

Water-stable MOFs and Hydrophobically Encapsulated MOFs for CO₂ Capture from Ambient Air and Wet Flue Gas

Xiaoyang Shi,^{1,2,3,†} Gahyun Annie Lee^{2,3,†}, Shuohan Liu⁴, Dongjae Kim^{1,3}, Ammar Alahmed⁵,
Aqil Jamal⁵, Lei Wang^{*4}, Ah-Hyung Alissa Park^{*1,2,3}

¹ Department of Earth and Environmental Engineering, Columbia University, New York, NY 10027, USA

² Department of Chemical Engineering, Columbia University, New York, NY 10027, USA

³ Lenfest Center for Sustainable Energy, The Earth Institute, Columbia University, New York, NY 10027, USA

⁴ National Laboratory of Solid-State Microstructures, School of Physics and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

⁵ Research and Development Center, Saudi Aramco, Dhahran 31311, Saudi Arabia

[†] These authors contributed equally

*Corresponding authors: ap2622@columbia.edu, Leiwang@nju.edu.cn

Abstract:

The extra CO₂ that has already been released into the atmosphere has to be removed in order to create a world that is carbon neutral. Technologies have been created to remove carbon dioxide from wet flue gas or even directly from ambient air, however these technologies are not widely deployed yet. New generations of creative CO₂ capture sorbents have been produced as a consequence of recent improvements in material assembly and surface chemistry. We summarize recent progress on water-stable and encapsulated metal-organic frameworks (MOFs) for CO₂ capture under a wide range of environmental and operating conditions. In particular, newly developed water-stable MOFs and hydrophobic coating technologies are discussed with insights into their materials discovery and the synergistic effects between different components of these hybrid sorbent systems. The future perspectives and directions of water-stable and encapsulated MOFs are also given for Direct Air Capture of CO₂ and CO₂ capture from wet flue gas.

1. Introduction:

The main cause of global warming is the buildup of carbon dioxide (CO₂) in the atmosphere¹. The Intergovernmental Panel on Climate Change (IPCC) scenario RCP 8.5 states that, in the absence of action, CO₂ emissions would increase from the current level of 49 GtCO₂eq/yr to between 85 and 136 GtCO₂eq/yr by the year 2050². Global mean temperatures might rise by 3.8 to 6.0 °C from their pre-industrial level (1880–1900) to 2100 as a result of growing CO₂ concentrations. While supplying the increasing energy demand, CO₂ emissions might be reduced through CO₂ collection from wet flue gas mixes produced by industrial producers and power plants, or from the ambient air directly³⁻⁶.

Metal-organic frameworks (MOFs) are three-dimensional (3D) materials made of metal ions or clusters connected by organic ligands (linkers). MOFs exhibit high CO₂ capacity and selectivity for CO₂⁷ due to their high surface functionality and porosity⁸⁻¹¹, and highly unusual tunability¹²⁻¹³. It has been demonstrated that some metal-organic frameworks' separation capacities are on par with or better than those of zeolite or carbon adsorbents^{7, 14-16}. However, several investigations show that MOFs have serious stability problems¹⁷⁻²², especially concerning their interactions with water²³⁻²⁴, severely limiting their practical potential. Comparing the usual chemical properties of post-exposure and pristine samples will reveal if a MOFs structure is still stable in the water stability test. Indicating whether the MOFs loses its crystallinity or structural porosity following exposure to moisture or humid streams are the chemical properties of the powder X-ray diffraction (PXRD) pattern and BET surface area based on gas adsorption capability. MOFs structures are often vulnerable to hydrolysis, which might result in ligand displacement, phase shifts, and structural breakdown.

When evaluating sorbents for CO₂ collection, it is important to take into account the presence of water vapor, which is present in ambient air (0.2 percent–4 percent) and industrial flue gases (10 percent). Increasing MOFs stability has been a major objective of current research²⁵⁻³⁷. In order to strengthen the bonding in the material, most of this research has focused on altering the chemical makeup of the MOFs itself (either the metal node or the organic linker). Using high-oxidation metal ions, like Zr⁴⁺ in MOFs like UiO-66²⁵, or changing the linker units with other functional groups, such pyrazolate²⁶, both boost the metal-linker bond strengths, are successful examples in this field. Other techniques involve post-synthetic changes to shield the MOFs from water

intrusion, such as hydrophobic coatings or mixed-matrix composites³⁸⁻⁴⁰. These methods alter the chemistry of the substance while boosting MOFs stability. Such chemical alterations frequently cause a diminution in the solid's functioning, sometimes gravely jeopardizing its practicability¹⁷. As a result, there is a critical need to create MOFs with the ideal chemical structure for CO₂ collection and sufficient hydrolytic stability for practical use. This paper examines techniques that have been suggested to be effective for CO₂ collection in humid environments and gives a general overview of the factors to take into account when coming up with a fresh strategy to increase MOFs stability in humid environments.

2. Design and synthesis of MOFs

Strong coordination bonds (thermodynamic stability) or considerable steric hindrance (kinetic stability) are typically present in MOFs structures with outstanding stability to prevent the damaging hydrolysis process that destroys the metal-ligand connections¹⁷. Numerous research articles on water-stable MOFs are now witnessing a rise, and many more water-stable MOFs are published every year thanks to ongoing efforts and greater understanding of MOFs structural stability in humid surrounding. Due to the important work done by Burtch *et al.*¹⁷, Canivet *et al.*⁴¹, Howarth *et al.*⁴² *etc*, a comprehensive database of water-stable MOFs has so far been created. Direct synthesized water-stable MOFs may be divided into three main groups: (1) High-valence metal ion-based metal carboxylate frameworks; (2) Metal azolate frameworks with nitrogen-donor ligands; and (3) MOFs with hydrophobic pore surfaces or metal centers that are not exposed. Methods for stabilization of MOFs in water according to direct synthesis are shown in Figure 1.

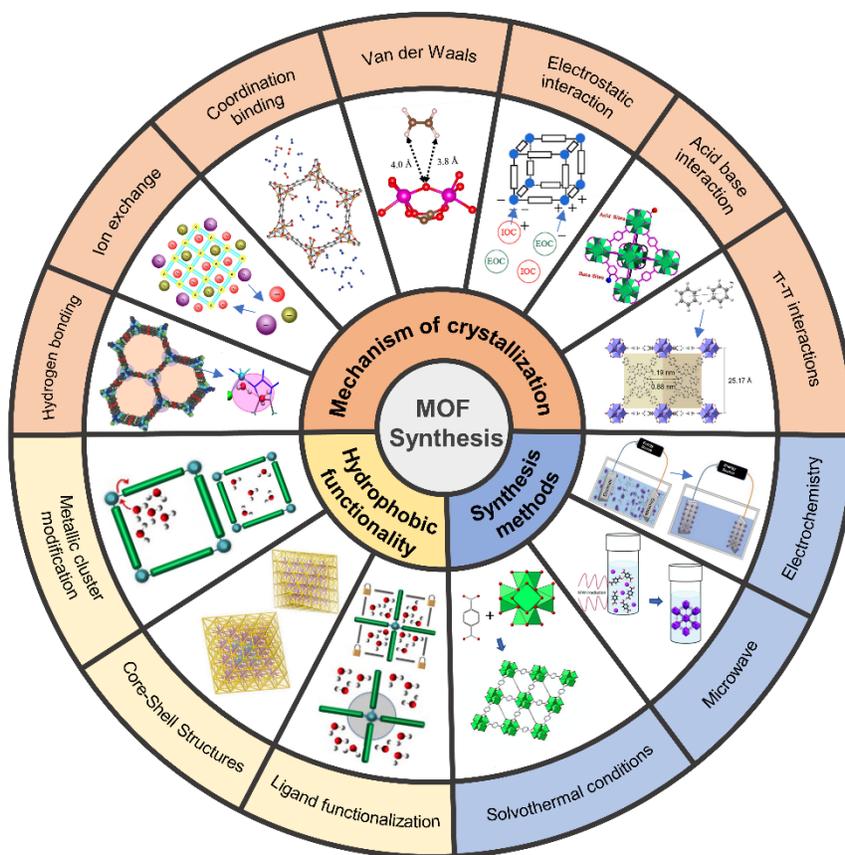


Figure 1. Mechanisms, reaction conditions and incorporation of hydrophobic functionality of MOF synthesis.

2.1 Metal Carboxylate Frameworks

High-valence metal ions including Fe^{3+} , Cr^{3+} , and Zr^{4+} have been employed as common carboxylate-type ligands to create water-stable MOFs. Due to their great aqueous stability, the combination of aromatic carboxylate molecules with a cluster caused steric hindrance in MOFs, which resulted in a significant deactivation of H^+ (or OH^-) ion activity on its surface⁴³. For instance, Ferey and his colleagues created the renowned Cr-based MIL-101, which offered reasonable chemical stability and could withstand multiple solvents and ambient conditions for months²⁰. These characteristics make MIL-101 an appealing choice for the adsorption of gas, in addition to its high adsorption capabilities. At 78 K, the MIL-101 nitrogen gas sorption isotherm is approximately $1200 \text{ cm}^3/\text{g}$, or $5900 \text{ m}^2/\text{g}$.

Additionally, high-valence Zr^{4+} cation-containing MOFs such as the well-known UiO-66 and the PCN family, which includes PCN-222, PCN-223, and PCN-224, exhibit extraordinary hydro-stability even in the presence of water^{25, 44}. The Zr MOFs structures made with linear ligands are shown in Figure 2A. The structural resilience to various solvents was also examined. A desolvated sample was agitated at room temperature in various solvents for 24 hours. A modest quantity of Si was added to each sample in order to examine alterations in the unit cell parameters. Figure 2B demonstrates the results achieved.

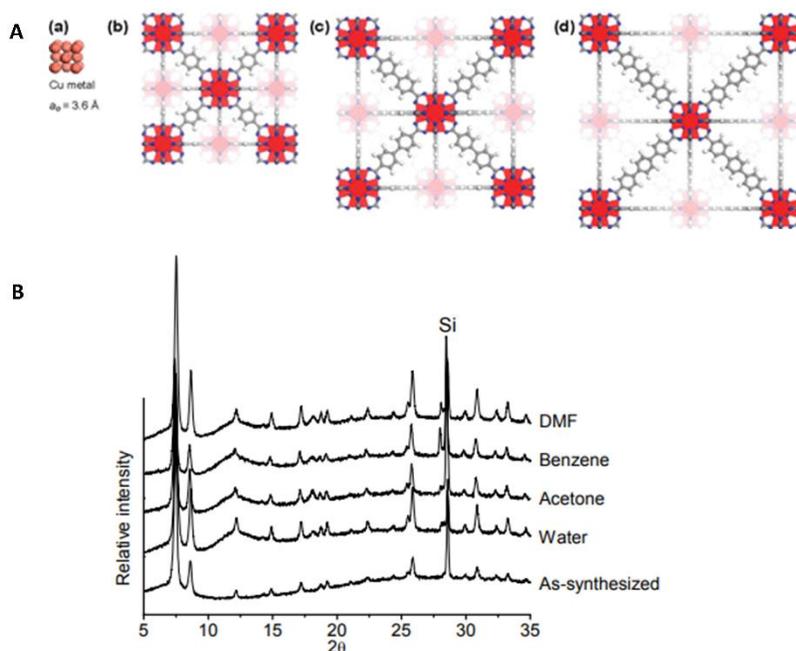


Figure 2 **A.** (a) One unit cell of copper drawn to scale with: (b) Zr–MOFs with 1,4-benzene-dicarboxylate (BDC) as linker, UiO-66, (c) Zr–MOFs with 4,4' biphenyl-dicarboxylate (BPDC) as linker, UiO-67, (d) Zr–MOFs with terphenyl dicarboxylate (TPDC) as linker, UiO-68. Zirconium, oxygen, carbon, and hydrogen atoms are red, blue, gray, and white, respectively. **B.** Powder XRD patterns of assynthesized UiO66 and UiO66 treated with different solvents following desolvation²².

In recent years, a variety of water-stable MOFs have been synthesized and described using this method⁴⁵⁻⁶⁴. *Le et al.*⁶⁵, for instance, describe the utilization of water-stable lanthanide (Ln)-based MOFs as catalysts for converting CO_2 into products with added value. The authors discuss the fixing of carbon dioxide into the epoxy ring of propylene oxide for the creation of cyclic carbonates using these MOFs.

2.2 Metal Azolate Frameworks

Utilizing azolate ligands (such as imidazoles, pyrazoles, triazoles, and tetrazoles) is an additional technique for the synthesis of water-stable MOFs, in addition to the use of high-valence metals as hard acids⁶⁶. As these nitrogen-containing ligands are typically softer, they can interact with the softer divalent metal ions to produce more robust MOFs structures. The establishment of a strong coordination connection between organic ligands and central metal ions may best explain this observation.

