂, respectively, under 1000 ppm dry NO₂, and the capacity of UiO-67 was further augmented to 11.8 wt% under 71% RH, presumably due to NO₂ dissolution into pore-confined water. Further, amino-functionalization of the linker of UiO-66 resulted in a nearly fivefold improvement in the static NO₂ capacity.^{209,210} However, IR and NMR spectroscopy revealed evidence of amine diazotization as well as nitrosation of the phenyl C-H bonds, revealing the complex reaction pathways possible upon NO₂ adsorption.²¹⁰ Indeed, NO₂ adsorption is not reversible in UiO-66-type frameworks, and it was proposed that NO₂ reacts at the Zr-O-Zr bridges resulting in partial framework collapse.²⁰⁹

Reversible NO₂ capture was achieved in the Al³⁺ carboxylate MOF, MFM-300, which adsorbs 14.1 mmol NO₂ g⁻¹ MOF over five cycles with no loss in capacity or crystallinity. Analysis of an NO₂ loaded sample using synchrotron powder x-ray diffraction revealed a 1D helical chain of NO₂ and N₂O₄ units within the pores. Each NO₂ forms five distinct weak

interactions with the framework, a consequence of the precisely tailored pore size providing stabilization for the helical chain. Additionally, the material exhibits preferential binding of NO₂ over CO₂ and SO₂. Notably, under wet conditions (0.5% NO₂ in N₂) the NO₂ breakthrough time decreases by ~10% compared to dry conditions, a decline postulated to result from competitive binding between H₂O and NO₂. Analysis of the material post-breakthrough experiment was not detailed.²¹¹

Leveraging the chemistries of the daughter products of NO₂ reactivity, the addition of NO₂ to a Zr⁴⁺ carboxylate MOF featuring a calixarene linker results in partial formation of N₂O₄, leading to the disproportionation products NO⁺ and NO₃⁻. The resulting NO⁺ transfers to the calixarene linker, generating a strongly adsorbed donor-acceptor complex detected using calorimetry. Interestingly, the process appears to be reversible and the material retained crystallinity after repeated NO₂ exposure.²¹²

Halogens

Occurrence, Applications

Most research on the adsorption of halogens by metal-organic frameworks has focused on I₂, which is motivated by the capture of volatile radioisotopes of I₂ from nuclear waste streams.^{213–220} Here, we focus on the more volatile lighter halogens Cl₂ and Br₂, which are much less commonly explored even though the capture and reversible storage of the highly toxic halogen elemental gases is of great interest to improve personal protective equipment, as well as to more safely handle, store, and transport X₂.

MOFs for X₂ Adsorption

Unfunctionalized carboxylate frameworks, including MOF-5, UiO-66, and Al-MIL-53, exhibit negligible Cl₂ uptake under dynamic conditions. Addition of an -NH₂ group to the terephthalate linker greatly enhances the irreversible Cl₂ uptake, to 35.5 wt% in the case of MOF-5-NH₂.¹⁸⁰ Similarly, both UiO-66-NH₂ (154 wt%) and Al-MIL-53-NH₂ (56 wt%) have orders of magnitude larger Cl₂ uptakes than their parent materials UiO-66 (3 wt%) and MIL-53 (1 wt%).²²¹ By contrast, functionalization with a hydroxy group in the case of UiO-66-OH (5 wt%), does not significantly improve chlorine uptake. Mechanistically, these enhancements are due to the amino groups, which promote electrophilic aromatic substitutions in positions ortho to themselves, resulting in a chlorinated ring and -NH₃Cl. Clearly, this is an irreversible process that cannot be utilized cyclically.

