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RECEIVED 24 May 2025

ACCEPTED 18 June 2025

PUBLISHED 08 July 2025

CITATION

Cammarere C, Cortés J, Glover TG, Snurr RQ,
Hupp JT and Liu J (2025) Water-enhanced CO₂
capture in metal–organic frameworks.
Front. Chem. 13:1634637.
doi: 10.3389/fchem.2025.1634637

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Water-enhanced CO₂ capture in metal–organic frameworks

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CO₂ capture from post-combustion flue gas originating from coal or natural gas power plants, or even from the ambient atmosphere, is a promising strategy to reduce the atmospheric CO₂ concentration and achieve global decarbonization goals. However, the co-existence of water vapor in these sources presents a significant challenge, as water often competes with CO₂ for adsorption sites, thereby diminishing the performance of adsorbent materials. Selectively capturing CO₂ in the presence of moisture is a key goal, as there is a growing demand for materials capable of selectively adsorbing CO₂ under humid conditions. Among these, metal–organic frameworks (MOFs), a class of porous, highly tunable materials, have attracted extensive interest for gas capture, storage, and separation applications. The numerous combinations of secondary building units and organic linkers offer abundant opportunities for designing systems with enhanced CO₂ selectivity. Interestingly, some recent studies have demonstrated that interactions between water and CO₂ within the confined pore space of MOFs can enhance CO₂ uptake, flipping the traditionally detrimental role of moisture into a beneficial one. These findings introduce a new paradigm: water-enhanced CO₂ capture in MOFs. In this review, we summarize these recent discoveries, highlighting examples of MOFs that exhibit enhanced CO₂ adsorption under humid conditions compared to dry conditions. We discuss the underlying mechanisms, design strategies, and structural features that enable this behavior. Finally, we offer a brief perspective on future directions for MOF development in the context of water-enhanced CO₂ capture.

KEYWORDS

CO₂ capture, metal-organic framework, nanoporous material, water, humidity

1 Introduction

The growing concentration of greenhouse gases, primarily carbon dioxide (CO₂), in the atmosphere, has led to significant global warming and climate changes. Anthropogenic CO₂ emissions are largely attributable to the increasing combustion of fossil fuels and various industrial processes designed to satisfy construction, energy, and manufacturing demands. Major contributors include coal- and gas-fired power plants, petrochemical facilities, hydrogen production via steam methane reforming followed by the water-gas shift reaction, and cement manufacturing using calcium carbonate as the primary raw material (Goel et al., 2016; Mukherjee et al., 2019; Dehimi et al., 2025; Park et al., 2021). To keep the atmospheric CO₂ concentration from rising further, two primary

strategies have been pursued. One focuses on developing alternative, clean energy sources that produce little to no CO₂ (Davis et al., 2018). The other centers on the design of energy-efficient processes for CO₂ capture, followed by either chemical conversion (Mukherjee et al., 2019; Wang et al., 2017; Sumida et al., 2012; Ran et al., 2018) or geological sequestration (Lin et al., 2024; Massarweh and Abushaikh, 2024; Spurin et al., 2025).

A variety of solid materials have been developed to achieve high CO₂ uptake and high selectivity for CO₂ over N₂, including activated carbons (Jedli et al., 2024), zeolites (Mukherjee et al., 2019; Kumar et al., 2020), metal–organic frameworks (MOFs) (Ghanbari et al., 2020; Schoedel et al., 2016; Lin et al., 2021), polymers (Song et al., 2022), and metal oxides (Yong et al., 2002). Among these, MOFs stand out due to their diverse topologies, large pore volumes, and broadly tunable pore sizes, which can be adjusted by modifying metal nodes and/or organic linkers (Zhou et al., 2012; Horike et al., 2009; Alezi et al., 2016; Wang et al., 2016). Owing to their high surface area, large pore volume and particularly the presence of a high density of open metal sites (Britt et al., 2009), certain MOFs have demonstrated excellent CO₂ uptake at room temperature. However, high CO₂ capacity and selectivity in the presence of N₂ are not enough, as CO₂ typically coexists with other components, water vapor being one of the most challenging (Siegelman et al., 2019). Water and CO₂ often target the same adsorption sites, with water typically binding more strongly, thus outcompeting CO₂ and reducing uptake capacity. This competition becomes critical in applied CO₂ capture scenarios. For instance, flue gas from natural gas combined cycle (NGCC) power plants contains approximately 75% N₂, 4% CO₂, 12% O₂, and 9% H₂O by volume (Siegelman et al., 2019; Zhang et al., 2020). At this concentration, water vapor can significantly impair CO₂ capture by blocking adsorption sites, and must, therefore, be carefully considered in material design and application.

The earliest systems developed for selective CO₂ capture in the presence of water were aqueous amine solutions, which rely on acid–base reactions to form carbamates (Li and Keeners, 2016). However, these liquid-phase systems suffer from several limitations, including low working capacities, high regeneration energies, and thermal instability (Zhao et al., 2012). To address these issues, researchers developed molecularly porous solid systems incorporating amine functionalities to enhance the selective adsorption of CO₂ in the presence of water. These approaches include grafting amine groups onto porous materials, such as porous polymers, silica, alumina, and carbon (Filburn et al., 2005; Wurzbacher et al., 2011; Kuwahara et al., 2012; Chai et al., 2016; Li, et al., 2010), as well as functionalizing MOFs with diamine-containing molecules (Choe et al., 2019; Li et al., 2015; Kang et al., 2019; Choi et al., 2012; Demessence et al., 2009; McDonald et al., 2011; Liao et al., 2016; McDonald et al., 2012; Planas et al., 2013; McDonald et al., 2015; Siegelman et al., 2017; Milner et al., 2018; 2017). In diamine-appended MOFs, one end of the diamine molecule binds to an open metal site in the MOF, while the other end remains available for CO₂ chemisorption. These diamine-functionalized MOFs introduce chemisorption sites, enhancing selectivity for CO₂ over H₂O. However, their overall CO₂ uptake capacity and uptake kinetics may be affected, as the diamine molecules partially occupy the available pore volume.

Several studies have now demonstrated that interactions between water and CO₂ within confined pore spaces can, in fact, enhance CO₂ capture. These findings represent a new paradigm, revealing that certain MOFs can convert the traditionally negative impact of moisture into a beneficial factor for improving CO₂ adsorption performance. This review highlights these key discoveries and examines the unique mechanisms underlying enhanced CO₂ adsorption under humid conditions. We conclude with a brief perspective on future directions for MOF design and research in the field of water-enhanced CO₂ capture.