The best illustration of this group is zeolitic imidazolate frameworks (ZIFs). Using Zn^{2+}/Co^{2+} and imidazolate linkers, scientists fabricated a variety of stable crystals with zeolite-like structure⁶⁷⁻⁶⁹. The chemical stability of the samples was evaluated by heating them in different solvents for seven days; these circumstances match probable harsh industrial needs. Several ZIFs with heterolinks have a high porosity that can impede the collection and storage of CO_2 with outstanding selectivity. Figure 3 depicts the chemical structures of ZIF-68, 69, and 70, as well as their gas adsorption isotherms and CO_2 capture characteristics. The Langmuir surface areas for ZIF-68, 69, and 70 were 1220, 1070, and 1970 $m^2 g^{-1}$, respectively.

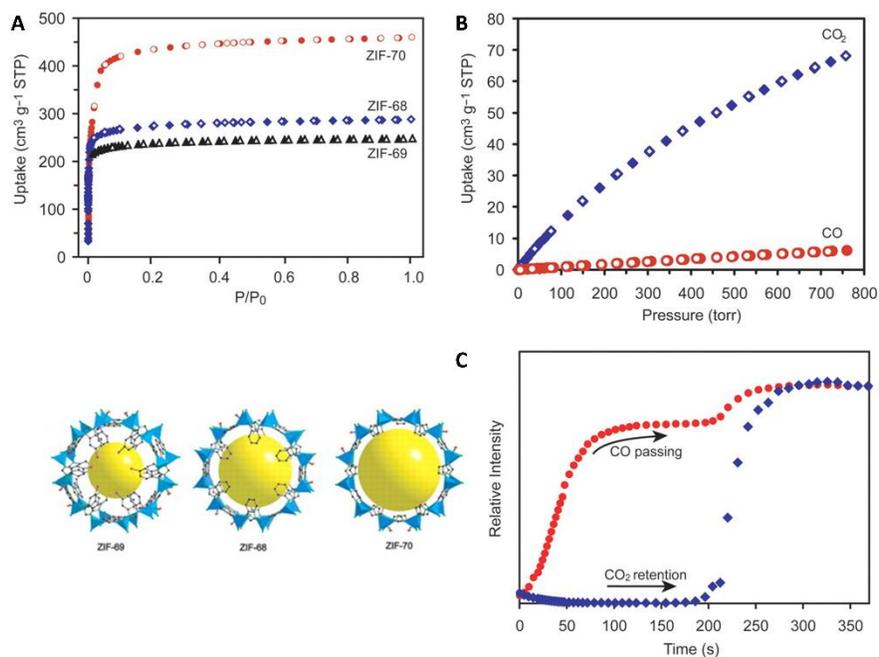


Figure 3. Isotherms of gas adsorption and CO₂ capture characteristics of ZIFs. **A.** The N₂ adsorption isotherms for heterolinked ZIF-68, 69, and 70 at 77 K. P/P_0 , relative pressure; STP, standard temperature and pressure. **B.** The CO₂ and CO adsorption isotherms for ZIF-69 at 273 K. For **A** and **B**, the gas uptake and release are indicated by solid and open symbols, respectively. **C.** Breakthrough curves of a stream of CO₂/CO combination that went through a sample of ZIF-68 demonstrate the retention of CO₂ in the pores and passage of CO⁶⁷.

In addition, Colombo *et al.*²⁶ produced the microporous pyrazolate-based MOFs, M₃(BTP)₂ (M = Ni, Cu, Zn, Co), which demonstrated superior hydrothermal stability compared to most carboxylate-based MOFs. As a result of this approach, an increasing number of azolate-based MOFs exhibit a respectable level of hydro-stability that was produced in recent years⁷⁰⁻⁸⁸.

In order to produce a flexible porous coordination polymer with a high CO₂ adsorption enthalpy and CO₂/N₂ selectivity, Liao *et al.*⁷¹ functionalized it with two uncoordinated triazolate N-donor pairs. Metal Azolate Framework (MAF-23) is seen in Figure 4B at 273 and 298 K, where it absorbs CO₂ at a rate of 74.2 and 56.1 cm³ g⁻¹ (14.6 and 11.0 wt percent, respectively) at 1 atm. MAF-23 only adsorbed 4.0 and 2.0 cm³ g⁻¹ of N₂ at 1 atm under the identical circumstances. Figure 4C demonstrates that even after refluxing in water for seven days, MAF-23 entirely maintained its crystallinity.

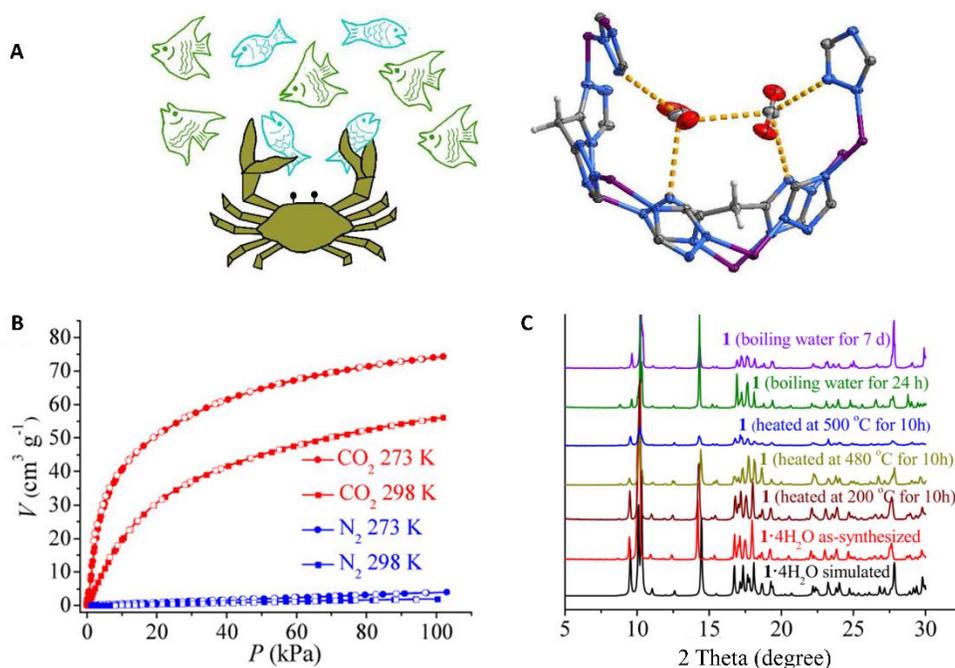


Figure 4A. Framework Structure of metal azolate. B. CO₂ and N₂ adsorption (solid) and desorption (open) isotherms. C. PXRD patterns of MAF-23⁷¹.

The bulk synthesis of high-quality MAF-6 with excellent purity, crystallinity, and thermal/chemical stability was accomplished by He *et al.*⁷⁴. When heated at 400 °C in a nitrogen environment for one hour or submerged in methanol, benzene, and water at ambient temperature for at least three days, the original crystallinity could still be maintained, according to PXRD. Figure 5A demonstrates that the surface of MAF-6 is very hydrophobic with a contact angle of $143 \pm 1^\circ$. At 77K, the N₂ sorption isotherm of MAF-6 revealed a Langmuir surface area of 1695 m²/g, a Brunauer–Emmett–Teller surface area of 1343 m² g⁻¹, as well as a pore volume of 0.61 cm³/g (Figure 5B).

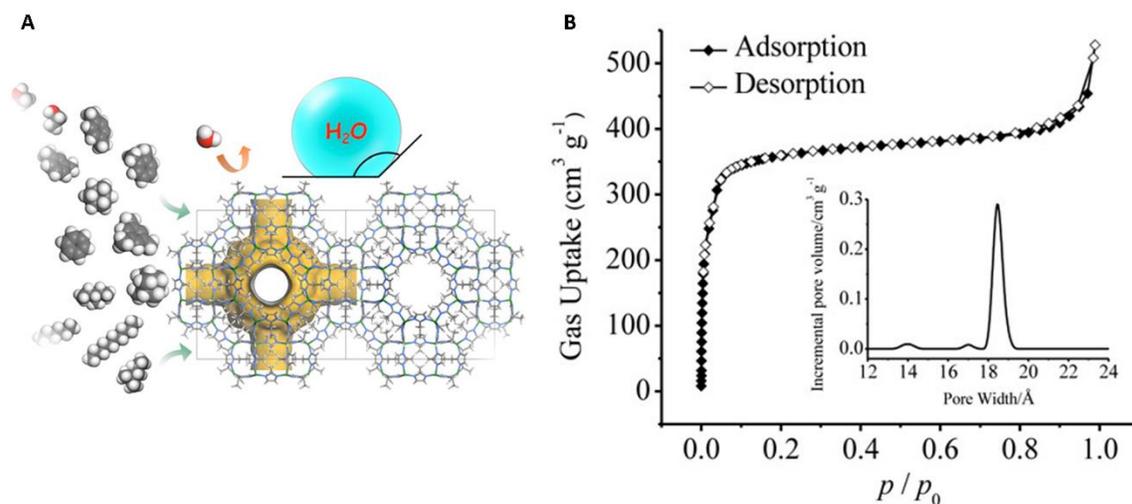


Figure 5. A. Hydrophobic structure of metal azolate framework. B. CO₂ and N₂ adsorption (solid) and desorption (open) isotherms⁷⁴.

Zhang *et al.*⁷⁹ described a coligand-bridging approach for manufacturing novel poly MOFs. These poly MOFs materials displayed reasonably strong CO₂ sorption but extremely low N₂ sorption, making them interesting for CO₂/N₂ separations. In addition, the hydrophobicity of polymer ligands and the cross-linking of the polymer chains inside the MOFs contributed to the excellent water stability of these poly MOFs, that were immersed in water at room temperature or 100 °C for 1 day. Five days of solvent exchange with methanol were followed by ten hours of activation at 130 °C under vacuum. PXRD indicated that, with the exception of Zn-pbdc-7a(bpe), all other

poly MOFs kept their crystallinity following water treatment. According to the CO₂ sorption results reported in Table 1, Zn-pbdc-11a(bpe), Zn-pbdc-12a(bpe), and Zn-pbdc-12a(bpy) demonstrated highly comparable CO₂ uptake values before and after water treatment, indicating outstanding water stability. Other poly MOFs materials exposed to water lost some porosity.

polyMOFs	contact angle (deg)	CO ₂ uptake (cm ³ /g) ^a	CO ₂ uptake (cm ³ /g) ^b
Zn-pbdc-8a(bpy)	0	91 ± 5	70 ± 5
Zn-pbdc-9a(bpy)	0	86 ± 3	72 ± 4
Zn-pbdc-12a(bpy)	119 ± 1	75 ± 5	78 ± 3
Zn-pbdc-7a(bpe)	0	72 ± 2	40 ± 7
Zn-pbdc-8a(bpe)	0	97 ± 5	70 ± 1
Zn-pbdc-9a(bpe)	0	80 ± 4	61 ± 5
Zn-pbdc-10a(bpe)	111 ± 1	140 ± 5	102 ± 6
Zn-pbdc-11a(bpe)	114 ± 1	106 ± 5	101 ± 5
Zn-pbdc-12a(bpe)	115 ± 1	105 ± 6	106 ± 5
MOF 1	N/A	156	N/A
MOF 1'	0	160 ± 6	N/A
MOF 2	110 ± 1	72 ± 6	N/A

Table 1. ^aAs-synthesized poly MOFs prior to water treatment. ^bpoly MOFs after room temperature water treatment⁷⁹.

2.3 Functionalized MOFs

In addition to improving the strength of the metal-ligand interaction, MOFs might be functionalized to create steric hindrance to maintain robustness in an aqueous media. By providing hydrophobic pore surfaces or inhibiting the metal ions, it is possible to prevent water molecules from accessing the lattice and damaging the framework structure.

Creating a hydrophobic surface on MOFs by post-synthetic alteration is an effective solution for the water sensitivity of MOFs. The process involves encapsulating hydrophobic guest molecules

(e.g., fluorinated compounds³⁹, polyoxometalates⁸⁹, and carbon nanotubes in MOFs pores⁹⁰) and functionalizing their exterior surfaces by ligand replacement and exchange⁹¹ or with carbon coatings by surface thermolysis⁹², *etc*⁹³.

Yang *et al.*⁹² discovered a basic technique for considerably enhancing MOFs' moisture resistance. The heat treatment of MOFs resulted in the creation of an amorphous carbon layer on the surface of the MOFs that inhibits hydrolysis. Figure 6A depicts a simple heat treatment at a certain temperature that resulted in coating the frameworks with an amorphous carbon layer, which acted as a moisture repellent when the MOFs were exposed to water, hence inhibiting hydrolysis. Figure 6B(a) demonstrates that the desolvated MOFs were exposed to ambient air (34% relative humidity) and then analyzed by measuring their PXRD patterns to acquire insight into the crystal structure in the presence of moisture. 14 days of exposure to desolvated IRMOF-1 to air (34% relative humidity) led to a shift in relative peak intensities and the emergence of new peaks, suggesting the initiation of hydrolysis.