Reversible storage of the lighter halogens was demonstrated using Co₂Cl₂(BTDD).²²² The cobalt metal centers are redox-active and feature an accessible Co(II/III) redox couple suitable for reactions with Cl₂ and Br₂. Exposure of Co₂Cl₂(BTDD) to either of the two elemental halogens results in the oxidation of five-coordinate Co²⁺ to octahedral Co³⁺, forming Co₂Cl₂X₂(BTDD) (X = Cl or Br), while maintaining crystallinity and porosity (**Figure 7**). Heating the Co³⁺ material to 275 °C (X = Cl) or 195 °C (X = Br), results in the reductive release of X₂ gas, and reformation of the parent Co₂Cl₂(BTDD). The capture and release of Br₂ was repeated over three cycles with reproducible yields of 75–80% on the initial cycle and 100% yield on subsequent ones.²²² The exceptional stability of Co₂Cl₂(BTDD) towards X₂ is attributed to strong M–L bonds, open metal sites with an accessible Co(II/III) redox couple, and particularly strong aromatic C–H bonds that are not susceptible to radical X· attack. Indeed, after oxidation, the framework stability may increase due to the eight orders of magnitude slower rate of ligand exchange for Co³⁺ as compared to Co²⁺.

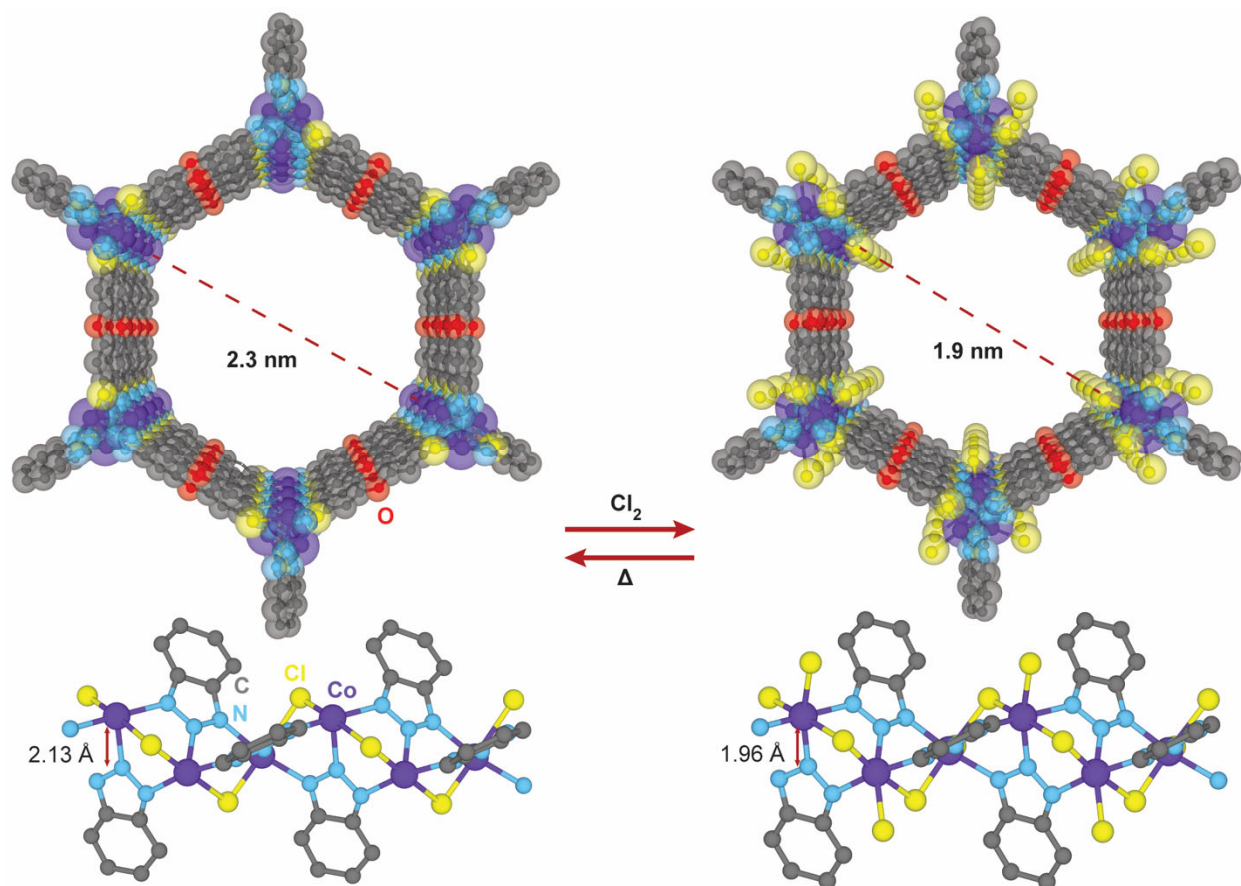


Figure 6: **Oxidative Capture of X₂**. Co₂Cl₂BTDD captures Cl₂ (or Br₂) via reversible oxidation to Co₂Cl₄BTDD (or Co₂Cl₂Br₂BTDD). H atoms omitted for clarity.

Conclusions and Outlook

It is frequently cost-prohibitive to remove all H₂O, NH₃, H₂S, or SO_x/NO_x from the atmosphere or from feed gas streams. Therefore, the use of MOFs in applications such as CO₂ removal from flue gas requires long-term stability to coordinating and corrosive species. Additionally, although we have divided this review into separate sections containing each analyte gas, these species are often present together, which may present other challenges, such as the formation of H₂SO₄ from SO_x, water, and oxygen. Multicomponent stability testing has largely been overlooked thus far, but it is vital. The design of frameworks for the capture of these challenging gases pushes the boundaries of sorbent robustness and advances our understanding of the fundamental kinetics and thermodynamics of MOF stability.

