

CD-MOFs for CO₂ Capture and Separation: Current Research and Future Outlook [†]

Edgar Clyde R. Lopez ^{1,2,*}  and Jem Valerie D. Perez ^{1,*}

- ¹ Nanotechnology Research Laboratory, Department of Chemical Engineering, University of the Philippines Diliman, Quezon City 1101, Philippines
- ² Department of Chemical Engineering, University of Santo Tomas, España, Manila 1015, Philippines
- * Correspondence: edgarclydelopez09@gmail.com (E.C.R.L.); jdperez@up.edu.ph (J.V.D.P.)
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Abstract: Carbon dioxide (CO₂) capture and separation constitute an important field of research as we seek to reduce the effects of climate change. Because of their porosity, resilient crystallinity, high adsorption capacity, and affinity for CO₂, cyclodextrin-based metal-organic frameworks (CD-MOFs) have emerged as attractive materials for carbon capture. This paper gives an overview of CD-MOFs and their applications in CO₂ capture and separation. Several studies have been conducted to synthesize and characterize CD-MOFs for CO₂ capture. The causes of the high binding affinity of CO₂ in CD-MOFs were discovered through mechanistic studies on CO₂ adsorption. Furthermore, CD-MOF modifications have been carried out to improve the sorption capacity and selectivity of CO₂ adsorption. Meanwhile, several researchers have reported using CD-MOFs for gaseous CO₂ membrane separation. This paper also highlights the current gaps in CD-MOF research and future outlooks in carbon capture and separation using CD-MOFs.

Keywords: cyclodextrin metal–organic frameworks; carbon dioxide capture; adsorption; separation

1. Introduction

Carbon dioxide (CO₂) concentrations in the atmosphere are increasing, causing global warming and climate change. A crucial strategy for lowering CO₂ emissions from industrial processes and power plants is carbon capture and storage (CCS).

In the carbon capture and storage (CCS) field, there has been a lot of interest in cyclodextrin metal–organic frameworks (CD-MOFs), a relatively young class of materials. These materials are attractive for gas separation applications because of their significant surface area and varied pore sizes. CD-MOFs are made of cyclodextrin (CD) molecules bonded with metal ions. Cyclodextrins are cyclic oligosaccharides containing six to twelve glucose units depending on the type. Hydrophobic holes in the centers of these molecules can house extracellular molecules like CO₂. Metal ions and CD molecules combine to form a porous network with a wide surface area and variable pore size. One of the major advantages of CD-MOFs for CO₂ capture is their high selectivity for CO₂ over other gases, including nitrogen (N₂) and methane (CH₄). Additionally, CD-MOFs have a high CO₂ adsorption capacity, allowing them to remove a sizable amount of CO₂ from a gas mixture.

This paper will discuss the current research on CD-MOFs for CO₂ capture. Current research gaps and future research outlooks are also highlighted.

2. CD-MOFs for Carbon Dioxide Capture

Cyclodextrin-based MOFs have found applications in carbon capture due to their porosity, robust and permanent crystallinity, high uptake and low pressure, and good



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affinity. The combination of chemisorption and physisorption allows CD-MOFs to have unprecedented uptake capacities superior to those of traditional MOFs and other adsorbents. Table 1 shows the summary of the CO₂ performances of various CD-MOFs.

CD-MOF-1 was created by Yan et al. via the vapor diffusion of methanol into a KOH solution of γ -cyclodextrin [1]. According to their CO₂ adsorption measurements, a completely evacuated CD-MOF-1 has an adsorption capacity of 24 mg of CO₂ g⁻¹. In the CD-MOF crystal, they discovered 0.7 adsorbed CO₂ molecules for every γ -CD molecule. The activation energy of CO₂ adsorption was determined to be -58.22 kJ mol⁻¹, which was close to the enthalpy of reaction for bicarbonate formation, proving that the primary adsorption mechanism is CO₂ chemisorption due to interaction with the most reactive primary hydroxyl groups located on each γ -CD torus, resulting in carbonic acid formation.