In contrast, the patterns of all thermally modified MOFs remained essentially unchanged, even after 14 days of humidity exposure. The thermally-treated MOFs displayed significantly better N₂ adsorption retention after 14 days of exposure to ambient air, demonstrating enhanced stability in the presence of moisture. In contrast, despite being exposed to humidity for 14 days, all thermally altered MOFs' patterns remained mostly unaltered. The thermally-treated MOFs showed noticeably improved N₂ adsorption retention, indicating improved stability in the presence of moisture.

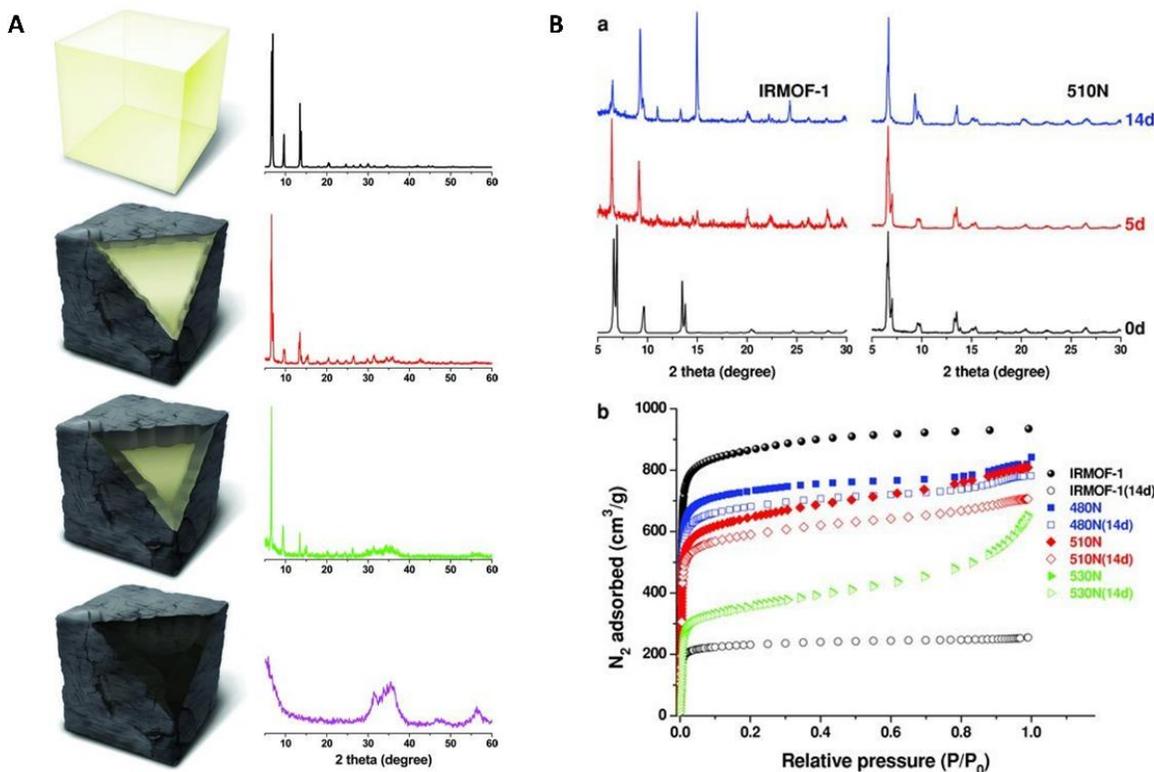


Figure 6 **A.** a Schematic illustration of IRMOF-1 (above) and IRMOF-1 following thermal alteration to create amorphous carbon-coated MOFs (middle) and, at higher temperature, ZnO nanoparticles@amorphous carbon (bottom). The corresponding XRD patterns are shown on the right. **B.** a) PXRD patterns and b) nitrogen adsorption isotherms of IRMOF-1 and the thermally-modified MOFs after exposure to ambient conditions. 480N, 510N, and 530N denote a sample heated at 480 °C, 510 °C, and 530 °C under a nitrogen atmosphere⁹².

Numerous studies on the increased hydrothermal stability of MOFs have been published. Taylor *et al.*⁹⁴ created CALF-25, a novel porous MOFs. The MOFs has a three-dimensional structure with one-dimensional rectangular pores lined with ethyl ester groups from the ligand. The presence of ethyl ester groups caused the pores to become hydrophobic. The ethyl ester groups inside the pores also prevent CALF-25 against breakdown by water vapor, preserving crystallinity and porosity after exposure to extreme humid environments (90% relative humidity at 353 K).

Omary and his colleagues created a variety of superhydrophobic and water-stable fluorinated metal-organic frameworks (FMOFs)⁹⁵⁻⁹⁶. Post-synthetic techniques, such as ligand modification⁹⁷

(Figure 7A), and ligand^{91, 98} and metal exchange reactions⁹⁹ (Figures 7B and 7C), were developed to significantly improve the hydrophobicity and hydrothermal stability of the existing MOFs structures.

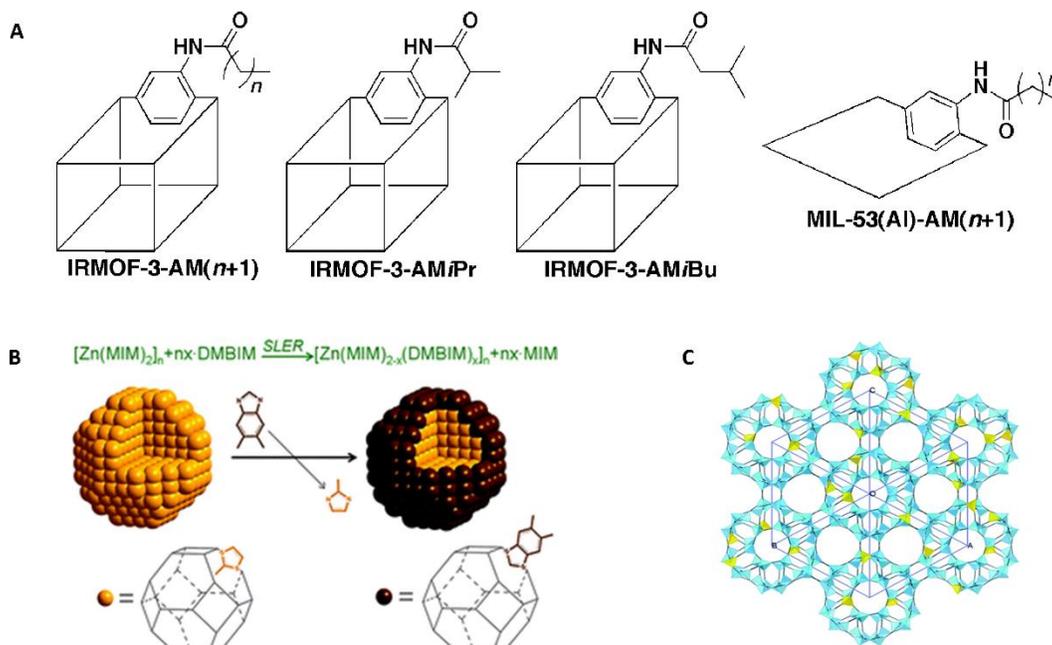


Figure 7. **A.** Schematic representations of substituted organic ligands⁹⁷. **B.** Schematic illustration of ZIF-8's shell-ligand-exchange reaction (SLER) mechanism⁸⁷. **C.** Cyan tetrahedrons and yellow tetrahedrons representing Zn^{2+} and Cu^{2+} nodes, respectively, to demonstrate the doped structure of STU-1⁹⁹.

3. Coating and supporting of MOFs using hydrophobic materials

The introduction of hydrophobic groups, such as methyls, long alkyl chains, and carbon coatings, would effectively obstruct the pores of MOFs, resulting in a significant reduction in specific surface area and porosity. It is crucial to preserve or even enhance the pore structure of modified MOFs, since it determines the adsorption and diffusion characteristics of adsorbate in porous materials. Coating the crystals of MOFs with hydrophobic polymers to form MOF@polymer composites that display greater structural stability in water-containing conditions than the equivalent MOFs alone is another intriguing post-synthetic modification¹⁰⁰⁻¹⁰⁵. Methods for stabilization of MOFs in water by hydrophobic materials are shown in Figure 8.

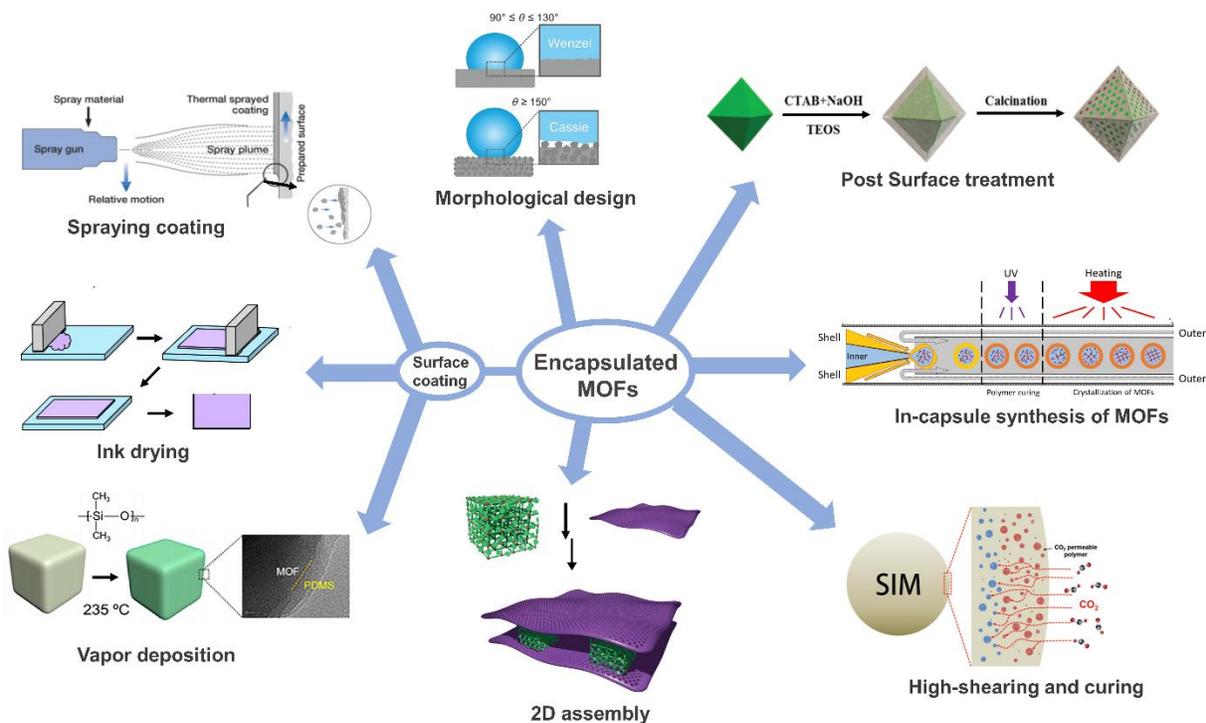


Figure 8. Methods of MOF encapsulation.

Fernandez *et al.* covered the outside surface of MOFs with a layer of hydrophobic Pluronic P123 polymer by physical adsorption¹⁰². The water stability of polymer-functionalized MOFs is greater than that of unmodified MOFs. However, the contact angle of the coated MOFs is between 22 and 27 degrees, which is insufficient for hydrolysis protection. Jiang *et al.* recently established a comprehensive coating technique to deposit hydrophobic polydimethylsiloxane (PDMS) on the surfaces of MOFs, which significantly improved their moisture/water stability¹⁰¹. Sun *et al.* also proposed a technique for imparting amphiphobicity to single-crystalline MOFs using 1H,1H,2H,2H-perfluorodecanethiol¹⁰⁴. Qian *et al.* proposed a solution-immersion procedure for depositing a layer of hydrophobic organosilicone on the exterior surface of MOFs with better water stability¹⁰⁶. Utilizing UV-curable coating technique, Nanoparticle Organic Hybrid Materials (NOHMs)¹⁰⁷⁻¹⁰⁸ have been encapsulated. The technique is applicable to MOFs¹⁰⁹ as well. Because they have the potential to be utilized in the field of CO₂ capture, the examples provided below are described in details.

Zhang *et al.* created a broad method to change hydrophobic PDMS on the surface of MOFs materials in order to considerably improve their resistance to moisture or water using a simple

vapor deposition technique¹⁰¹. Their research demonstrated that the PDMS protective covering had no effect on the existing structure, porosity, or adsorption site use of MOFs. This unique coating method might make MOFs useful in the presence of water or humidity in a variety of applications, including gas sorption and catalysis, where they have not been utilized previously. MOF-5, HKUST-1, and ZnBT, which are archetypal susceptible MOFs, were effectively coated with PDMS, and the coated samples retained their original crystalline nature and pore properties. Nearly 100% percent of the surface regions of these MOFs were preserved after PDMS coating.