2 Water-enhanced CO₂ capture

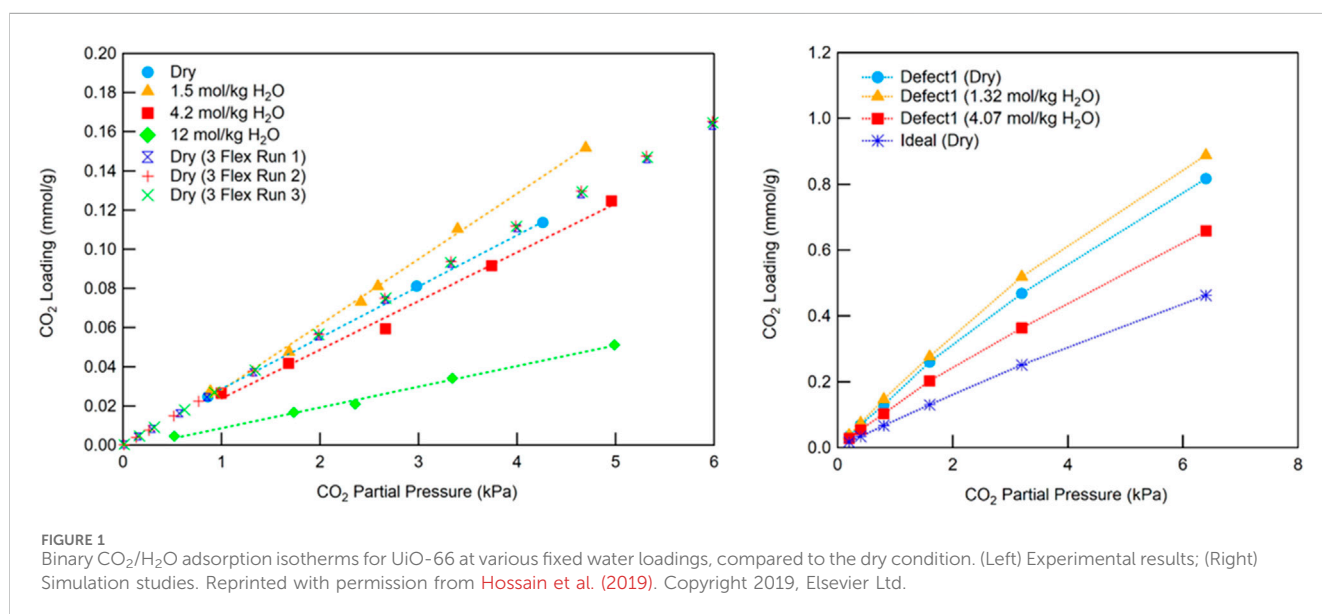
2.1 Dipole–quadrupole interaction

In a high-throughput screening study (Chanut et al., 2017), Chanut et al. investigated the effect of pre-equilibrated water on CO₂ uptake in 45 MOFs using thermogravimetric analysis. The MOFs were grouped into various categories based on the extent to which pre-adsorbed H₂O influenced CO₂ uptake. One category, which included MIL-110(Al), MIL-163(Zr), Cu-HKUST-1 and UiO-66(Zr) (Table 1), exhibited a slight increase in CO₂ uptake with a certain amount of pre-adsorbed water. For example, Cu-HKUST-1 showed an approximately 5 wt% increase in CO₂ uptake in the presence of 2–4% relative humidity (RH). This observation is consistent with Yazaydin's report that CO₂ uptake and its selectivity over N₂ increased in 4 wt% hydrated Cu-HKUST-1 due to the presence of water molecules coordinated to the framework open-metal sites (Yazaydin et al., 2009). This enhancement was initially predicted through molecular simulations and later validated by experiments. Detailed examination of interaction energies using grand canonical Monte Carlo simulations suggested that Coulombic interactions are responsible for the increased CO₂ adsorption—specifically interactions between the quadrupole moment of CO₂ and the electric field generated by water molecules bound to open metal sites. The LeVan group reported similar findings for Cu-HKUST-1 through volumetric measurements (Liu et al., 2010). Collectively, these results suggest an unexpected approach for enhancing CO₂ capture in the presence of water. However, at high humidity levels, Cu-HKUST-1 undergoes structural degradation, which likely explains why enhanced CO₂ uptake was not observed under conditions of high RH. Yu et al. (2016) investigated the effect of water on CO₂ capture in an isostructural series of M-HKUST-1 frameworks (M = Zn, Co, Ni, and Mg) through simulation studies evaluating water coordination within the MOFs. Water-coordination enhanced CO₂ uptake, similar to that observed in Cu-HKUST-1, was found for the Zn-, Co-, and Ni-based analogues. However, for Mg-HKUST-1, water coordination reduced CO₂ adsorption at higher pressures.

Another water-stable MOF, UiO-66, was reported by Hossain et al. to show a similar result, exhibiting a slight enhancement in CO₂ adsorption at low water loading (1.5 mol/kg) under low CO₂ partial pressure (below 5 kPa) at 25°C. This observation was based on experimental binary adsorption isotherms measured volumetrically using a mass balance approach (Hossain et al., 2019). However, increasing the co-adsorbed water loadings to 4.2 and 12 mol/kg led

TABLE 1 MOFkey and MOFid codes for some MOFs mentioned in this paper (Bucior et al., 2019).

MOF Name	MOFkey	MOFid
Cu-HKUST-1	Cu.QMKYBPDZANOJGF.MOFkey-v1.tbo	[Cu][Cu].[O-]C(=O)c1cc(cc(c1)C(=O)[O-])C(=O)[O-] MOFid-v1.tbo.cat0
UiO-66	Zr.KKEYFWRCBNTPAC.MOFkey-v1.fcu	[O-]C(=O)c1ccc(cc1)C(=O)[O-].[O]12[Zr]34[OH]5[Zr]62[OH]2[Zr]71[OH]4[Zr]14[O]3[Zr]35[O]6[Zr]2([O]71)[OH]43 MOFid-v1.fcu.cat0
MIL-100	Cr.QMKYBPDZANOJGF.MOFkey-v1.moo	F[Cr][O]([Cr])[Cr].F[Cr][O]([Cr]F)[Cr].[Cr][O]([Cr])[Cr].[O-]C(=O)c1cc(cc(c1)C(=O)[O-])C(=O)[O-] MOFid-v1.moo.cat0
Mg-MOF-74	Mg.YXUXCIBWQAOXRL.MOFkey-v1.UNKNOWN	[Mg].[O-]C(=O)c1cc([O])c(cc1[O])C(=O)[O-] MOFid-v1.UNKNOWN.cat0
MOF-808	Zr.QMKYBPDZANOJGF.MOFkey-v1.spn	O[Zr]123([OH2])[OH]4[Zr]56([O]3[Zr]37([OH]2[Zr]28([O]1[Zr]14([O]6[Zr]([OH]53)([OH]21)([O]78)([OH2])O)([OH2])(O)O)[OH2])([OH2])(O)O)[OH2].[O-]C(O)c1cc(cc(c1)C(O)[O-])C(O)[O-] MOFid-v1.spn.cat0
NOTT-400	Sc.QURGMSIQFRADOZ.MOFkey-v1.UNKNOWN	[O-]C(=O)c1cc(cc(c1)C(=O)[O-])c1cc(cc(c1)C(=O)[O-])C(=O)[O-].[OH].[Sc] MOFid-v1.UNKNOWN.cat0
Mg-CUK-1	Mg.WAYLQVWVRREMCZ.MOFkey-v1.UNKNOWN	[Mg].[O-]C(=O)c1ccc(cc1)c1ccn(c1)C(=O)[O-].[OH] MOFid-v1.UNKNOWN.cat0



to reduced CO₂ uptake (Figure 1 Left). Molecular simulations supported these findings and further revealed that the effect depends on the type of defect sites within the MOF: missing linker defects promoted the enhancement (Figure 1 Right), whereas missing cluster defects didn't show this behavior. Expanding on this work, Hernandez et al. conducted computational studies on three amine-linker UiO-66 materials and found that water molecules bridge between metal-oxide clusters by occupying missing linker positions (Hernandez et al., 2021). These water bridges reduce the pore size in defect-laden MOFs and enhance CO₂ adsorption in the presence of co-adsorbed water. Experimental binary isotherm data were consistent with these predictions. These studies underscore the importance of considering defect sites when evaluating CO₂ capture performance in humid conditions.