According to Gassensmith et al. [2,3], CD-MOF-2 exhibits an exceptional selectivity of 3000-fold for CO₂ adsorption versus CH₄, a figure that has not been matched in recent studies. At the inflection point, it shows a significant affinity for CO₂, indicating chemisorptive CO₂ capture with a sorption capacity of about 23 cm³/g between 273 and 298 K. Isotherm measurements have revealed that the abrupt shift in higher-pressure regimes (>1 Torr) becomes significantly more dependent on temperature. This is in accordance with covalent bond formation happening preferentially at low pressures and giving way to physisorption at rising pressures. The authors proposed that CO₂'s observed favorable reactivity results from CD-MOF-2's abundance of readily accessible hydroxyl groups, which define the perimeter of the material's large pores (1.7 nm in diameter) and can act as reactive functional groups for the reversible formation of carbonic acid. Their solid-state NMR experiments supported this idea. As a result, the production of bound CO₂ molecules is made more accessible by these high local concentrations of hydroxyl groups. This is similar to the improved reactivity in supramolecular host/guest complexes, in which reactivity is increased by orders of magnitude as a result of the higher local concentration within a supramolecular ensemble. Using a methyl red indicator found in CD-MOF-2 that changes color when exposed to CO₂, they were also able to demonstrate that the primary mechanism for CO₂ uptake is the creation of a carbonate ester via interaction with a hydroxyl group of a γ -CD. The transitory carbonic acid function returned to the alcohol, releasing CO₂ in a manner similar to Le Chatelier's principle, but when the source of CO₂ was removed, the crystals changed back to a yellow tint. Furthermore, it is interesting that CD-MOF-2's strong CO₂ absorption was lost upon pulverization since it became amorphous [2,3].

To better understand the process of CO₂ adsorption in CD-MOF-2, Wu et al. [3] used a calorimetric technology to directly evaluate the enthalpy of gas uptake as a function of coverage. According to isotherm investigations, CD-MOF-2 exhibits a type I isotherm with steep gas absorption in the early low-pressure zone, suggesting a powerful chemical interaction between CD-MOF-2 and CO₂ molecules. Studies using microcalorimetry have revealed that as coverage increases, the differential enthalpy of CO₂ adsorption becomes less exothermic. The strongest interaction between CO₂ and any MOF, amine, or zeolitic sorbent at room temperature has been measured at near-zero coverage, where the differential enthalpy of adsorption is 113.5 kJ per mole of CO₂. This supports the formation of strong chemical bonds between the most reactive primary hydroxyl groups of CD-MOF-2 and adsorbed CO₂. When the surface coverage is between 0.1 and 0.3 CO₂ per nm², the enthalpy of CO₂ adsorption reaches a first plateau (-65.4 kJ/mol CO₂), which they attributed to the adsorption of CO₂ onto the majority of the less-reactive hydroxyl groups, which may include both primary and secondary hydroxyls. The first plateau of the differential enthalpy curve abruptly changes to the second plateau at roughly -40.1 kJ/mol CO₂, after which the CO₂ adsorbed is thought to be physisorbed as the coverage of CD-MOF-2 rises over 0.3 CO₂ per nm². According to the authors, the predominant adsorption mechanism is CO₂ adsorption on the structural sugar alcohol groups rather than interaction with accidental OH⁻ in the pores. They also demonstrated that, whereas all other adsorbed CO₂ is reversible, the CO₂ attached to the most reactive primary hydroxyl groups is bound

irreversibly at about 0% coverage, even when applying a strong vacuum throughout the desorption process.

It was recently reported [4] that the vapor-diffusion of methanol in a Teflon-lined autoclave at 353 K for 15 h enabled the quick synthesis of nanoporous CD-MOF. Following various experimental cycles, it was discovered that CO₂ adsorption is completely reversible based on matching isotherms. CD-MOF's free hydroxyl groups interact with CO₂ in NMR tests, increasing the CO₂ absorption capacity (44 mg g⁻¹) at pressures below 1.32 mbar and temperatures between 273 and 298 K. This notion was subsequently supported by microcalorimetry experiments, which revealed that the adsorption energy recorded at zero-coverage was comparable to the enthalpy of reaction between aqueous hydroxide and gaseous CO₂ (66.4 kJ mol⁻¹ at 25 °C) and that the adsorption energy decreases with coverage, indicating that the interaction between CO₂ and KOH is not the primary adsorption mechanism. Finally, it was demonstrated that CO₂ uptake rises with pressure and falls with temperature. At 303 and 323 K, CD-MOF had maximum sorption capacities of 326 and 268 mg g⁻¹, respectively.