Typically, the coating procedure involves heating MOFs in the presence of PDMS stamps in a sealed glass container at 235 °C, which is appropriate for the majority of MOFs (which are typically stable up to 300 °C). The volatile and low-molecular-weight silicone molecules, which emerge from the thermal decomposition of PDMS, would settle on the surface of MOFs and then cross-link to produce a hydrophobic silicone coating. The coated MOFs would be produced upon cooling to room temperature.

A high-resolution transmission electron microscopy (HRTEM) picture reveals a 10 nm PDMS coating layer on the surface of the MOFs in Figure 9A. It is well known that MOF-5, HKUST-1, and ZnBT are all water-sensitive to variable degrees and are hydrophilic materials with water contact angles near 0°. All PDMS-coated samples have water contact angles of $130 \pm 2^\circ$, indicating their hydrophobic nature (Figure 9B, a–f). Figure 9C depicts the N₂ sorption isotherms for three kinds of uncoated and PDMS-coated MOFs before to and after treatment with moisture/water. After exposure to water, the amount of N₂ adsorbed by uncoated MOFs has reduced dramatically, but the amount adsorbed by PDMS-coated MOFs remains consistent.

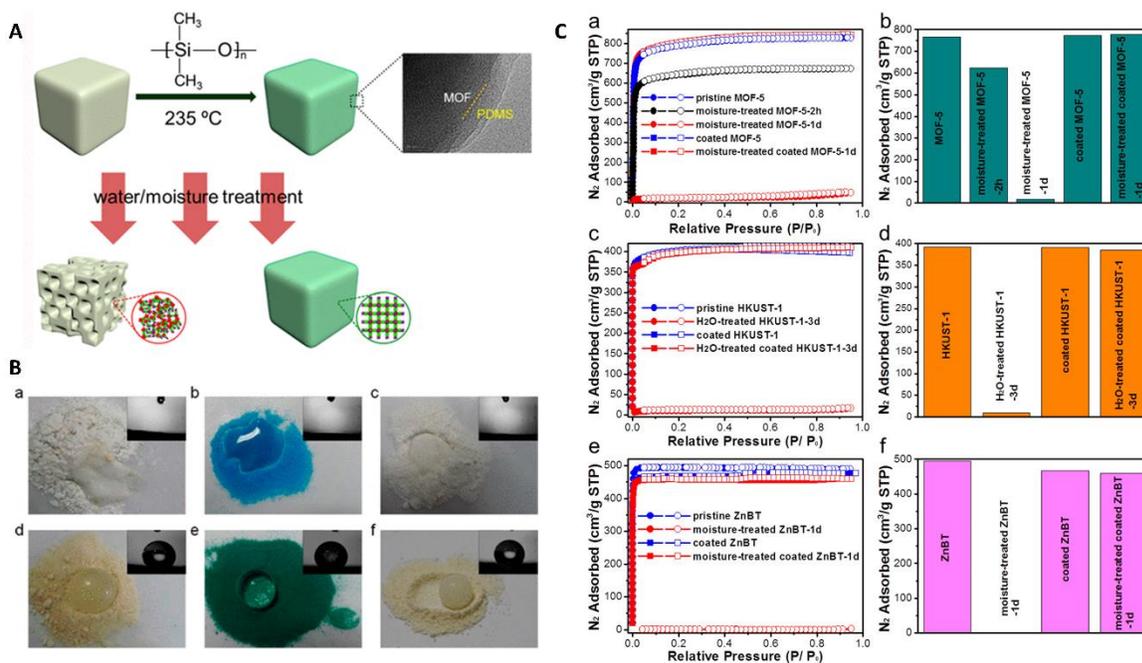


Figure 9. **A.** Illustration of PDMS-Coating on the surface of MOFs and the enhancement of moisture resistance of MOFs. **B.** (a–f) Digital photographs of (a) MOF-5, (d) coated MOF-5, (b) HKUST-1, (e) coated HKUST-1, (c) ZnBT, and (f) coated ZnBT after a drop of water was placed onto the samples. Inset shows contact angle measurement for each sample, respectively (coated MOF-5, 128°; coated HKUST-1, 130°; coated ZnBT, 130°). **C.** (a, c, and e) N₂ sorption isotherms for pristine and PDMS-coated MOFs before and after moisture/water treatment (MOF-5 and ZnBT were treated in the air at 55% relative humidity for 1 d; HKUST-1 was treated in water for 3 d). (b, d, and f) N₂ sorption capacity of samples at relatively low pressure (P/P_0 equal to 0.1)¹⁰¹.

Qian *et al.* established a simple solution-immersion method for depositing a hydrophobic coating on the outside surface of MOFs without obstructing the MOFs' inherent pores¹⁰⁶. The method can be performed at room temperature and without heating. Three exemplary MOFs, NH₂-MIL-125(Ti), ZIF-67, and HKUST-1, have been chosen for in-depth examination to highlight the adaptability of the method. Figure 10A (a)-(c) demonstrate that water droplets may spread and absorb rapidly on MOFs. (d)-(f) demonstrates that spherical water droplets may stand freely on hydrophobic coating samples without being absorbed. Figure 10B (a), (d), and (g) depict the morphology of three MOF types before to exposure to water. After five days of exposure to water, the crystals in (b), (e), and (h) are almost ruined and full of fractures and voids. (c), (f), and (i)

demonstrate that the hydrophobic coating on the surface of MOFs is well retained, as is their crystal shape.

Figure 10C depicts a type I isotherm for the N₂ sorption and desorption isotherms of three as-synthesized (AS) MOFs at 77 K. Five days after being exposed to water, the N₂ adsorption and desorption curves of three AS MOFs had diminished. N₂ sorption curves for hydrophobic-coated MOFs (SS) indicate just a modest reduction. Approximately 85% of capacity remains after the same time span. Figure 10D depicts the similar pattern for the adsorption and desorption curves of CO₂.

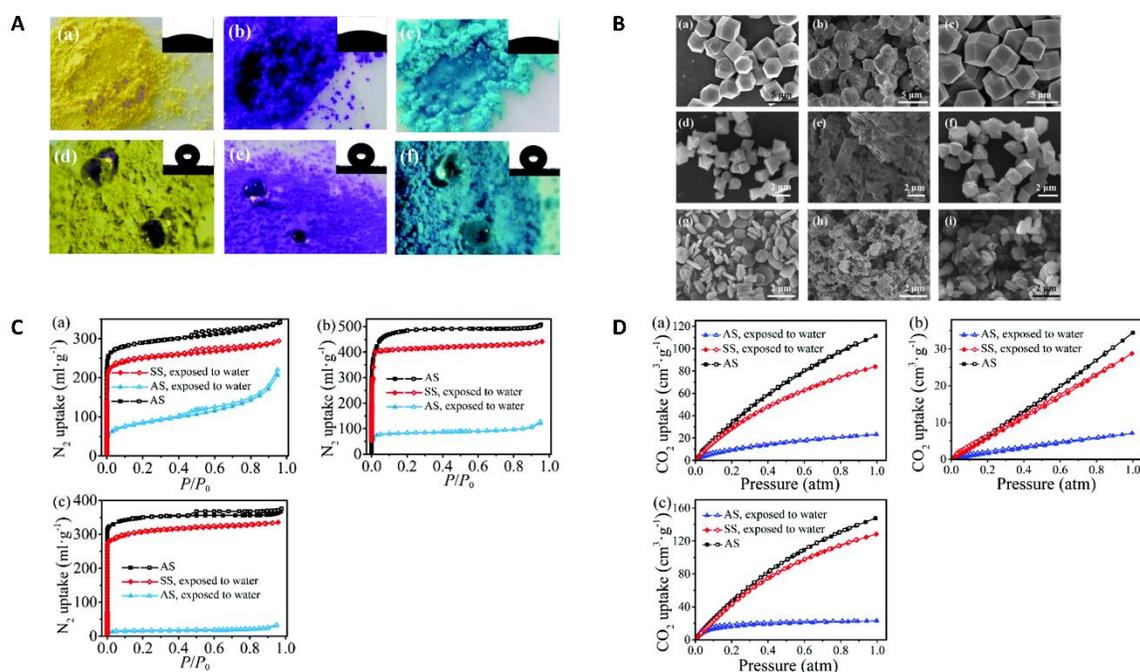


Figure 10. **A.** Digital photographs of the as-synthesized samples (a) NH₂-MIL-125(Ti), (b) ZIF-67, (c) HKUST-1, and the SH (d) NH₂-MIL-125(Ti), (e) ZIF-67, (f) HKUST-1. The inset shows the contact angle image. **B.** SEM images of (a) the AS ZIF-67, (b) and (c) the AS ZIF-67 and SH ZIF-67 after exposure to water for 5 days, respectively, (d) the AS HKUST-1, (e) and (f) the AS HKUST-1 and SH HKUST-1 after exposure to water for 5 days, respectively, (g) the AS NH₂-MIL-125(Ti), (h) and (i) the AS NH₂-MIL-125(Ti) and SH NH₂-MIL-125(Ti) after exposure to water for 5 days, respectively. **C.** N₂ sorption isotherms for (a) NH₂-MIL-125(Ti), (b) ZIF-67 and (c) HKUST-1 after exposure to liquid water for 5 days. **D.** CO₂ sorption isotherms for (a) NH₂-MIL-125(Ti), (b) ZIF-67 and (c) HKUST-1 after exposure to liquid water for 5 days¹⁰⁶.

As illustrated in Figure 11A, Carne-Sanchez *et al.*¹⁰⁰ demonstrated a technique of spray-dry encapsulation of HKUST-1 crystals in polystyrene microspheres to produce water-resistant composites that preserve the majority of HKUST-1's superior gas sorption capability. The MOFs crystals encased in a polymeric matrix do not require any purifying or filtering operations because the composites are formed in a dry, pure state (Figure 11B). The N₂ isotherm at 77 K demonstrated that the composite's value after incubation in water was around 80 percent (Figure 11C). In contrast, HKUST-1 crystals entirely lost their sorption ability under equal circumstances.

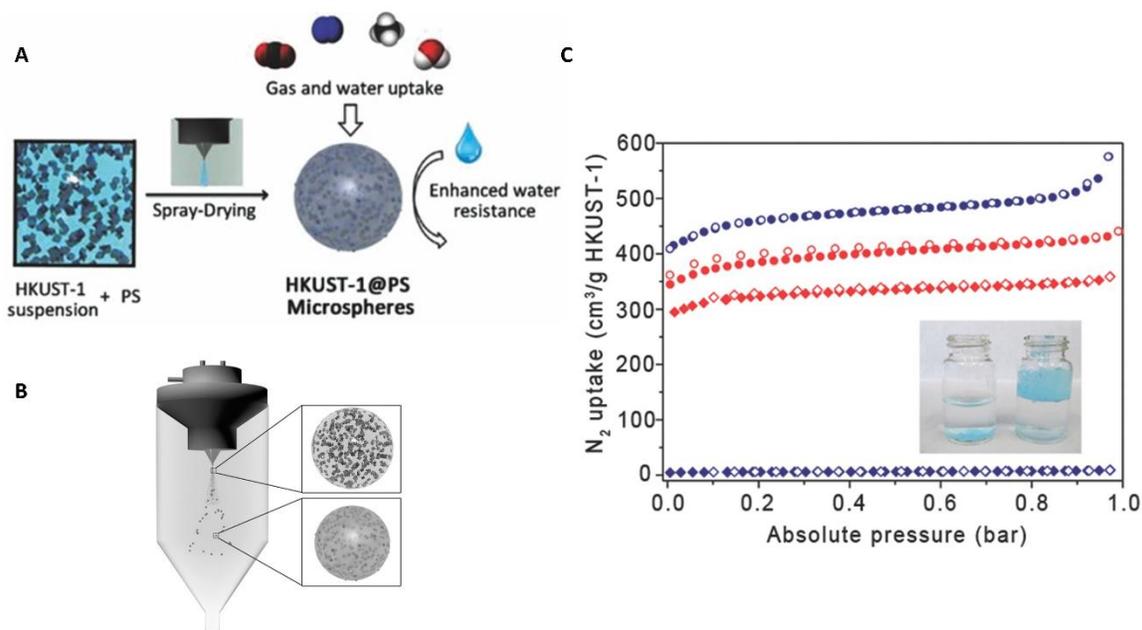


Figure 11. **A.** Spray-dry encapsulation of HKUST-1 crystals into polystyrene microspheres. **B.** Schematic of the spray-drying synthesis of HKUST-1@PS composites. **C.** N₂ isotherms at 77 K of HKUST-1 (blue) and HKUST-1@PS₆₃ (red) before (circles) and after (diamonds) incubation in water¹⁰⁰.

4. Water-stable MOFs and Encapsulated MOFs for CO₂ Capture from Wet Flue Gas

Due to the intense interest in employing MOFs as sorbents for lowering greenhouse gas emissions, extensive research has been conducted on CO₂ capture. CO₂ capture in the presence of water is difficult. Although MOFs are capable of capturing large quantities of CO₂ under dry conditions, the capture efficiency is drastically reduced in the presence of water because water molecules compete with CO₂ molecules for the same binding sites, and in some cases they can even destroy

the MOFs framework¹¹⁰⁻¹¹¹. For example, after exposure to water vapor, the CO₂ adsorption capacity of [Mg₂(dobpdc)] decreases by approximately 50% when tested under dry circumstances¹¹⁰⁻¹¹¹.