2.2 H₂O dissociation leading to new adsorption sites

MIL-100(Fe) was evaluated by Soubeyrand-Lenoir et al., who reported a five-fold increase in CO₂ uptake (105 mg/g) at low pressure (200 mbar) under moderate humidity (40% RH) (Soubeyrand-Lenoir et al., 2012). They hypothesized that water molecules coordinate to the Lewis-acidic metal sites, forming water channels, while CO₂ adsorption occurs in the center of these channels without carbonate formation. In addition to the water stability of the materials, its mesoporosity was highlighted as a key factor contributing to the observed enhancement, as it allows for the formation of microporous water pockets that can subsequently be filled with CO₂ (see Figure 2).

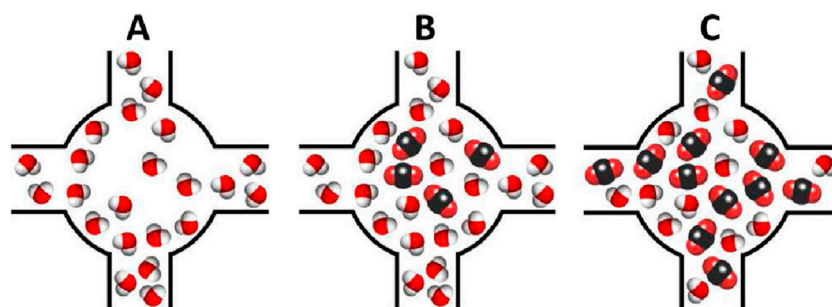


FIGURE 2

Schematic representation of the water channel formed in MIL-100(Fe) to enhance the CO₂ adsorption (A) Adsorbed water molecules create pockets that can (B) adsorb CO₂ molecules, which can in turn (C) displace some of the water molecules. Reprinted with permission from Soubeyrand-Lenoir et al. (2012). Copyright 2012, American chemical society.

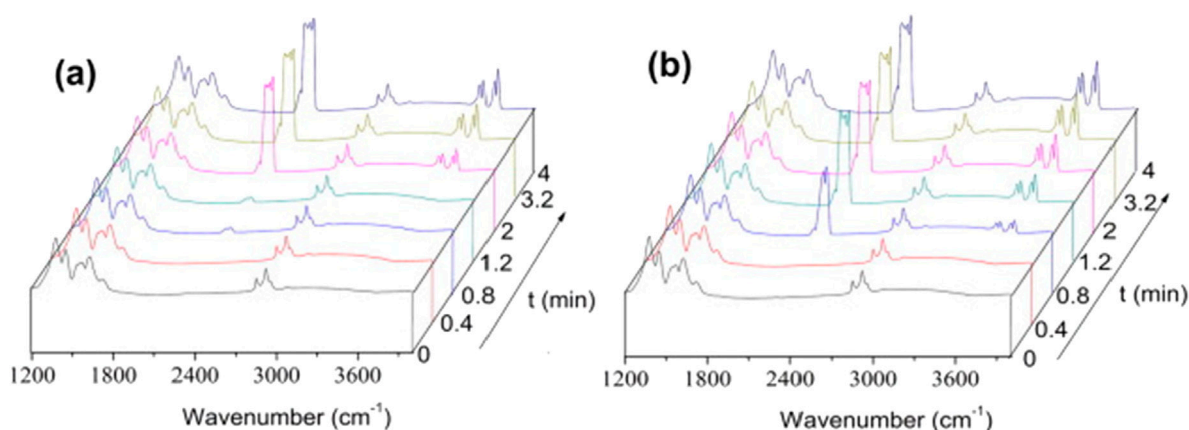


FIGURE 3

In situ IR spectra of MIL-100(Fe) loaded with CO₂ in the spectral region between 1,200 and 4,000 cm⁻¹. (a) CO₂ gas flow rate 40 mL/min, 298 K in dry condition. (b) CO₂/H₂O gas flow rate 40 mL/min, 298 K, 50% RH. Reprinted with permission from Xian et al. (2015). Copyright 2015, Elsevier Ltd.

Xian et al. further investigated this idea in MIL-100(Fe) using CO₂ temperature programmed desorption (TPD) and *in situ* Fourier transform infrared spectroscopy (FTIR) (Xian et al., 2015). TPD measurements revealed two CO₂ desorption peaks in the hydrated sample (50% RH), compared to only one in the dehydrated sample, indicating the creation of an additional adsorption site in the presence of water. The authors proposed that water molecules dissociate to form node hydroxyl groups, which serve as extra adsorption sites for CO₂, thereby leading to an additional adsorption site to enhance the material's uptake capacity. *In situ* FTIR results supported this conclusion by revealing faster CO₂ adsorption under humid conditions, as evidenced by the more rapid appearance of CO₂ stretching mode peaks (see peaks at 2,350, 3,600, and 3,700 cm⁻¹ in Figure 3). The water dissociation hypothesis is worthy of further investigation.

2.3 Water nanopocket confinement effects

For MOFs containing bridging hydroxo ligands as components of nodes, computational studies have predicted that at low water

loadings, H₂O molecules can be efficiently packed through strong hydrogen bonding to the -OH groups (Liu et al., 2023; He et al., 2023). These well-ordered water molecules can, in turn, improve CO₂ adsorption by forming favorable hydrogen bonds with CO₂ within the microchannels. In other words, the hydroxo ligands act as directing agents for efficient water arrangement, and the pre-adsorbed water molecules introduce confinement effects that further promote CO₂ uptake.

Building on this principle, the Ibarra group investigated a series of MOFs containing μ_2/μ_3 -OH ligands, including NOTT-400 (Gonzalez et al., 2015), NOTT-401 (Lara-García et al., 2015; Sánchez-González et al., 2016), InOF-1 (Peralta et al., 2015), and Mg-CUK-1 (Sagastuy-Breña et al., 2018), and demonstrated that their CO₂ capture capacities were enhanced to varying degrees under moderate humidity (RH < 40%) at 30°C. In a combined experimental and computational study, Breña et al. further reported humidity-enhanced CO₂ adsorption in Mg-CUK-1, a framework featuring one-dimensional microporous channels (Sagastuy-Breña et al., 2018). Using static CO₂ adsorption isotherms and thermogravimetric analysis under a constant CO₂ flow (60 mL/min), they observed a maximum CO₂ uptake

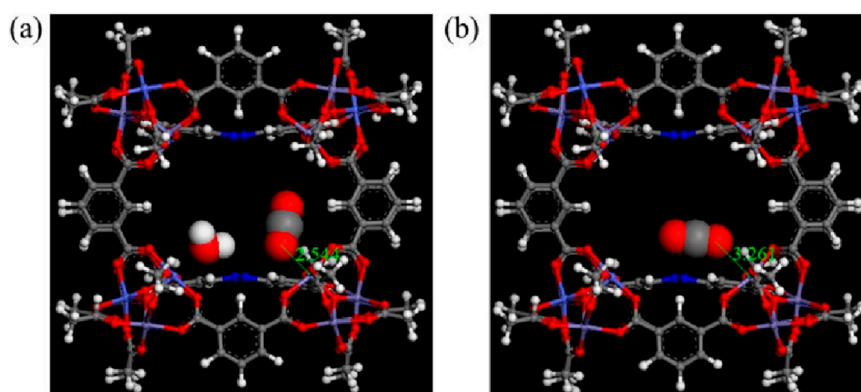


FIGURE 4
Binding sites of CO₂ in PCN-250(Fe₂Co) structure (a) with and (b) without H₂O. Reprinted with permission from [Chen et al. \(2018\)](#). Copyright 2018, American chemical society.

of 8.5 wt% at 18% RH, compared to 4.6 wt% under dry conditions. However, beyond 20% RH, a rapid decline in CO₂ adsorption was observed, with almost negligible CO₂ uptake at 25% RH.