MOFs are most often synthesized from weakly donating ligands, such as carboxylates, in combination with labile metal ions such as Zn²⁺ and Cu²⁺. Together, these favor reversible ligand binding to promote ideal crystal growth. The crystallization of MOFs using inert metal ions, such as Cr³⁺, or more strongly donating ligands, such as pyrazolates, is more difficult because the reversible sampling of configurations towards the local minimum energy state is not as efficient. Therefore, harsh synthetic conditions such as high temperature, high pressure, and the use of mineralizers such as HF are often required.³⁰ Consequently, it becomes more difficult to obtain large crystals, which may complicate structure determination. Indeed, the structures in original reports of Cr-MIL-53 and Cr-MIL-101 were solved using powder refinement rather than by more

straightforward single-crystal methods which require larger crystals.^{30,31} Although the synthesis of MOFs containing inert metals, or ligands that are more strongly donating, can be challenging,^{223,224} it may lead to structures capable of withstanding demanding conditions relevant for many applications, such as gas storage and separations involving impure gas streams containing water vapor, ammonia, or acid gases. Ultimately, nothing good comes easy. By and large, MOFs that crystallize very easily and grow as large single crystals tend to be less stable to water or other corrosive and coordinating gases.

Porous materials are kinetically stable. Currently, the default vocabulary for describing the stability of MOFs is a binary scale: stable versus unstable. Moving forward, our view is that MOFs will be ranked on a continuum of kinetic stability. Quantitative benchmarking of all MOFs using a broadly applicable stability rating, such as those already employed using water vapor or steam temperature,^{50,225} could significantly advance the field. Recent research has followed two main paths to stabilize the porous phase, either by engineering heterolytically stronger metal ligand bonds, or by using more inert metals. This has led to exceptionally robust frameworks, and portends the use of MOFs for applications requiring extensive stability toward harsh gases and vapors, as well as in areas requiring long-term lower level stability. Future progress in this direction will enable MOFs to fulfill their promise as designer multifunctional materials for diverse applications.

Acknowledgements

Studies of small molecule interactions with metal nodes in MOFs are supported through a CAREER grant from the National Science Foundation to M.D. (DMR-1452612). A.J.R. is supported by the Martin Family Fellowship for Sustainability. We thank the Abdul Latif Jameel World Water and Food Security Lab for seed funding for water capture.

Competing Interests Statement

The authors declare no competing interests

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