DFT simulations on CD-MOF-2 were conducted to understand the mechanism of CO₂ adsorption in CD-MOFs. While CO₂ adsorption on negatively charged alkoxide groups happens spontaneously, it is thermodynamically impossible for CO₂ to bind with neutral alcohol groups on CD-MOF-2's cyclodextrin units. It was shown that the hydrogen bonds formed by the adsorption sites and the alkylcarbonic adducts with the surrounding alcohol groups significantly impacted the strength of CO₂ binding. CD-MOF-2's hydroxyl counterions pull protons away from the cyclodextrin alcohol groups to increase the nucleophilic strength of the cyclodextrin alcohol groups and transform them into strongly binding alkoxide chemisorption sites. In contrast to earlier experiments, it was observed that CO₂ molecules bound to primary and secondary sites. Additionally, it was shown that the previously identified physisorption of weak CO₂ binding can be attributed to weak chemisorption [5].

The first amino-functionalized CD-MOF-2 was created by Hartlieb et al. [6]. They discovered that the BET surface area of NH₂-CD-MOF-2 is lower (963 m² g⁻¹) than that of CD-MOF-2 (1030 m² g⁻¹). At low pressures, there is significant affinity between the framework and CO₂, indicating chemisorption, which leads to the formation of carbonic acid functionalities on the primary face's free hydroxyl groups. At high pressures, physisorption occurs, with a point of inflection of 16 cm³ g⁻¹. Additionally, they discovered that NH₂-CD-MOF-2 can permanently store CO₂ in the form of carbamates or bicarbonates while still being capable of being recycled by simply dissolving the framework in water to hydrolyze the carbamic acid groups, followed by recrystallization with ROH or Me₂CO vapor to recreate the NH₂-CD-MOF-2 framework [6].

According to Xu et al. [7], the synthesis of NH₂-β-CD-MOF utilizing 6-NH₂-β-CD was accomplished using ultrasound. Using p-toluenesulfonyl, which has a stronger leaving ability than hydroxyl, the hydroxyl group at the C6 position of β-CD was replaced with a toluenesulfonyl group to create 6-OTs-β-CD, which was then converted into 6-NH₂-β-CD through a substitution process with ammonia. According to their method, the sonic cavitation brought on via ultrasonication raised the temperature, quickened the cooling rate, and sped up the fabrication of NH₂-γ-CD-MOF, cutting the synthesis time in half, leaving it at about two hours. However, this did not produce single crystals but mesoporous, polycrystalline shell-like particles with pore diameters concentrated at 2 nm. The particle size was around 25 nm. Additionally, utilizing the vapor diffusion approach and the empirical formula of [C₄₂H₇₀NO₃₄K]_n, they were able to create NH₂-β-CD-MOF, which crystallized on the P₂₁ space group via the coordination of potassium cations with hydroxyl and amino groups on the -CD. The maximal adsorption capacity of NH₂-β-CD-MOF (12.3 cm³/g) is 10 times greater than that of β-CD-MOF (1.2 cm³/g), according to their CO₂ adsorption/desorption studies. Because carbon dioxide and the amino group in NH₂-β-CD-MOF have such a great affinity for one another at lower pressures (0–200 mmHg), they were able to permanently fix CO₂ and increase the CO₂ gas uptake via the chemisorption

process to $7.8 \text{ cm}^3/\text{g}$. With increasing pressure, the NH_2 - β -CD-MOF selectivity of CO_2/N_2 (1:1, v/v) increased noticeably. It reached a maximum value of 947.52 at 273 K. According to the findings of their DFT study, adding amino groups as polar functional groups improved the water stability of NH_2 - β -CD-MOF because these groups can more successfully compete with foreign water molecules than hydroxyl groups, preventing water molecules from attacking metal sites ($-\text{OH}\cdots\text{K}^+\cdots\text{O}$). NH_2 - β -CD-MOF can be recycled using a secondary ultrasonic technique while retaining its full CO_2 adsorption capacity.

Table 1. Summary of CO_2 capture performances of CD-MOFs.