[Chen et al. \(2018\)](#) reported unusual moisture-enhanced CO₂ adsorption in PCN-250(Fe₃) and PCN-250(Fe₂Co). These compounds are constructed from trimetallic-oxo clusters, i.e., Fe₃(μ₃-O)(CH₃COO)₆ or Fe₂Co(μ₃-O)(CH₃COO)₆, as nodes, and ABTC⁴⁻ units as linkers (H₄ABTC = 3,3',5,5'-azobenzene-tetracarboxylic acid). For PCN-250(Fe₃), the uptake of CO₂ increases by 54% under 50% RH, compared to dry conditions (from 1.18 to 1.82 mmol/g). PCN-250(Fe₂Co) exhibited a 69% increase in CO₂ uptake under the same conditions (from 1.32 to 2.23 mmol/g). Even at 90% RH, significant increases in CO₂ adsorption were observed (44% for PCN-250(Fe₃) and 70% for PCN-250(Fe₂Co)) compared to their respective uptakes under dry conditions. Molecular simulations revealed that node-based, bridging oxo ions (μ₃-O) act as directing agents for H₂O adsorption. These water molecules, in turn, help position CO₂ molecules closer to metal centers on the opposite side of the pore, enhancing CO₂ adsorption via confinement effects. The CO₂/MOF interaction is further strengthened by what the authors term a “plier effect”, where coordinated water molecules appear to “clamp” CO₂ molecules onto open metal sites (see [Figure 4](#)), increasing the efficiency of adsorption under unsaturated conditions by maximizing the use of available adsorption sites. The plier effect, involving CO₂, H₂O, and the MOFs, enables effectively use of more of the candidate adsorption sites by CO₂; in turn, the amount of CO₂ adsorbed increases. The mechanism behind the enhanced CO₂ uptake at 90% RH is less clear, as such high humidity would presumably saturate the pores with water, leaving little space for CO₂.

[Shi et al. \(2020\)](#) reported a series of metal-triazolate MOFs, constructed from ZnF rods and 1,2,4 triazolate linkers functionalized with various groups (e.g., -NH₂ and -CH₃), among which the MOF featuring a 3,5-diamino-1,2,4-triazolate linker (ZnF(daTZ)) exhibited a CO₂/N₂ thermodynamic adsorption selectivity of 120 at 298K and 0–101 kPa, and a CO₂/H₂O kinetic adsorption selectivity of 70 at 298K and 33% RH. DFT calculations revealed a 25%–30% increment in the heat of CO₂ adsorption in the presence of co-adsorbed water, indicating stronger CO₂ binding under

humid conditions (see [Figure 5](#)). This enhancement was attributed to the preferential localization of water and CO₂ molecules within the MOF framework, i.e., water molecules tended to occupy the corner sites, while CO₂ molecules were primarily located at the center of the channels. However, this study does not fully elaborate on how this spatial distribution contributes to the enhanced CO₂ adsorption under humid conditions. A similar spatial preference was reported in amine-functionalized UiO-66, where H₂O and CO₂ adsorbed at different sites ([Hernandez et al., 2021](#)). The authors proposed that water molecules formed hydrogen-bonded bridges between metal nodes by occupying missing linker positions, effectively reducing the pore size and enhancing CO₂ adsorption.

2.4 Ammonium carbamate, carbamic acid and bicarbonate formation

Functionalizing MOFs with diamines allows one amine group to coordinate to an open metal site, while the other points into the pore to interact with CO₂ molecules. For instance, diamine-modified MOF-74 materials have displayed selective CO₂ adsorption over water due to the formation of carbamate species, particularly at low CO₂ concentrations ([Milner et al., 2018](#)). However, carbamate formation typically requires two amine groups to react with one single CO₂ molecule, which limits the overall CO₂ uptake capacity.

The impact of RH on the performance of amine-appended MOFs remains relatively underexplored, with few studies reporting CO₂ uptake across a broad range humidity levels. [Holmes et al. \(2023\)](#) investigated this effect on (2-ampd)₂Mg₂(dobpdc) MOF (2-ampd is 2-(aminomethyl)piperidine) using both gravimetric and breakthrough adsorption techniques. Their findings identified three distinct RH regions based on the influence of water on CO₂ uptake: competitive adsorption from 0%–20% RH, enhanced adsorption between 20%–40% RH, and hindered adsorption due to pore saturation at RH levels above 40%, see [Figure 6](#). A significant enhancement in CO₂ uptake at 1 bar and 40°C was observed at 30% RH (5.7 ± 0.2 mmol/g), compared to 3.35 mmol/g under dry conditions, see [Figure 6](#). This increase was attributed to a mixed adsorption mechanism, wherein CO₂ binds to both primary and secondary amines in 2-ampd, forming ammonium

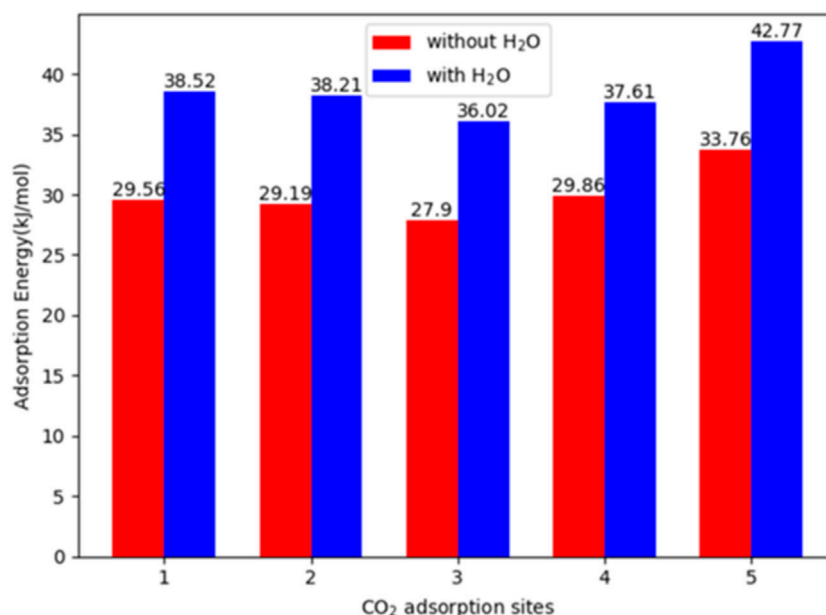


FIGURE 5

Comparison between CO₂ adsorption energies without H₂O and with H₂O for five distinct CO₂ adsorption sites in ZnF(daTZ). Reprinted with permission from Shi et al. (2020). Copyright 2020, American chemical society.