Despite the fact that water content is frequently harmful to CO₂ extraction when utilizing MOFs materials, there are instances where water has a negligible effect. Fracaroli *et al.*¹¹¹ employed IRMOF-74-III-CH₂NH₂ to selectively collect CO₂ at a relative humidity of 65%. The experimental findings demonstrate that this MOFs is exceptionally effective at absorbing CO₂ (3.2 mmol of CO₂ per gram at 800 Torr). However, IRMOF's structure is not stable after 14 days of exposure to water⁹². In addition, Zhang *et al.* noted that their created Zn-pbdc-12a(bpe) and Zn-pbdc-12a(bpy) display CO₂ uptakes of 2.2 and 1.8 mmol/g, respectively, under the condition of 1 bar of CO₂, which is extremely near to the uptake values before water vapor treatment⁷⁹.

In addition, McDonald and colleagues emphasized that the mmen-M₂(dobpdc) (M = Mg, Mn, Fe, Co, Zn) compounds, referred to as 'phase-change' adsorbents, show extremely desired properties for the effective capture of CO₂¹¹². Figure 12 demonstrates that the Langmuir-type CO₂ adsorption behavior may be maintained quite well after exposure to water at different temperatures.

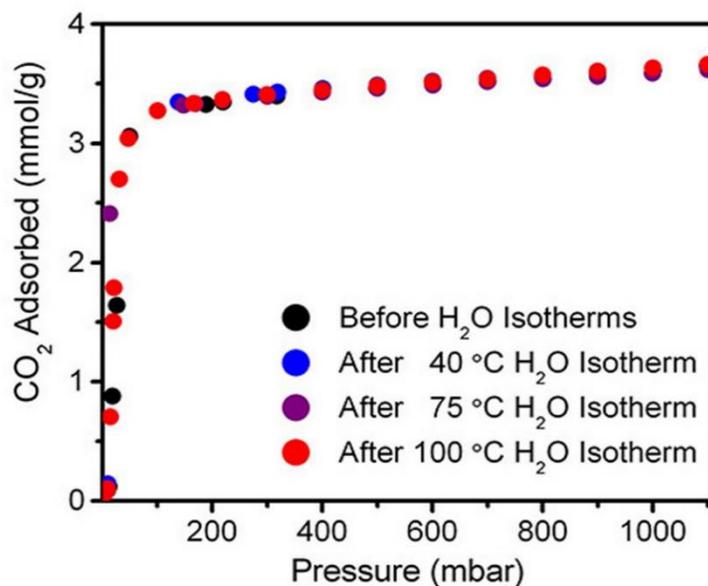


Figure 12. Isothermal adsorption measurements of CO₂ with a sample of mmen-Mg₂(dobpdc) before exposure to water and after water isotherms at 40, 75 and 100 °C¹¹².

In addition, Liao *et al.*¹¹³ shown that functionalizing MOFs with monodentate hydroxide on their pore surfaces may significantly improve CO₂ capture performance. The MOFs materials can absorb up to 4.2 mmol/g or 13.4 wt % of CO₂ from simulated flue gases, even at high relative humidity (82 %), and then rapidly desorb it under mild regeneration conditions (N₂ purge at 358 K). Moon *et al.*⁵⁰ synthesized [Mg₂(dobpdc)(DMF)₂] and soaked it in polystyrene (PS) solution for one day (150 mg PS in 5 mL N,N-dimethylformamide (DMF)). [Mg₂(dobpdc)(DMF)₂]@PS was washed three times with DMF to remove excess PS from crystals before being dried under vacuum. One day was spent activating the material under vacuum at 250 °C. Figure 13 depicts the composite's remarkable moisture stability after one day of exposure to 90% humidity.

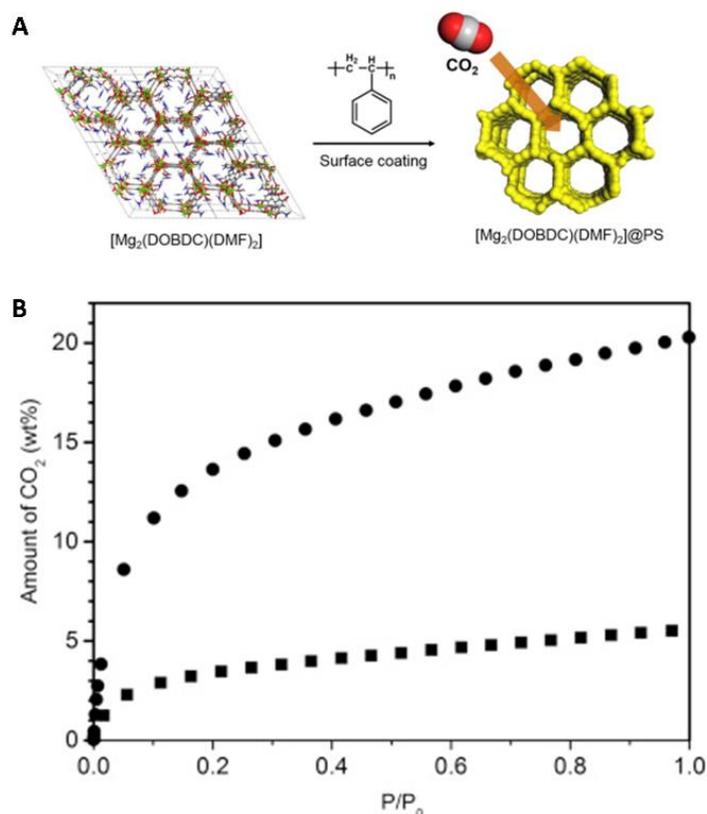


Figure 13. **A.** The structure of [Mg₂(dobpdc)(DMF)₂]. **B.** CO₂ sorption isotherms of [Mg₂(dobpdc)(DMF)₂] (squares) and [Mg₂(dobpdc)(DMF)₂]@PS (circles) after humidity exposure⁵⁰.

Using an innovative in-situ microencapsulated synthesis, Yu *et al.*¹¹⁴ reported the production of a new MOFs-based hybrid sorbent. Figure 14 depicts the production of double emulsions of MOFs

precursor solutions and UV-curable silicone shell fluid using a custom-made double capillary microfluidic setup. Microscopic photos of encapsulated HKUST-1 are shown in Figure 15. As illustrated in Figure 15, the geometry and size of the microcapsules are quite uniform^{105, 114}. Depending on the system parameters of the microfluidic device and the fluid characteristics, the average capsule diameter is between 300 and 500 microns and the shell thickness is between 35 and 75 microns.

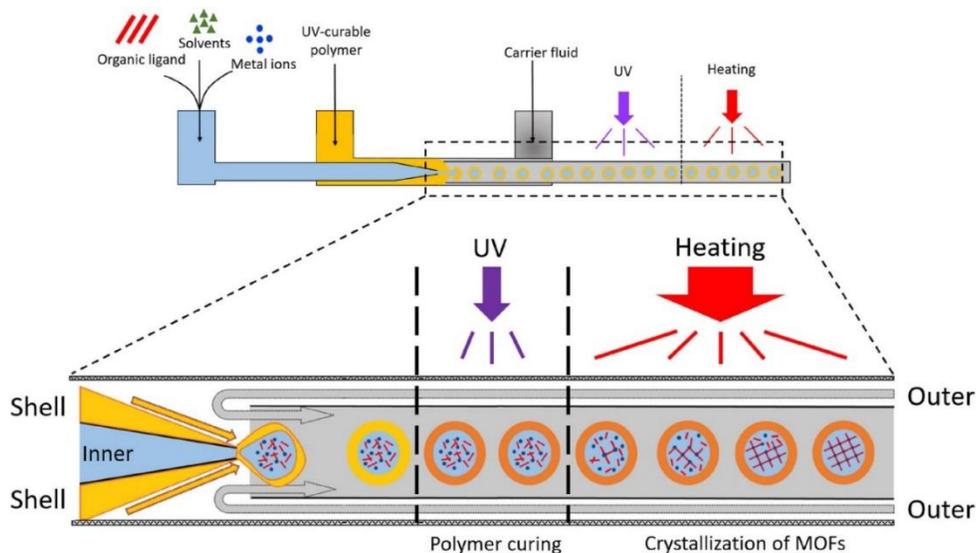


Figure 14. Schematic of the microfluidic system for in-situ encapsulated synthesis of MOFs¹¹⁴.

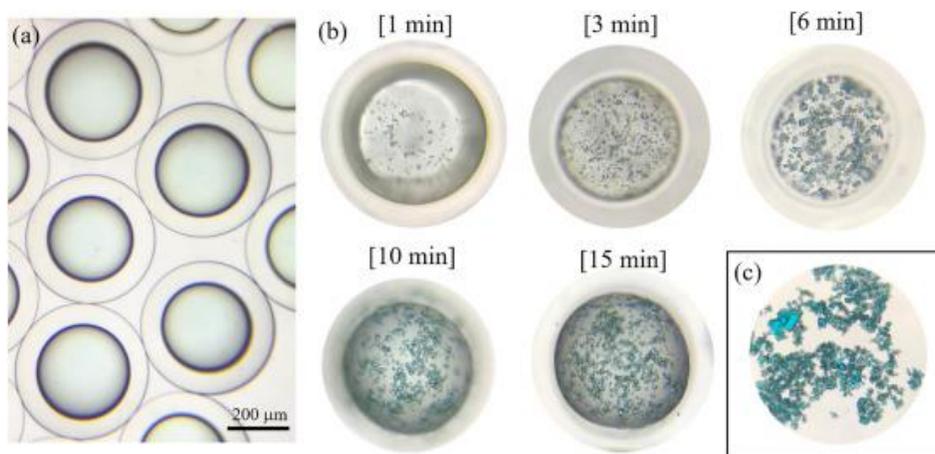


Figure 15. Images of HKUST-1 contained within a capsule. (a) Produced microcapsules containing HKUST-1 precursor solutions; (b) The stages of HKUST-1 crystal formation during the in-situ

thermal reaction within the microcapsules (reaction time: 1–15 min); (c) A comparison image of HKUST-1 crystals synthesized via the conventional solvothermal method using a bulk solution¹¹⁴.

Consequently, HKUST-1 is effectively produced within the encapsulated droplets of gas-permeable microcapsules. Through TGA analysis, the CO₂ capture behavior of encapsulated HKUST-1 is examined. As demonstrated in Figure 16, the CO₂ capacity is up to 4 mmol CO₂/g MOFs and remains stable after 10 cycles. Microencapsulation is regarded as a potential technique to enhance the stability of sorbents in humid surroundings for CO₂ capture^{16, 115}.

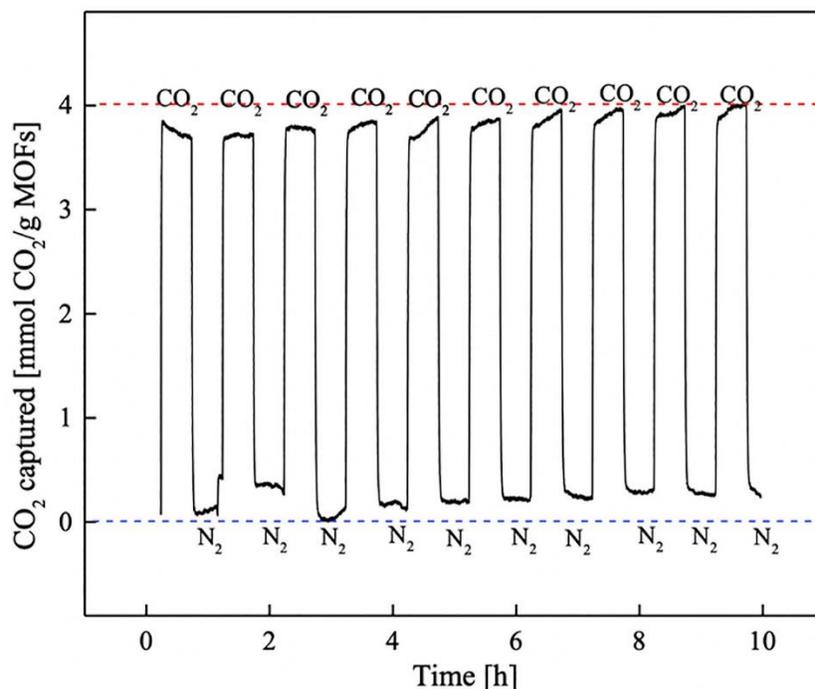


Figure 16. Cyclic study of CO₂ capture by encapsulated HKUST-1¹¹⁴.