MOF	Synthesis Method	Metal Precursors	CD	Remarks	Ref.
CD-MOF-1	Vapor diffusion	KOH	γ -CD	Completely evacuated CD-MOF reached $24 \text{ mg of CO}_2 \text{ g}^{-1}$	[1]
CD-MOF-2	Vapor diffusion	RbOH	γ -CD	Selectivity for CO_2 vs. CH_4 was nearly 3000-fold	[2]
CD-MOF-2	Vapor diffusion	RbOH	γ -CD	Recorded the strongest interaction between CO_2 and any MOF, amine, or zeolitic sorbent at room temperature.	[3]
γ -CD-MOF	Solvothermal Vapor diffusion	KOH	γ -CD	Maximum CO_2 adsorption capacity = 326 mg g^{-1} at 303 K	[4]
CD-MOF-2	Ultrasonic	RbOH	6- NH_2 - β -CD	Sorption capacity was 10 times that of β -CD-MOF CO_2/N_2 selectivity = 947.52 (max)	[7]
CD-HF-1	Vapor diffusion	K-4-methoxy-salicylate	γ -CD	CD-HF-1 does not adsorb N_2 gas, i.e., fully selective for CO_2	[8]
Li/K-CD-MOF	Vapor diffusion	KOH LiOH	γ -CD	CD-MOF-1 = 4.2 mmol g^{-1} Li/K-CD-MOF = 4.5 mmol g^{-1}	[9]
γ -CD-MOF/PEI	Vapor diffusion	KOH	γ -CD	Branched PEI 600- γ -CD-MOFs exhibited the highest CO_2 sorption of 0.9 mmol/g	[10]
CD-MOF-1 CD-MOF-2	Vapor diffusion	KOH RbOH	γ -CD	Uptake at 100 kPa and 298 K: CD-MOF-1 = 2.87 mmol g^{-1} CD-MOF-2 = 2.67 mmol g^{-1}	[11]

Cyclodextrin-based MOFs are starting to diversify since earlier research revealed various intriguing features that might be applicable to various applications. Recently, a hybrid framework (CD-HF) using 4-methoxysalicylate anions as the secondary building blocks and γ -CD as the primary building blocks was created by combining coordinative, electrostatic, and dispersive forces. Shen et al.'s [8] method entailed the use of an organic counteranion co-assembly technique to incorporate organic counterions during the crystallization of cationic MOFs. They used potassium 4-methoxysalicylate (4-MSK) as a source of organic anions (4-MS), K^+ for alkali cation coordination sites, and γ -CD as organic ligands. Their results suggested that the hydrogen bonds in the frameworks improve the crystalline structure's durability and that the solvent is not as crucial for structural stabilization. Temperature-dependent PXRD investigations revealed that CD-HF-1 was stable after being heated to $100 \text{ }^\circ\text{C}$. At 77 K, CD-HF-1 cannot absorb N_2 gas molecules because the size of the channels is similar to the kinetic size of N_2 , preventing N_2 from diffusing into the channels. At pressures below 300 mmHg, the CO_2 gas sorption isotherms of CD-HF-1 (BET surface area of $270 \text{ m}^2 \text{ g}^{-1}$) at 195 K demonstrated a greater CO_2 uptake than CD-MOF-1 (BET surface area of $306 \text{ m}^2 \text{ g}^{-1}$).

By co-crystallizing LiOH and KOH with -CD, Patel et al. [9] created a multivariate CD-MOF. The CO_2 adsorption capabilities of CD-MOF-1 and Li/K-CD-MOF at 273 K and 298 K, respectively, were 4.2 and 4.5 mmol g^{-1} and 3.0 and 3.1 mmol g^{-1} , respectively, in their research. The majority of the CO_2 sorption capacity was seen at low partial pressures or below 0.15 bar, regardless of temperature, as with other CD-MOFs, indicating a chemisorption process. At 77 K and 1 bar, respectively, Li/K-CD-MOF and CD-MOF-1 demonstrated H_2 adsorption capacities of 126 and $121 \text{ cm}^3 \text{ g}^{-1}$, which are greater than CD-MOF-2's ($100 \text{ cm}^3 \text{ g}^{-1}$) capacity. In both cases, Li/K-CD-MOF has a higher sorption

capacity than CD-MOF-1 because of the lower density of Li^+ ions compared with that of K^+ ions and their open metal sites.