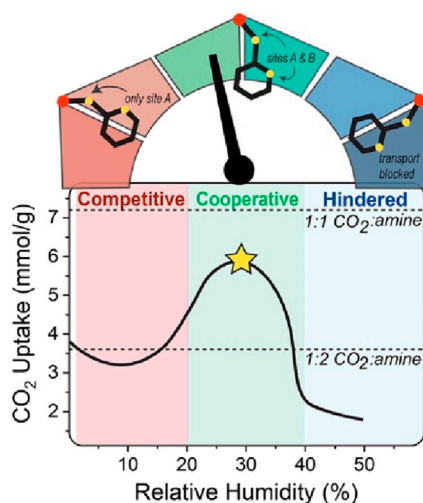


FIGURE 6

Three distinct RH regions for CO₂ uptake by (2-ampd)₂Mg₂(dobpdc): competitive adsorption from 0%–20% RH, enhanced adsorption between 20%–40% RH, and hindered adsorption at RH levels above 40% at 1 bar and 40°C. Reprinted with permission from Holmes et al. (2023). Copyright 2023, Elsevier Ltd.

carbamate and carbamic acid, respectively. This mechanism was supported by TPD data showing co-desorption of water and CO₂, as well as DRIFTS measurements revealing the loss of N-H stretching from secondary amines and the emergence of O-H stretching in humid samples.

Didas et al. (2014) reported that co-adsorption of CO₂ and water on mesoporous silica with low amine surface coverage leads to

bicarbonate formation. Recently, Lyu et al. (2022) and Chen et al. (2024) both demonstrated that bicarbonate formation within MOFs can enhance CO₂ uptake. In their studies, they developed amine-functionalized MOF-808 materials: one featuring amino acids coordinated to Zr ions (MOF-808-AAs), first reported by Lyu et al. (2022), and the other incorporating polyamines covalently attached to a chloro-functionalized framework (MOF-808-PAs), reported by Chen et al. (2024), see Figure 7 (top). Both series exhibited improved CO₂ capture performance under humid conditions for direct air capture of CO₂, where the CO₂ concentration is approximately 420 ppm in the atmosphere. At 50% RH, the l-lysine- and tris(3-aminopropyl)amine-functionalized variants exhibited remarkable uptakes of 1.205 and 0.872 mmol/g at 400 ppm CO₂ and 25°C corresponding to 97% and 75% increases compared to the dry uptakes, respectively. The detailed sorption study using solid-state NMR revealed that for the wet conditions, MOF-808-Lys exhibited a single signal at 167 ppm under 50% RH attributed to ammonium bicarbonate formation. The presence of water enhanced the amine utilization efficiency by forming bicarbonate species (see Figure 7 (bottom)), resulting in increased CO₂ uptake compared to the dry conditions.

3 Conclusion

The presence of water vapor, long considered a challenge in CO₂ capture, is now recognized as a potential partner in enhancing CO₂ adsorption performance in certain MOFs. A growing body of experimental and computational studies has revealed several mechanisms through which water can improve CO₂ uptake, including dipole–quadrupole interactions, water-assisted formation of new adsorption sites, confinement effects via water

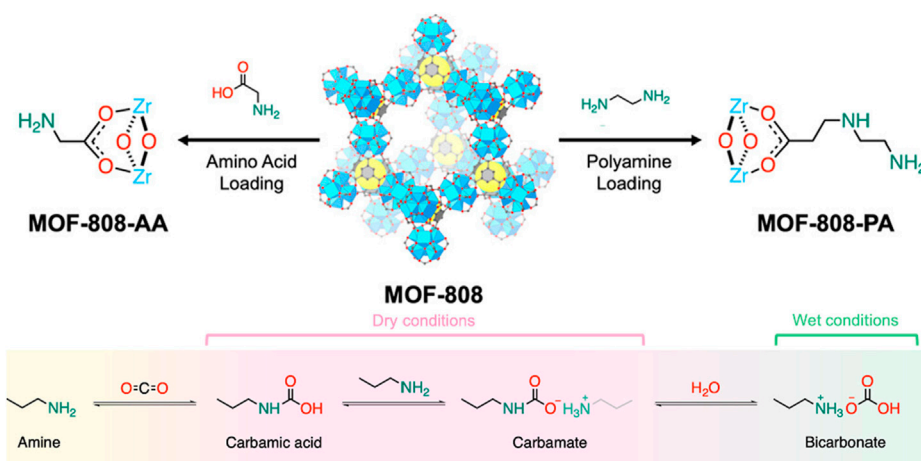


FIGURE 7
(Top) Two series of amine-functionalized MOF-808: MOF-808-AAs and MOF-808-PAs. (Bottom) Proposed chemisorption mechanism of amines with CO₂ under dry and wet conditions. Reprinted with permission from [Chen et al. \(2024\)](#). Copyright 2024, American chemical society.

nanopockets, and ammonium carbamate, carbamic acid and bicarbonate formation at reactive amine sites. These mechanisms, observed in a diverse range of MOFs, such as HKUST-1, MIL-100(Fe), PCN-250, and MOF-808, demonstrate that well-designed frameworks can convert water from a disruptive presence into a cooperative one. While many of these enhancements occur under low or moderate humidity, challenges remain in boosting performance under high relative humidity, where water saturation can reduce pore accessibility. Continued exploration of MOF structures, functional groups, and water-CO₂ interactions will be key to designing next-generation materials for practical CO₂ capture, especially in humid environments such as flue gas streams and ambient air. The development of MOFs exhibiting high CO₂ selectivity, capacity, and stability under humid conditions represents a promising path forward in advancing scalable carbon capture technologies.

4 Perspectives

The emerging understanding of water-enhanced CO₂ capture in MOFs presents an exciting opportunity to rethink the role of moisture in gas capture. While water vapor has traditionally been viewed as a challenge, competing with CO₂ for adsorption sites and destabilizing frameworks, recent findings demonstrate that, under specific structural and chemical conditions, water can become a cooperative agent that enhances CO₂ uptake. Mechanisms such as dipole-quadrupole interactions, molecular confinement, water-induced site activation, and bicarbonate formation at amine-functionalized sites have all been shown to improve performance in humid environments. The simple dipole-quadrupole interaction model between water and CO₂ molecules suggests that positively charged adsorption sites formed via water coordination can promote CO₂ uptake. If a framework offers an environment that facilitates the creation of such sites, enhanced CO₂ adsorption can be achieved. Rational incorporation of hydrophilic functional groups, such as μ_2/μ_3 -OH bridges and open metal sites, can facilitate structured water

adsorption, promoting CO₂ capture. Additionally, frameworks with hierarchical pore structures may provide the spatial freedom to accommodate water and CO₂ without compromising access to active sites. The “plier effect” and the formation of new reactive sites from water dissociation further suggest that cooperative interactions can be engineered to improve performance under humid conditions.