5. MOFs and Encapsulated MOFs for Direct Air Capture of CO₂

According to estimates, only 47% of CO₂ emission sources are amenable to traditional carbon capture and storage¹¹⁶, with the remainder coming from diffuse sources such as isolated industrial sites and transportation. This has led to study interest in the contentious topic of CO₂ collection directly from the atmosphere or direct air capture (DAC). Lackner suggested the idea of trapping CO₂ from the air for climate change mitigation in 1999¹¹⁷. DAC has acquired tremendous momentum during the past several years¹¹⁸⁻¹⁴⁷. However, acceptability of these technologies remains restricted¹⁴⁸⁻¹⁴⁹. Cost and technical difficulties have been cited as important problems. The

idea is now widely defined as the direct air capture (DAC) of CO₂, and the IPCC created the name "Negative Emission" for such technologies¹⁵⁰. Several approaches employing various media have been described for DAC, including: physical sorption¹⁵¹⁻¹⁵⁷, sorption by strong bases^{118, 120, 151, 158-164}, sorption by amine-modified materials in a thermal-swing process^{5, 165-172}, sorption by aqueous amino acid solution and followed by precipitation into a guanidine compound¹⁷³⁻¹⁸¹, sorption by ion exchange resin in a moisture-swing process^{128, 149, 182-196}, and also sorption by polyanthraquinone-carbon nanotube composite in a electrochemical-swing process¹⁹⁷⁻²⁰¹.

It is essential to develop sorbent materials for CO₂ sorption from ambient air in order to mitigate climate change and complete the carbon cycle. The utilization of sorbent materials, such as MOFs²⁰²⁻²⁰⁵, is key to most direct air capture methods. However, few research has investigated the use of MOFs for Direct Air Capture of CO₂. Unlike CO₂ capture from high concentration streams^{112, 206-209}, CO₂ is diluted in the atmosphere. Any procedure for collecting CO₂ must avoid using considerable amounts of energy on CO₂ removal from bulk air. This excludes heating, cooling, and compressing air. Also, the issue of MOFs' stability in the presence of water must be resolved.

5.1 MOFs for Physisorption of CO₂:

In the presence of physical sorbents, the interactions between CO₂ and the surface of the material are controlled by van der Waals or ion quadrupole forces. Because physisorption relies on physical interactions to bind CO₂, this process normally takes place on the surface and inside the pores of a sorbent¹⁵². This indicates that materials having a large surface area, such as those with a high porosity or nanoscale dimensions¹⁵³⁻¹⁵⁵, are desirable. Among these substances are zeolites, activated carbon, alumina, and metal-organic frameworks¹⁵¹. However, surface area alone cannot ensure significant CO₂ physisorption capacity.

Regeneration with solid sorbents by physisorption requires less energy than regeneration with typical amine solvents. On the other hand, the thermodynamic drivers for CO₂ capture are diminished, making physisorption at ambient CO₂ levels problematic due to losses in selectivity and absorption capacity. Water vapor is common in ambient air, and MOFs have a very strong affinity for it. Therefore, water's competitive adsorption can greatly lower their CO₂ absorption.

As illustrated in Figure 17, Zaworotko and colleagues investigated the CO₂ sorption capabilities of zeolite 13X, tetraethylenepentamine-impregnated SBA-15, and microporous and ultramicroporous MOFs physisorbents. Results indicate that physisorbents are capable of capturing CO₂ from CO₂-rich gas mixtures, shown as Table 2; however, competition and reactivity with ambient moisture greatly limited their DAC performance. The CO₂ and H₂O sorption data indicated that controlling the pore size and pore chemistry by crystal engineering may be an effective technique for enhancing CO₂ capture performance. The quicker and less energy-intensive recycling of physisorbents might compensate for the lower uptake values, which is a benefit of physisorbents.

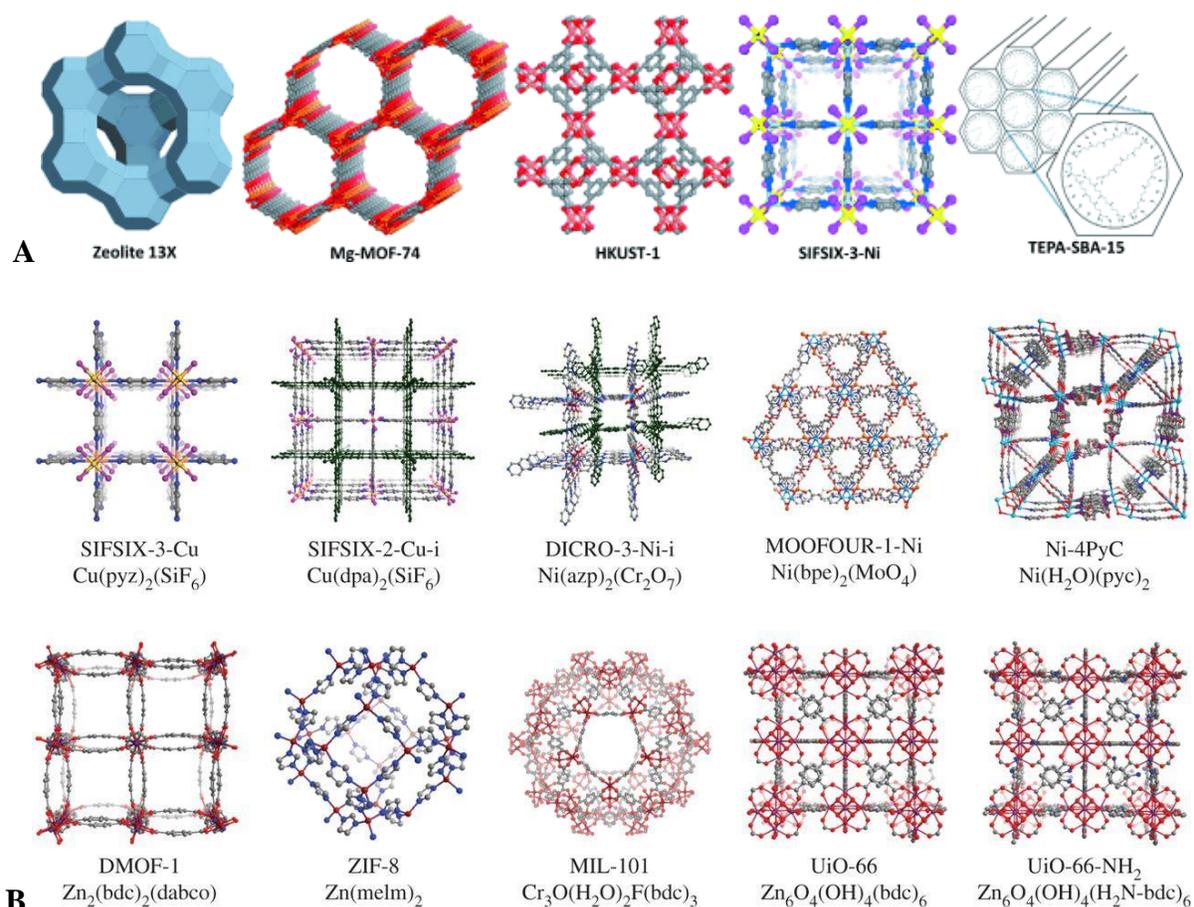


Figure 17. Representative structures of sorbent materials investigated by **A** Amrit Kumar et al.²¹⁰ and **B** David G. Madden et al.²¹¹

Porous Materials	Capacity (mmol CO ₂ /g)	Ref.
SIFSIX-3-Ni	0.182	210
HKUST-1	0.048	
Mg-MOF-74	0.143	
Zeolite 13X	0.034	
SIFSIX-3-Cu	0.320	211
DICRO-3	0.043	
SIFSIX-2-Cu-i	0.036	
MOOFOUR-1-Ni	0.056	
Ni-4-PyC	0.075	
DMOF-1	0.030	
ZIF-8	0.052	
MIL-101	0.023	
UiO-66	0.016	

Table 2. Physisorption Materials under 400 ppm CO₂ and 49% relative humidity under 1 atm pressure at room temperature.

Typically, the MOFs with high CO₂ temperatures of adsorption featured positively charged open-metal sites or metal-oxygen metal bridges. This resulted in powerful electrostatic interactions between the positively charged sites and the negatively charged O atoms in both CO₂ and H₂O. Findley *et al.*²¹² tested the computationally-ready, experimental metal-organic framework (CoRE MOFs) database from 2014 for DAC in humid circumstances, as seen in Figure 18. The performance of zeolite in terms of heat of adsorption is superior to that of MOFs.

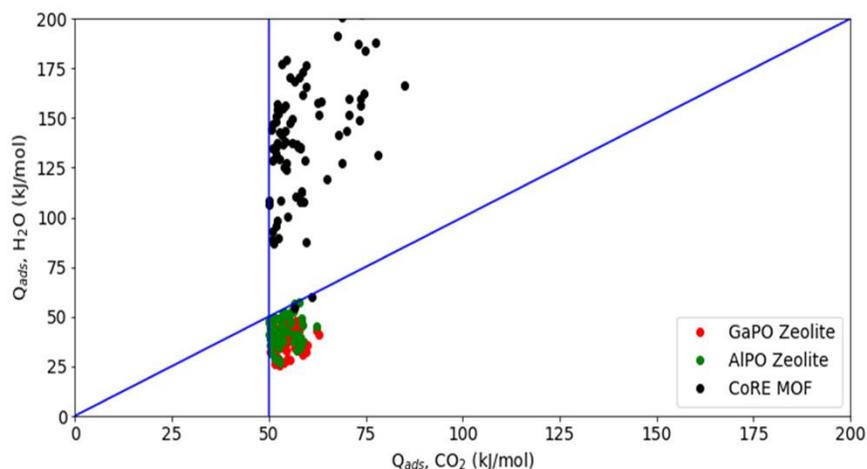


Figure 18. Parity plot showing CO₂ and H₂O heats of adsorption at zero loading in GAPO zeolites (red), AlPO zeolites (green), and CoRE MOFs (black). Adsorbents to the right of the vertical line (50 kJ/mol) and below the parity line (blue) were considered further for direct air capture.

Adjusting the pore size of MOFs might maximize physisorption. SIFSIX-3-Cu was tuned to improve the electrostatic van der Waals contact between CO₂ and the SIFSIX pillars, making it one of the most promising MOFs for DAC in this class²¹³. Using short pyrazine linkages and Cu, the pore size has been reduced to 3.5 relative to structurally comparable precursors. As illustrated in Figure 19, the F-CO₂ distance is short and four fluorine atoms point directly into the square channels, allowing for a high charge density. This MOFs has outstanding adsorption characteristics. At 400 ppm CO₂, the material had an adsorption capacity of 1.24 mmol/g and exhibited good carbon selectivity over N₂ and CH₄. However, the influence of humidity on CO₂ collection was not mentioned in the study.

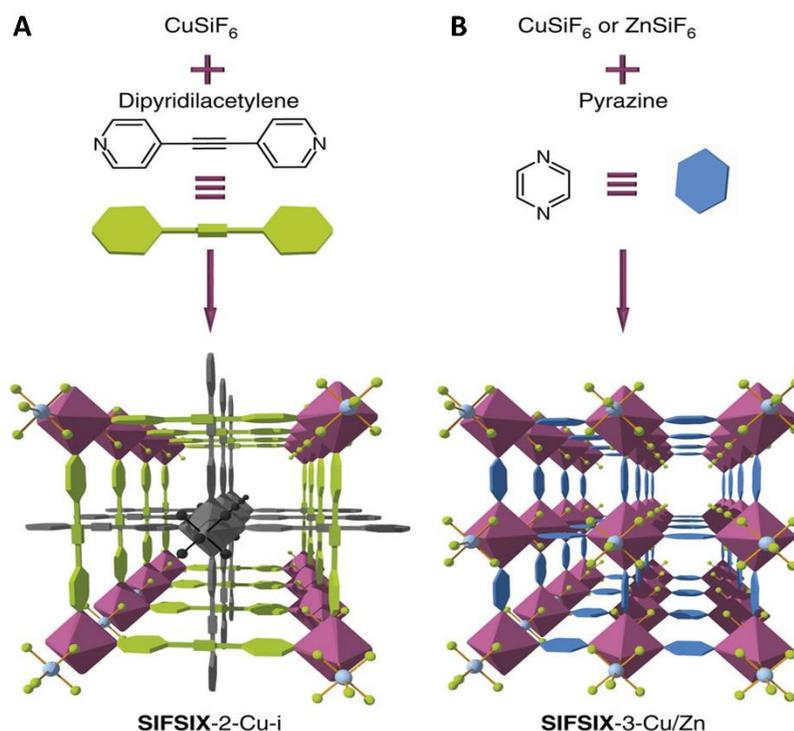


Figure 19. Pore size tuning of the channel structures of **A** SIFSIX-2-Cu-i, **B** SIFSIX-3-Zn or/and SIFSIX-3-Cu. **A** SIFSIX-2-Cu-i; pores size 5.15 Å. **B** SIFSIX-3-Zn; pores size 3.84 Å, BET apparent surface area $250 \text{ m}^2 \text{ g}^{-1}$; SIFSIX-3-Cu; pores size 3.50 Å²¹³.