Watson et al. modified CD-MOFs with polyethyleneimine to enhance their CO_2 sorption capacity and selectivity. According to their research, the linear PEI- γ -CD-MOFs had a CO_2 sorption capacity of 0.12 mmol/g, whereas the branched PEI 600- γ -CD-MOFs displayed the highest CO_2 sorption at 0.9 mmol/g. As a result of the more efficient spatial distribution of the CO_2 binding sites inside γ -CD-MOF pores in branched PEI, it has a greater sorption capacity than linear PEI. Higher-molecular-weight PEIs were found to clog pores, which reduced their ability to absorb CO_2 [10].

There are limited studies on CO_2 capture from flue gases and other gas mixtures to date, primarily because CD-MOFs are a relatively new family of MOFs. This opens a wide range of possible research avenues ranging from synthesizing new CD-MOFs, modifying existing CD-MOFs to improve their properties and develop a renewable solution to CO_2 capture, and exploring other applications in environmental engineering and other fields.

3. CD-MOFs for Carbon Dioxide Separation

CD-MOFs have also been used to separate carbon dioxide in gaseous mixtures. For instance, Li et al. [11] used CD-MOF-1 and CD-MOF-2 to study the adsorptive separation of C_2H_2 and CO_2 . They noticed high affinity between CO_2 molecules and the CD-MOFs that was demonstrated by the fact that CD-MOF-1 and CD-MOF-2 displayed extremely steep adsorption isotherms for CO_2 at low pressures below 10 kPa. Their absorption amounts peaked at 2.87 mmol g^{-1} at 298 K and 2.67 mmol g^{-1} at 100 kPa, respectively. The selectivity values of $\text{CO}_2/\text{C}_2\text{H}_2$ (1:2, v/v) on CD-MOF-1 and CD-MOF-2 at 100 kPa and 298 K were 6.6 and 16.0, respectively, based on the Ideal Adsorbed Solution Theory (IAST). These results reveal that the newly created materials outperform previously reported porous materials that exhibit inverse adsorption during $\text{CO}_2/\text{C}_2\text{H}_2$ separation. The fourth type of porous material to date with inverse $\text{CO}_2/\text{C}_2\text{H}_2$ adsorption under ambient settings comprise CD-MOF-1 and CD-MOF-2. The Clausius–Clapeyron equation results for the Langmuir isotherms of CO_2 at almost-zero coverage on CD-MOF-1 and CD-MOF-2 were 41.0 kJ mol^{-1} and 67.2 kJ mol^{-1} , respectively. The organic ligand of CD-MOFs was shown to have hydroxyl groups and hydroxide anions, which played a crucial role in the interaction with CO_2 in chemisorption and physisorption, according to a mechanistic investigation of CO_2 sorption. Their dynamic sorption investigations demonstrated the reversibility of the reaction between CO_2 and C_2H_2 , allowing for the one-step removal of trace CO_2 from C_2H_2 .

Additionally, CD-MOFs have been added to composite membranes for CO_2 capture. In a recent study, two-step spin coating was employed to construct PAN- γ -CD-MOF-PU membranes, which were subsequently used in gas permeation tests. The corresponding results showed that PAN- γ -CD-MOF-PU outperformed all currently available PU-based membranes and MOF layer membranes, with a CO_2/N_2 selectivity of 253.46 and a CO_2/O_2 selectivity of 154.28. However, it was observed that the membranes' high selectivity is directional, meaning that gases should pass through the membrane from the PAN side [12].

In another study, CD-MOF was used as a filler in mixed matrix gas separation membranes made of polyurethane. These MMMs were used to separate CO_2 from CH_4 , and the results showed that the PU/ γ -CD-MOF membrane had higher CO_2 and CH_4 permeability than pure PU membranes. A higher filler loading of more than 1 wt.% led to higher methane permeability and decreased CO_2/CH_4 selectivity because the filler in the polymeric matrix did not disperse well, formed holes, and accumulated. As the filler loading in the PU increased, the permeability of both gases dropped. The permeability for CO_2 and CH_4 at an optimal CD-MOF loading of 0.2 wt.% was attained at pressures of 5 bar and 214 and 7.49 barrer, respectively. All the membrane samples displayed a decrease in permeability with increased CO_2/CH_4 selectivity as pressure increased. Tests with mixed gases showed a decrease in permeability and selectivity. At 5 bar of 181 barrer and 26.19, respectively,

the greatest CO₂ permeability and CO₂/CH₄ selectivity in PU/γ-CD-MOF (0.2 wt.%) were discovered [13].