Despite these advances, significant knowledge gaps remain. For instance, systematic studies of water-enhanced CO₂ capture across a range of relative humidities are lacking. Likewise, the effect of varying CO₂ concentrations, such as those relevant to direct air capture, has not been thoroughly explored in humid conditions. Advanced *in situ* techniques, such as solid-state NMR, IR spectroscopy, and X-ray scattering, coupled with multiscale computational modeling, will be vital for unraveling these complex interactions at the molecular level. Furthermore, future research should include a focus on bridging the gap between fundamental discovery and practical deployment. This focus would include improving the stability and regenerability of MOFs under cyclic operation, scaling up synthesis methods, and integrating these materials into realistic gas separation processes, such as post-combustion carbon capture and direct air capture.

Author contributions

CC: Writing – original draft. JC: Writing – original draft. TG: Writing – review and editing. RS: Writing – review and editing. JH: Writing – review and editing. JL: Funding acquisition, Writing – review and editing.

Funding

The author(s) declare that financial support was received for the research and/or publication of this article. RS and JH gratefully acknowledge research support from the National Science

Foundation under grant no. 2119433. TG gratefully acknowledges research support from the National Science Foundation under grant no. 2119033. JL gratefully acknowledges a startup research grant from the College of Science, Rochester Institute of Technology.

Conflict of interest

RS and JH have a financial interest in Numat, a company that is commercializing MOFs. TG has a financial interest in Atoco Inc., which is seeking to commercialize related technologies.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

- Alezi, D., Spanopoulos, I., Tsangarakis, C., Shkurenko, A., Adil, K., Belmabkhout, Y., et al. (2016). Reticular chemistry at its best: directed assembly of hexagonal building units into the awaited metal-organic framework with the intricate polybenzene topology, pbz-MOF. *J. Am. Chem. Soc.* 138, 12767–12770. doi:10.1021/jacs.6b08176
- Britt, D., Furukawa, H., Wang, B., Glover, T. G., and Yaghi, O. M. (2009). Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites. *Proc. Natl. Acad. Sci.* 106, 20637–20640. doi:10.1073/pnas.0909718106
- Bucior, B. J., Rosen, A. S., Haranczyk, M., Yao, Z., Ziebel, M. E., Farha, O. K., et al. (2019). Identification schemes for metal-organic frameworks to enable rapid search and cheminformatics analysis. *Cryst. Growth Des.* 19, 6682–6697. doi:10.1021/acs.cgd.9b01050
- Chai, S.-H., Liu, Z.-M., Huang, K., Tan, S., and Dai, S. (2016). Amine functionalization of micro-sized and nano-sized mesoporous carbons for carbon dioxide capture. *Ind. Eng. Chem. Res.* 55, 7355–7361. doi:10.1021/acs.iecr.6b00823
- Chanut, N., Bourrelly, S., Kuchta, B., Serre, C., Chang, J.-S., Wright, P. A., et al. (2017). Screening the effect of water vapour on gas adsorption performance: application to CO₂ capture from flue gas in metal-organic frameworks. *ChemSusChem* 10, 1543–1553. doi:10.1002/cssc.201601816
- Chen, O.I.-F., Liu, C.-H., Wang, K., Borrego-Marín, E., Li, H., Alawadhi, A. H., et al. (2024). Water-enhanced direct air capture of carbon dioxide in metal-organic frameworks. *J. Am. Chem. Soc.* 146, 2835–2844. doi:10.1021/jacs.3c14125
- Chen, Y., Qiao, Z., Huang, J., Wu, H., Xiao, J., Xia, Q., et al. (2018). Unusual moisture-enhanced CO₂ capture within microporous PCN-250 frameworks. *ACS Appl. Mater. Interfaces* 10, 38638–38647. doi:10.1021/acsami.8b14400
- Choe, J. H., Kang, D. W., Kang, M., Kim, H., Park, J. R., Kim, D. W., et al. (2019). Revealing an unusual temperature-dependent CO₂ adsorption trend and selective CO₂ uptake over water vapors in a polyamine-appended metal-organic framework. *Mater. Chem. Front.* 3, 2759–2767. doi:10.1039/c9qm00581a
- Choi, S., Watanabe, T., Bae, T.-H., Sholl, D. S., and Jones, C. W. (2012). Modification of the Mg/DOBDC MOF with amines to enhance CO₂ adsorption from ultradilute gases. *J. Phys. Chem. Lett.* 3, 1136–1141. doi:10.1021/jz300328j
- Davis, S. J., Lewis, N. S., Shaner, M., Aggarwal, S., Arent, D., Azevedo, I., et al. (2018). Net-zero emissions energy systems. *Science* 360, eaas9793. doi:10.1126/science.aas9793
- Dehimi, L., Alioui, O., Benguerba, Y., Yadav, K. K., Bhutto, J. K., Fallatah, A. M., et al. (2025). Hydrogen production by the water gas shift reaction: a comprehensive review on catalysts, kinetics, and reaction mechanism. *Fuel Process. Technol.* 267, 108163. doi:10.1016/j.fuproc.2024.108163