Dynamic breakthrough gas studies conducted on the ultramicroporous material SIFSIX-18-Ni indicate trace CO_2 removal from humid air (1000 to 10,000 ppm). Mukherjee *et al.*²¹⁴ credit the success of SIFSIX-18-Ni to two normally mutually contradictory factors: a new sort of strong CO_2 binding site and hydrophobicity comparable to ZIF-8. SIFSIX-18-Ni also has rapid sorption kinetics to permit selective capture of CO_2 over N_2 and H_2O , making it a prototype for a hitherto unidentified family of physisorbents that display successful trace CO_2 capture in both dry and wet environments.

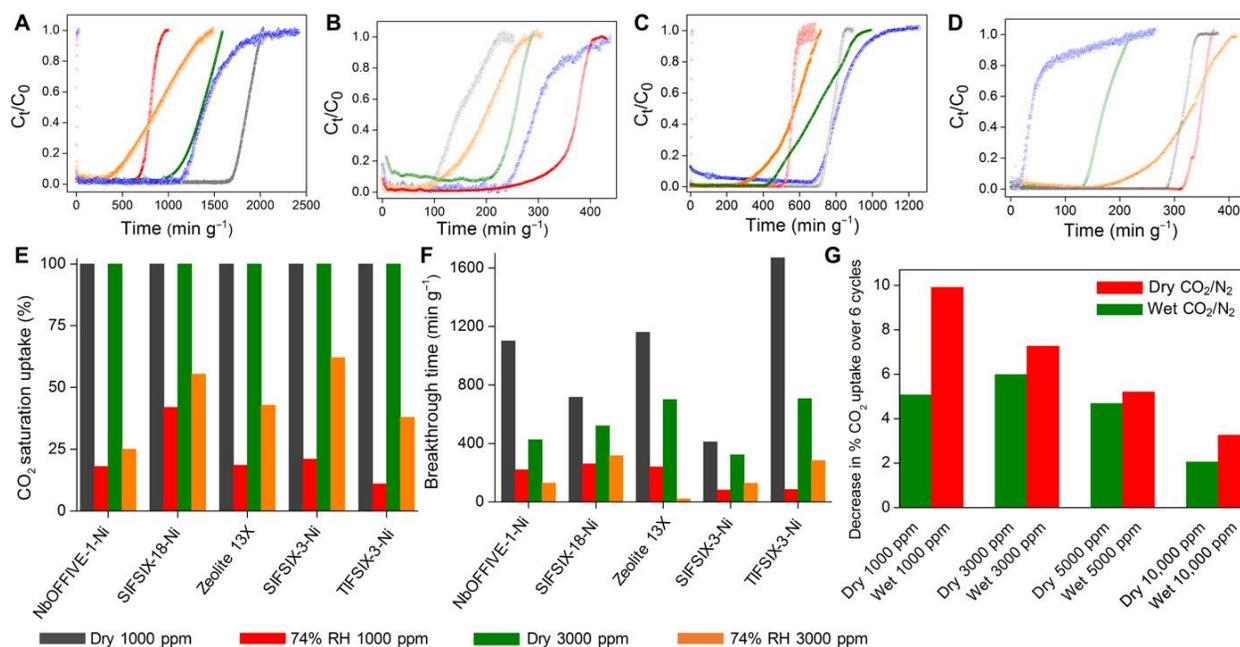
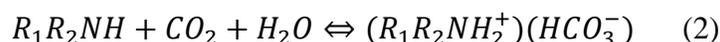


Figure 20. Dynamic gas breakthrough and recyclability tests. Dynamic gas breakthrough tests for SIFSIX-18-Ni- β (red), NbOFFIVE-1-Ni (green), Zeolite 13X (blue), SIFSIX-3-Ni (orange), TIFSIX-3-Ni (gray), and ZIF-8 (purple) using (A) dry 1000 ppm, (B) 74% RH 1000 ppm, (C) dry 3000 ppm, and (D) 74% RH 3000 ppm CO₂/N₂ [v/v = 0.1/99.9% for (A) and (B) and v/v = 0.3/99.7% for (C) and (D)] gas mixtures (298 K; 1 bar; flow rate, 20 cm³ min⁻¹). (E) Bar diagram exhibiting the relative decline in CO₂ saturation uptakes (%) of SIFSIX-18-Ni- β versus other physisorbents (dry/74% RH, 1000/3000 ppm CO₂/N₂). (F) Bar diagram of CO₂ retention times (min g⁻¹) under dry/74% RH, 1000/3000 ppm CO₂/N₂. (G) Decrease in % CO₂ uptakes over six consecutive adsorption-desorption cycles for SIFSIX-18-Ni- β (CO₂/N₂ dry/wet gas mixtures of the following composition: 1000, 3000, 5000, and 10,000 ppm CO₂, without/with 74% RH, saturated with N₂)

5.2 Amine-modified MOFs:

Direct Air Capture of CO₂ has been proposed utilizing amines and polyamines on solid supports. Due to their low energy consumption, chemical stability, and great reversibility, amine-modified solid materials have exhibited substantial promise for CO₂ extraction from ambient air. There are two distinct sorption mechanisms: (1) Under dry circumstances, the reaction between primary and secondary amines and CO₂ produces carbamate or carbamic acid²¹⁵⁻²¹⁸. (2) Under circumstances

of humidity, amines react with CO₂ to form bicarbonate²¹⁹⁻²²¹. Under dry and wet circumstances, secondary amines R₁R₂NH react with CO₂ according to Equations 1 and 2²²².



The most common methods for the preparation of supported amine sorbents are **(1)** impregnation of amines on porous materials, such as silica, alumina, activated carbon, MOFs, zeolites, and clays²²³⁻²⁴². This review focuses on MOFs²⁰²⁻²⁰⁵. **(2)** The method of functionalization of MOFs for post-combustion CO₂ collection and Direct Air Capture has been understood for a very long time¹³⁷. Particular MOFs are synthesized by coordinating certain solvent molecules, often DMF or H₂O, to the metal core. These can be eliminated by heating to around 400 degrees Celsius, leaving coordinately unsaturated areas (CUS). In typical MOFs carbon capture, these regions serve as adsorption sites, as the core metal is a strong Lewis acid. These CUS have been used to enable alkylamine-functionalization of DAC. After removing the solvent molecules, the MOFs is put in an organic solvent containing the alkylamine of choice, and the CUS are functionalized to variable degrees depending on the framework. The selected diamines are very basic and firmly coordinate to Lewis acidic metal centers, leaving one amine end unoccupied.

Choi *et al.*¹⁶⁸ introduced pendent amines into the MOFs micropores by modifying MOFs Mg/dobpdc with ethylene diamine (ED). Over four adsorption-desorption cycles with temperature fluctuation, the CO₂ capture below 390 ppm was evaluated. ED-Mg-MOF-74 had an adsorption capacity from 1.51 mmol/g to 1.55 mmol/g with no significant change over four cycles, which was higher than non-functionalized Mg-MOF-74 (which also experienced a 20% decrease in adsorption capacity) and close to the final value of PEI-silica at 1.65 mmol/g, which experienced a 29% decrease from 2.36 mmol/g.

Lee *et al.*¹¹⁰ shown that an ethylenediamine-functionalized metal-organic framework (MOFs) can collect CO₂ from ambient air. As illustrated in Figure 21, the MOFs is mmen-Mg₂-(dobpdc), which is an equivalent of Mg-MOF-74 with expanded linker ligands (4,4'-dioxido-3,3'-biphenyldicarboxylate) that increased the pore space from 11 to 18.4. The CO₂ absorption capability of the sorbent is 2.83 mmol/g from a 390 ppm CO₂/N₂ combination at 25 °C. This study also revealed that amine-functionalized MOFs are not significantly affected by humidity, with en-

Mg₂(dobpdc) and mmen-Mg₂(dobpdc) exhibiting near-perfect performance after capturing dilute CO₂ from humid air, whereas Mg-MOF-74 experienced a significant decrease, likely due to water molecules binding to CUS and being difficult to remove. However, temperature swing research revealed a 6% decrease in adsorption capacity following 5 cycles.

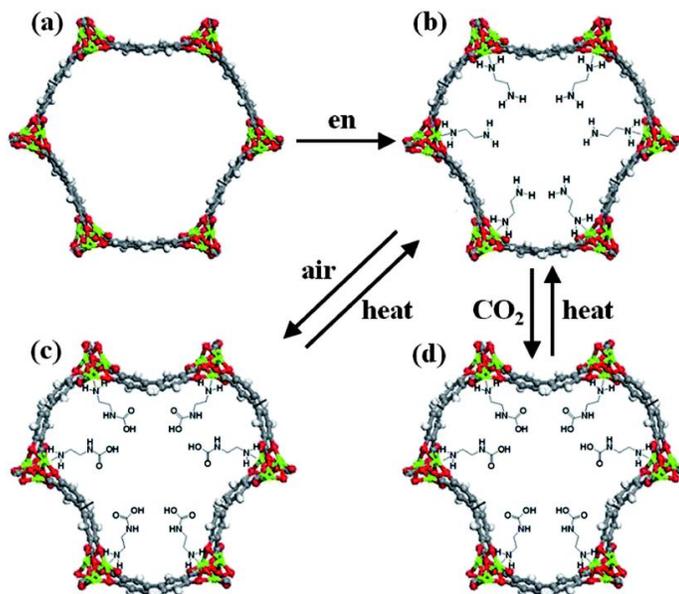


Figure 21. Structures of (a) activated Mg₂(dobpdc) (M=Zn,Mg; dobpdc=4,4'-dioxido-3,3'-biphenyldicarboxylate), (b) en-functionalized Mg₂(dobpdc) (en=ethylenediamine), (c) CO₂ capture from ambient air, and (d) CO₂ capture from flue gas. A reversible transformation between en-functionalized Mg₂(dobpdc) and en-functionalized Mg₂(dobpdc) occurs during heat treatment with CO₂¹¹⁰.

Darunte *et al.*²⁴³ investigated the kinetics of CO₂ sorption by the sorbent using step-function isotherms. The stepped isotherm is adjustable, and the system may be optimal for DAC applications. CO₂ adsorption in Mg₂(dobpdc) was investigated under ultra-dilute circumstances utilizing a breakthrough adsorption setup as a surrogate for real flow systems. The shape of the isotherm and kinetic parameters significantly lowered the CO₂ capture percentage at low concentrations, hence diminishing the feasibility of Mg₂(dobpdc) for practical DAC applications. Liao *et al.*²⁴⁴ observed that the CO₂ sorbent reported by Lee *et al.*¹¹⁰ did not attain saturation at 400 ppm CO₂ in air. This is attributed to the strong intermolecular hydrogen bonds between two neighboring amine groups, which must be broken by higher pressure CO₂^{112, 245}. Liao *et al.*²⁴⁴

resolved this issue by replacing the ethylenediamine molecule with an even shorter diamine: hydrazine (H_2N_4) The authors demonstrate that the novel material $[\text{Mg}_2(\text{dobpdc})(\text{H}_2\text{N}_4)_{1.8}]$ absorbs 3.89 mmol/g CO_2 at 400 ppm, 298 K, under dry conditions.

5.3 Potential of water-stable and encapsulated MOFs as moisture-swing CO_2 capture sorbent:

Lackner¹²⁸ presented a method for capturing CO_2 from ambient air utilizing moisture-swing sorbents in order to offset the high energy cost associated with amine-based sorbents. They bind CO_2 in dry environments and release it in moist environments. Water is crucial to the CO_2 sorption-desorption mechanism. These sorbents are composed of an anion-exchange resin with quaternary ammonium cations coupled to a polymer network with hydroxide or carbonate anions as mobile counterions. As shown in Figure 22 for a wet resin without CO_2 loading, termed State 1 by Shi *et al.*¹⁴⁹, stable carbonate anions are the predominant counterions. As the resin dries, its water content decreases, and the carbonate ion becomes less stable. It causes one of the remaining water molecules to separate into an HCO_3^- ion and an OH^- ion. State 2, which contains OH^- ions, has a significant affinity for CO_2 . The resin absorbs CO_2 from air even at low partial pressure. Consequently, State 3 is a completely bicarbonated state. State 4 results from the complete hydration of the bicarbonate ions caused by wetting the resin. This causes CO_2 to escape from the moist condition (desorption), which leads to State 1 and the completion of the cycle.