For the separation of CO₂/CH₄ gases, mixed matrix membranes based on cellulose acetate/gamma-cyclodextrin MOFs have been used. As the percentage of γ-CD-MOF grew, the permeability of CO₂ and CH₄ in the CA matrix decreased gradually. These results are consistent with the Maxwell model. The ideal CO₂/CH₄ selectivity values were 36.79 and 38.49 at 0.2 and 0.4 wt.% CA/γ-CD-MOF, respectively. As with other membranes, CO₂ and CH₄'s permeability reduced as the pressure rose. Raising the input pressure improved the CO₂/CH₄ selectivity for all the CA/γ-CD-MOF membrane samples in single-gas permeation testing. In the CA/γ-CD-MOF (0.4 wt.%) sample, the highest selectivity was reached at 5 bars. When comparing mixed-gas testing to single-gas testing, the competitive impact of one gas over the other when interacting with the membrane surface affects permeability and selectivity [14].

4. Future Research

Despite CD-MOFs' potential for CO₂ capture, numerous hurdles must be overcome before these materials can be deployed on a large scale. CD-MOFs' lack of stability in the presence of moisture and acidic gases, which can cause the framework to deteriorate over time, is one of the critical problems. Researchers are actively working on generating more stable CD-MOFs by altering the synthesis conditions and employing alternative metal ions and CD molecules. It is critical to highlight that for CD-MOFs to be employed in industrial applications, they must be stable under the severe conditions of the flue gas environment.

Another issue is the scalability of CD-MOF synthesis, which is currently a time-consuming and costly process. Researchers are investigating alternative synthesis approaches, such as microwave-assisted synthesis and spray drying, to increase the scalability and efficiency of CD-MOF manufacturing. Most CD-MOFs that have been synthesized are based on alkali and alkaline-earth metals. CD-MOFs based on other metals, such as copper [15], iron [16], and lead [17], have already been successfully synthesized.

Future research priorities include the development of sustainable synthesis techniques for CD-MOFs. Currently, CD-MOF synthesis necessitates using hazardous solvents and high temperatures, which can harm the environment. To lessen the environmental effect of CD-MOF synthesis, researchers should investigate using green solvents and alternate synthesis methods such as sonochemical synthesis.

Advanced characterization techniques are needed to better understand CD-MOFs' structure and behavior. Techniques including X-ray diffraction (XRD), nuclear magnetic resonance (NMR) spectroscopy, and electron microscopy can be used to obtain detailed information about the structure and stability of CD-MOFs. Researchers could develop new characterization techniques or use existing ones to better understand CD-MOFs and how they might be modified for CO₂ capture.

Most of the studies on CD-MOFs focus on synthesizing and characterizing their structures. So far, the studies that include applications of CD-MOFs are limited to the encapsulation of bioactive molecules [18–22] due to their biocompatibility, solubility, and porous structure. Attempts to extend their use for carbon dioxide separation have succeeded on the laboratory scale. However, none so far have reported the use of transition-metal-based CD-MOFs for carbon dioxide applications.

Aside from stability and scalability, researchers are working to improve CD-MOFs' performance for CO₂ capture. This involves optimizing the framework's pore size and surface area to improve CO₂ adsorption and selectivity. Researchers are also examining how varied operating variables, such as temperature and pressure, affect CD-MOF efficacy for CO₂ capture.

CD-MOFs might be used with membrane separation technologies to generate hybrid CO₂ capture materials. The CD-MOF would be employed as a selective layer in the membrane in this system, allowing for the effective separation of CO₂ from other gases.

This might result in improved CO₂ capture efficiency and reduced energy needs compared to typical amine-based capture systems.

CD-MOFs' performance for CO₂ capture under various operating circumstances might be predicted using computer modeling and simulation. Researchers may then tweak the design and operating parameters of CD-MOFs for optimal CO₂ capture efficiency. Modeling might also be utilized to estimate the long-term stability of CD-MOFs under various environmental conditions.

Finally, real-world testing of CD-MOFs for CO₂ capture is required to fully grasp their potential. This entails putting CD-MOFs through rigorous testing in various working circumstances, such as varied temperatures and pressures and in the presence of other gases. Researchers might also test the scalability and economic feasibility of CD-MOFs in pilot-scale CO₂ capture systems.

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