- Demessence, A., D'Alessandro, D. M., Foo, M. L., and Long, J. R. (2009). Strong CO₂ binding in a water-stable, triazolate-bridged metal-organic framework functionalized with ethylenediamine. *J. Am. Chem. Soc.* 131, 8784–8786. doi:10.1021/ja903411w
- Didas, S. A., Sakwa-Novak, M. A., Foo, G. S., Sievers, C., and Jones, C. W. (2014). Effect of amine surface coverage on the co-adsorption of CO₂ and water: spectral deconvolution of adsorbed species. *J. Phys. Chem. Lett.* 5, 4194–4200. doi:10.1021/jz502032c
- Filburn, T., Helble, J. J., and Weiss, R. A. (2005). Development of supported ethanolamines and modified ethanolamines for CO₂ capture. *Ind. Eng. Chem. Res.* 44, 1542–1546. doi:10.1021/ie0495527
- Ghanbari, T., Abnisa, F., and Daud, W. M. A. W. (2020). A review on production of metal organic frameworks (MOF) for CO₂ adsorption. *Sci. Total Environ.* 707, 135090. doi:10.1016/j.scitotenv.2019.135090
- Goel, C., Bhunia, H., and Pramod, B. K. (2016). Novel nitrogen enriched porous carbon adsorbents for CO₂ capture: breakthrough adsorption study. *J. Environ. Chem. Eng.* 4, 346–356. doi:10.1016/j.jece.2015.11.017
- Gonzalez, M. R., González-Estefan, J. H., Lara-García, H. A., Sánchez-Camacho, P., Basaldella, E. I., Pfeiffer, H., et al. (2015). Separation of CO₂ from CH₄ and CO₂ capture in the presence of water vapour in NOTT-400. *New J. Chem.* 39, 2400–2403. doi:10.1039/C4NJ01933D
- He, M., Zhao, H., Yang, X., Jia, J., Liu, X., Qu, Z., et al. (2023). Reconsideration about the competitive adsorption of H₂O and CO₂ on carbon surfaces: the influence of oxygen functional groups. *J. Environ. Chem. Eng.* 11, 111288. doi:10.1016/j.jece.2023.111288
- Hernandez, A. F., Impastato, R. K., Hossain, M. I., Rabideau, B. D., and Glover, T. G. (2021). Water bridges substitute for defects in amine-functionalized UiO-66, boosting CO₂ adsorption. *Langmuir* 37, 10439–10449. doi:10.1021/acs.langmuir.1c01149
- Holmes, H. E., Ghosh, S., Li, C., Kalyanaraman, J., Realff, M. J., Weston, S. C., et al. (2023). Optimum relative humidity enhances CO₂ uptake in diamine-appended M₂ (dobpdc). *Chem. Eng. J.* 477, 147119. doi:10.1016/j.ccej.2023.147119
- Horike, S., Shimomura, S., and Kitagawa, S. (2009). Soft porous crystals. *Nat. Chem.* 1, 695–704. doi:10.1038/nchem.444
- Hossain, M. I., Cunningham, J. D., Becker, T. M., Grabicka, B. E., Walton, K. S., Rabideau, B. D., et al. (2019). Impact of MOF defects on the binary adsorption of CO₂ and water in UiO-66. *Chem. Eng. Sci.* 203, 346–357. doi:10.1016/j.ces.2019.03.053
- Jedli, H., Almonnef, M., Rabhi, R., Mbarek, M., Abdesslem, J., and Slimi, K. (2024). Activated carbon as an adsorbent for CO₂ capture: adsorption, kinetics, and RSM modeling. *ACS Omega* 9, 2080–2087. doi:10.1021/acsomega.3c02476
- Kang, M., Kim, J. E., Kang, D. W., Lee, H. Y., Moon, D., and Hong, C. S. (2019). A diamine-grafted metal-organic framework with outstanding CO₂ capture properties and a facile coating approach for imparting exceptional moisture stability. *J. Mater. Chem. A* 7, 8177–8183. doi:10.1039/C8TA07965J
- Kumar, S., Srivastava, R., and Koh, J. (2020). Utilization of zeolites as CO₂ capturing agents: advances and future perspectives. *J. CO₂ Util.* 41, 101251. doi:10.1016/j.jcou.2020.101251
- Kuwahara, Y., Kang, D.-Y., Copeland, J. R., Brunelli, N. A., Didas, S. A., Bollini, P., et al. (2012). Dramatic enhancement of CO₂ uptake by poly(ethyleneimine) using zirconosilicate supports. *J. Am. Chem. Soc.* 134, 10757–10760. doi:10.1021/ja303136e
- Lara-García, H. A., Gonzalez, M. R., González-Estefan, J. H., Sánchez-Camacho, P., Lima, E., and Ibarra, I. A. (2015). Removal of CO₂ from CH₄ and CO₂ capture in the presence of H₂O vapour in NOTT-401. *Inorg. Chem. Front.* 2, 442–447. doi:10.1039/C5QI00049A
- Li, L.-J., Liao, P.-Q., He, C.-T., Wei, Y.-S., Zhou, H.-L., Lin, J.-M., et al. (2015). Grafting alkylamine in UiO-66 by charge-assisted coordination bonds for carbon dioxide capture from high-humidity flue gas. *J. Mater. Chem. A* 3, 21849–21855. doi:10.1039/C5TA05997F
- Li, T., and Keeners, T. C. (2016). A review: desorption of CO₂ from rich solutions in chemical absorption processes. *Int. J. Greenh. Gas. Control* 51, 290–304. doi:10.1016/j.jggc.2016.05.030
- Li, W., Choi, S., Drese, J. H., Hornbostel, M., Krishnan, G., Eisenberger, P. M., et al. (2010). Steam-stripping for regeneration of supported amine-based CO₂ adsorbents. *ChemSusChem* 3, 899–903. doi:10.1002/cssc.201000131
- Liao, P.-Q., Chen, X.-W., Liu, S.-Y., Li, X.-Y., Xu, Y.-T., Tang, M., et al. (2016). Putting an ultrahigh concentration of amine groups into a metal-organic framework for CO₂ capture at low pressures. *Chem. Sci.* 7, 6528–6533. doi:10.1039/C6SC00836D