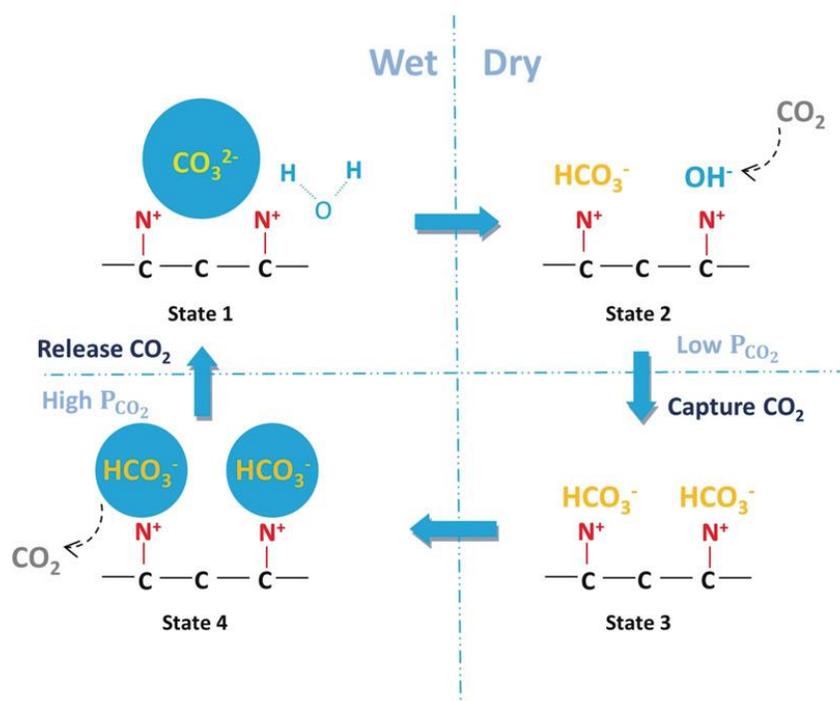


Figure 22. Moisture-swing sorbent for CO₂ capture from ambient air¹⁴⁹.

Recently, Shi *et al.*¹⁹² investigated the impacts of sorbent factors on CO₂ capture efficiency, paving the door for the future development of sorbents for DAC. Due to their large surface area, porosity, and controllable pore size, water-stable or encapsulated MOFs offer a great deal of promise for use as moisture-swing sorbents. Changing the pore size of MOFs might increase the CO₂ absorption capacity of moisture-swing in humid climates.

The CO₂ capacity of different types of MOFs discussed in the review under different conditions has been summarized in Figure 23.

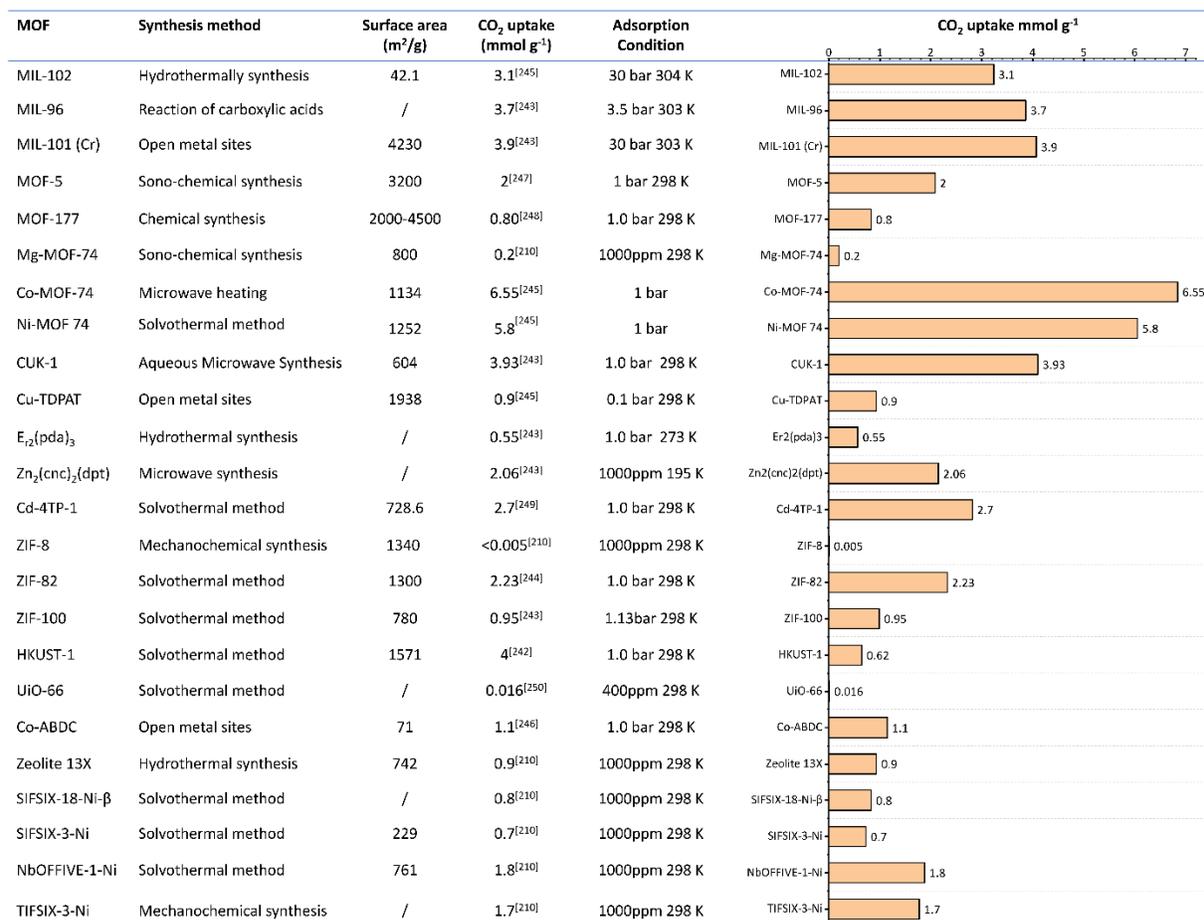


Figure 23: CO₂ capacity of different water-stable MOFs.

6. Summary and Outlook:

The benefits of MOFs include their form, pore structure, pore size, and surface characteristics adaptability. Temperature and humidity influence the sorption capacity and selectivity of the majority of sorbents. The performance of MOFs in a high-pressure CO₂ stream is exceptional, but their sorption capabilities are low when handling gas combinations. Currently, MOFs are badly impacted by water and have water stability difficulties, since the materials experience irreversible structural deterioration in an environment containing water. Therefore, synthesis of water-stable MOFs or encapsulation of MOFs with hydrophobic coatings are essential for CO₂ capture by MOFs from wet flue gas or ambient air.

With ongoing attempts to reveal the link between MOF structure and hydro-stability and to investigate methodologies for synthesizing water-stable MOFs, an increasing number of water-stable MOFs have been synthesized. They may be categorized into three groups: metal carboxylate frameworks containing high-valence metal ions, metal azolate frameworks, and MOFs with specialized functionalization. MOFs can also be protected by the hydrophobic coating approach. Certain constraints, such as high-temperature heating, lengthy manufacture, or costly hydrophobic polymers, must be avoided. All MOFs should be compared to one another and to other materials to determine which is now the most cost-effective and which areas require more investigation.

Thus far, technological advancements have been remarkable. However, considerable further study is required. In CO₂ capture from wet flue gas, the fundamental demand is for more chemically and thermally resistant materials that can tolerate the high quantities of water in the flue gas stream while simultaneously adjusting the temperature necessary for regeneration. In addition, although the majority of adsorption studies to date have evaluated the performance of materials using single-component CO₂ and N₂ adsorption isotherms or breakthrough experiments employing a CO₂/N₂ mixed gas, a greater understanding of the impact of the presence of water and other minor components in the flue gas is urgently required. For a comprehensive evaluation of the performance of a specific material, it is necessary to examine metal-organic frameworks in parameters that mimic real working conditions (gas composition, temperature, and pressure).

The development of MOFs for Direct Air Capture of CO₂ is still in its infancy, with several obstacles left. For the physisorption technique, it is vital to fine tune the MOFs ligands or MOFs metal centers in order to modify their pore size to match the diameter of the CO₂ molecule. CO₂ content in the air is extremely low. The optimal pore size of MOFs can improve its CO₂ storage ability. For the chemisorption process, there are particular enhancements that must be made: the high regeneration energy and synthesis cost of alkylamine-functionalized MOFs must be addressed, although performance is anticipated to increase when other ligands are tried with various frameworks. This is guided by the suggested mechanism, which predicts that altering the distance between surrounding amines and the core metal may increase performance. Sorption of a sorbent for DAC should be performed under actual ambient air conditions (78 percent N₂, 21 percent O₂, 1 percent inert gases and water vapors, under different humidity conditions). Almost no research has been conducted on MOFs for Direct Air Capture of CO₂ under real ambient air conditions.

In addition, if CO₂ capture can be paired with its later conversion, the overall sustainability of carbon capture and conversion systems can be substantially enhanced. The creation of catalytic MOFs is an additional field of ongoing study, and MOFs such as Lanthanide MOFs may be constructed to successfully convert CO₂ under aqueous-rich and mixed-gas conditions⁶⁵. The effective mass and energy transfer through these materials should be thoroughly explored. MOFs can be designed as hybrid systems that can host both CO₂ collection and conversion.

Future research directions of the development of water-stable and encapsulated MOFs for CO₂ capture has been shown in Figure 24. In conclusion, all aspects of MOFs for CO₂ collection from wet flue gas and ambient air should be evaluated, including sorbent stability, sorption kinetics, sorption capacity, selectivity, regeneration energy penalty, and cost. Developing water-stable, energy-efficient, and low-cost MOFs for CO₂ collection is necessary to combat global climate change.

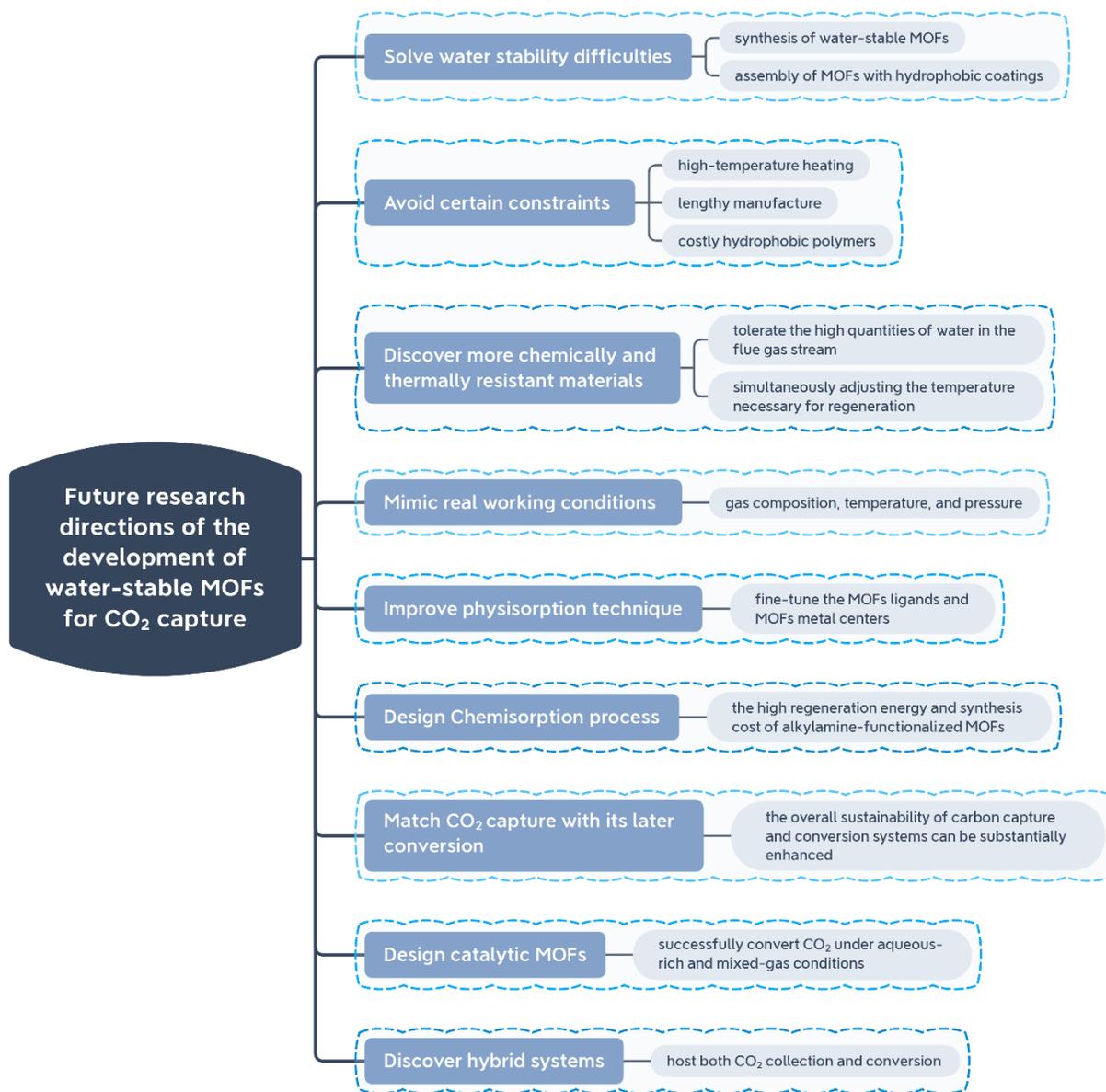


Figure 24. Future research directions of the development of water-stable MOFs for CO₂ capture

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DECLARATION OF INTERESTS

All authors declare no competing interests.

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