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- Lin, J., Nguyen, T. T. T., Vaidhyanathan, R., Burner, J., Taylor, J. M., Durekova, H., et al. (2021). A scalable metal-organic framework as a durable physisorbent for carbon dioxide capture. *Science* 374, 1464–1469. doi:10.1126/science.abi7281
- Lin, Z., Kuang, Y., Li, W., and Zheng, Y. (2024). Research status and prospects of CO₂ geological sequestration technology from onshore to offshore: a review. *Earth Sci. Rev.* 258, 104928. doi:10.1016/j.earscirev.2024.104928
- Liu, J., Prelesnik, J. L., Patel, R., Kramar, B. V., Wang, R., Malliakas, C. D., et al. (2023). A nanocavitation approach to understanding water capture, water release, and framework physical stability in hierarchically porous MOFs. *J. Am. Chem. Soc.* 145, 27975–27983. doi:10.1021/jacs.3c07624
- Liu, J., Wang, Y., Benin, A. I., Jakubczak, P., Willis, R. R., and LeVan, M. D. (2010). CO₂/H₂O adsorption equilibrium and rates on metal-organic frameworks: HKUST-1 and Ni/DOBDC. *Langmuir* 26, 14301–14307. doi:10.1021/la102359q
- Lyu, H., Chen, O. L., Hanikel, N., Hossain, M. I., Flaig, R. W., Pei, X., et al. (2022). Carbon dioxide capture chemistry of amino acid functionalized metal-organic frameworks in humid flue gas. *J. Am. Chem. Soc.* 144, 2387–2396. doi:10.1021/jacs.1c13368
- Massarweh, O., and Abushaikh, A. S. (2024). CO₂ sequestration in subsurface geological formations: a review of trapping mechanisms and monitoring techniques. *Earth Sci. Rev.* 253, 104793. doi:10.1016/j.earscirev.2024.104793
- McDonald, T. M., D'Alessandro, D. M., Krishna, R., and Long, J. R. (2011). Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework CuBTTri. *Chem. Sci.* 2, 2022–2028. doi:10.1039/C1SC00354B
- McDonald, T. M., Lee, W. R., Mason, J. A., Wiers, B. M., Hong, C. S., and Long, J. R. (2012). Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen-Mg₂(dobpdc). *J. Am. Chem. Soc.* 134, 7056–7065. doi:10.1021/ja300034j
- McDonald, T. M., Mason, J. A., Kong, X., Bloch, E. D., Gygi, D., Dani, A., et al. (2015). Cooperative insertion of CO₂ in diamine-appended metal-organic frameworks. *Nature* 519, 303–308. doi:10.1038/nature14327
- Milner, P. J., Martell, J. D., Siegelman, R. L., Gygi, D., Weston, S. C., and Long, J. R. (2018). Overcoming double-step CO₂ adsorption and minimizing water co-adsorption in bulky diamine-appended variants of Mg₂(dobpdc). *Chem. Sci.* 9, 160–174. doi:10.1039/C7SC04266C
- Milner, P. J., Siegelman, R. L., Forse, A. C., Gonzalez, M. I., Runčevski, T., Martell, J. D., et al. (2017). A diaminopropane-appended metal-organic framework enabling efficient CO₂ capture from coal flue gas via a mixed adsorption mechanism. *J. Am. Chem. Soc.* 139, 13541–13553. doi:10.1021/jacs.7b07612
- Mukherjee, A., Okolie, J. A., Abdelrasoul, A., Niu, C., and Dalai, A. K. (2019). Review of post combustion carbon dioxide capture technologies using activated carbon. *J. Environ. Sci.* 83, 46–63. doi:10.1016/j.jes.2019.03.014
- Park, S., Ahn, Y., Lee, S., and Choi, J. (2021). Calcium carbonate synthesis from waste concrete for carbon dioxide capture: from laboratory to pilot scale. *J. Hazard. Mater.* 403, 123862. doi:10.1016/j.jhazmat.2020.123862
- Peralta, R. A., Alcántar-Vázquez, B., Sánchez-Serratos, M., González-Zamora, E., and Ibarra, I. A. (2015). Carbon dioxide capture in the presence of water vapour in InOF-1. *Inorg. Chem. Front.* 2, 898–903. doi:10.1039/C5QI00077G
- Planas, N., Dzubak, A. L., Poloni, R., Lin, L.-C., McManus, A., McDonald, T. M., et al. (2013). The mechanism of carbon dioxide adsorption in an alkylamine-functionalized metal-organic framework. *J. Am. Chem. Soc.* 135, 7402–7405. doi:10.1021/ja4004766
- Ran, J., Jaroniec, M., and Qiao, S.-Z. (2018). Cocatalysts in semiconductor-based photocatalytic CO₂ reduction: achievements, challenges, and opportunities. *Adv. Mater.* 30, 1704649. doi:10.1002/adma.201704649
- Sagastuy-Breña, M., Mileo, P. G. M., Sánchez-González, E., Reynolds, J. E., Jurado-Vázquez, T., Balmaseda, J., et al. (2018). Humidity-induced CO₂ capture enhancement in Mg-CUK-1. *Dalton Trans.* 47, 15827–15834. doi:10.1039/C8DT03365J
- Sánchez-González, E., Álvarez, J. R., Peralta, R. A., Campos-Reales-Pineda, A., Tejeda-Cruz, A., Lima, E., et al. (2016). Water adsorption properties of NOTT-401 and CO₂ capture under humid conditions. *ACS Omega* 1, 305–310. doi:10.1021/acsomega.6b00102
- Schoedel, A., Ji, Z., and Yaghi, O. M. (2016). The role of metal-organic frameworks in a carbon-neutral energy cycle. *Nat. Energy* 1, 16034. doi:10.1038/nenergy.2016.34
- Shi, Z., Tao, Y., Wu, J., Zhang, C., He, H., Long, L., et al. (2020). Robust metal-triazolate frameworks for CO₂ capture from flue gas. *J. Am. Chem. Soc.* 142, 2750–2754. doi:10.1021/jacs.9b12879
- Siegelman, R. L., McDonald, T. M., Gonzalez, M. I., Martell, J. D., Milner, P. J., Mason, J. A., et al. (2017). Controlling cooperative CO₂ adsorption in diamine-appended Mg₂(dobpdc) metal-organic frameworks. *J. Am. Chem. Soc.* 139, 10526–10538. doi:10.1021/jacs.7b05858
- Siegelman, R. L., Milner, P. J., Forse, A. C., Lee, J.-H., Colwell, K. A., Neaton, J. B., et al. (2019). Water enables efficient CO₂ capture from natural gas flue emissions in an oxidation-resistant diamine-appended metal-organic framework. *J. Am. Chem. Soc.* 141, 13171–13186. doi:10.1021/jacs.9b05567
- Song, K. S., Fritz, P. W., and Coskun, A. (2022). Porous organic polymers for CO₂ capture, separation and conversion. *Chem. Soc. Rev.* 51, 9831–9852. doi:10.1039/D2CS00727D
- Soubeyrand-Lenoir, E., Vagner, C., Yoon, J. W., Bazin, P., Ragon, F., Hwang, Y. K., et al. (2012). How water fosters a remarkable 5-fold increase in low-pressure CO₂ uptake within mesoporous MIL-100(Fe). *J. Am. Chem. Soc.* 134, 10174–10181. doi:10.1021/ja302787x
- Spurin, C., Callas, C., Darraj, N., Rucker, M., and Benson, S. (2025). The importance and challenges associated with multi-scale heterogeneity for geological storage. *InterPore J.* 2, IPJ260225–2. doi:10.69631/ipj.v2i1nr76
- Sumida, K., Rogow, D. L., Mason, J. A., McDonald, T. M., Bloch, E. D., Herm, Z. R., et al. (2012). Carbon dioxide capture in metal-organic frameworks. *Chem. Rev.* 112, 724–781. doi:10.1021/cr2003272
- Wang, T. C., Vermeulen, N. A., Kim, I. S., Martinson, A. B. F., Stoddart, J. F., Hupp, J. T., et al. (2016). Scalable synthesis and post-modification of a mesoporous metal-organic framework called NU-1000. *Nat. Protoc.* 11, 149–162. doi:10.1038/nprot.2016.001
- Wang, Y., Zhao, L., Otto, A., Robinus, M., and Stolten, D. (2017). A review of post-combustion CO₂ capture technologies from coal-fired power plants. *Energy Procedia* 114, 650–665. doi:10.1016/j.egypro.2017.03.1209
- Wurbacher, J. A., Gebald, C., and Steinfeld, A. (2011). Separation of CO₂ from air by temperature-vacuum swing adsorption using diamine-functionalized silica gel. *Energy Environ. Sci.* 4, 3584–3592. doi:10.1039/C1EE01681D
- Xian, S., Peng, J., Zhang, Z., Xia, Q., Wang, H., and Li, Z. (2015). Highly enhanced and weakened adsorption properties of two MOFs by water vapor for separation of CO₂/CH₄ and CO₂/N₂ binary mixtures. *Chem. Eng. J.* 270, 385–392. doi:10.1016/j.cej.2015.02.041
- Yazaydin, A. Ö., Benin, A. I., Faheem, S. A., Jakubczak, P., Low, J. J., Willis, R. R., et al. (2009). Enhanced CO₂ adsorption in metal-organic frameworks via occupation of open-metal sites by coordinated water molecules. *Chem. Mater.* 21, 1425–1430. doi:10.1021/cm900049x
- Yong, Z., Mata, V., and Rodrigues, A. E. (2002). Adsorption of carbon dioxide at high temperature—a review. *Sep. Purif. Technol.* 26, 195–205. doi:10.1016/S1383-5866(01)00165-4
- Yu, J., Wu, Y., and Balbuena, P. B. (2016). Response of metal sites toward water effects on postcombustion CO₂ capture in metal-organic frameworks. *ACS Sustain. Chem. Eng.* 4, 2387–2394. doi:10.1021/acssuschemeng.6b00080
- Zhang, W., Sun, C., Snape, C. E., Sun, X., and Liu, H. (2020). Cyclic performance evaluation of a polyethylenimine/silica adsorbent with steam regeneration using simulated NGCC flue gas and actual flue gas of a gas-fired boiler in a bubbling fluidized bed reactor. *Int. J. Greenh. Gas. Control* 95, 102975. doi:10.1016/j.ijggc.2020.102975
- Zhao, B., Su, Y., Tao, W., Li, L., and Peng, Y. (2012). Post-combustion CO₂ capture by aqueous ammonia: a state-of-the-art review. *Int. J. Greenh. Gas. Control* 9, 355–371. doi:10.1016/j.ijggc.2012.05.006
- Zhou, H.-C., Long, J. R., and Yaghi, O. M. (2012). Introduction to metal-organic frameworks. *Chem. Rev.* 112, 673–674. doi:10.1021/cr300014x