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CD-MOFs for CO_2 Capture and Separation: Current Research, and Future Outlook †

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Abstract: Carbon dioxide (CO_2) capture and separation is 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 CO_2, 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 CO_2 capture and separation. Several studies have been conducted to synthesize and characterize CD-MOFs for CO_2 capture. The causes for the high binding affinity of CO_2 in CD-MOFs were discovered through mechanistic studies on CO_2 adsorption. Furthermore, CD-MOF modifications have been carried out to improve the sorption capacity and selectivity of CO_2 adsorption. Meanwhile, several researchers reported using CD-MOFs for gaseous CO_2 membrane separation. The 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

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1. Introduction

Carbon dioxide (CO_2) concentrations in the atmosphere are increasing, causing global warming and climate change. A crucial strategy for lowering CO_2 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. A hydrophobic hole in the center of these molecules could house extracellular molecules like CO_2. 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 CO_2 capture is their high selectivity for CO_2 over other gases, including nitrogen (N_2) and methane (CH_4). Additionally, CD-MOFs have a high CO_2 adsorption capability, allowing them to remove a sizable amount of CO2 from a gas mixture.

This paper will discuss the current research on CD-MOFs for CO_2 capture. Current research gaps and future research outlooks are also highlighted.

2. CD-MOFs for Carbon Dioxide Capture

Cyclodextrin-based MOFs found their application for carbon capture due to their porosity, robust and permanent crystallinity, high uptake and low pressure, and good affinity. The combination of chemisorption and physisorption allows CD-MOFs to have unprecedented uptakes capacities superior to traditional MOFs and other adsorbents.

CD-MOF-1 was created by vapor diffusion of methanol into a KOH solution of -cyclodextrin by Yan et al. [1]. According to their CO_2 adsorption measurements, a completely evacuated CD-MOF-1 has an adsorption capability of 24 mg CO_2 g^{-1}. In the CD-MOF crystal, they discovered 0.7 adsorbed CO_2 molecules for every -CD molecule. The activation energy of CO_2 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 CO_2 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 CO_2 adsorption versus CH_4, a figure that has not been matched in recent literature. At the inflection point, it shows a significant affinity for CO_2, indicating chemisorptive CO_2 capture with a sorption capacity of about 23 cm^3/g between 273 and 298 K. Isotherm measurements 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. They proposed that the observed CO_2's favorable reactivity results from CD-MOF-2's abundance of readily accessible hydroxyl groups, which define the perimeter of the material's large pore (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. As a result, the production of bound CO_2 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, which is increased by orders of magnitude and results from the higher local concentration within a supramolecular ensemble. Using a methyl red indicator found in CD-MOF-2 that changes color when exposed to CO_2, they were also able to demonstrate that the primary mechanism for CO_2 uptake is the creation of a carbonate ester by interaction with a hydroxyl group of a γ-CD. The transitory carbonic acid function had returned to the alcohol, releasing CO_2 in a manner similar to Le Chatelier's principle, but when the source of CO_2 was removed, the crystals changed back to a yellow tint. Furthermore, it is interesting that CD-MOF-2's strong CO_2 absorption is lost with pulverization since it became amorphous. [2,3].

To better understand the process of CO_2 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 a steep gas absorption in the early low-pressure zone, which suggests a powerful chemical interaction between CD-MOF-2 and CO_2 molecules. Studies using microcalorimetry revealed that as coverage increases, the differential enthalpy of CO_2 adsorption becomes less exothermic. The strongest interaction between CO_2 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 CO_2. This supports the formation of strong chemical bonds between the most reactive primary hydroxyl groups of CD-MOF-2 with absorbed CO_2. When the surface coverage is between 0.1 and 0.3 CO_2 per nm^2, the enthalpy of CO_2 adsorption reaches a first plateau (−65.4 kJ/mol CO_2), which they attributed to the adsorption of CO_2 onto the majority of 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 CO_2, after which the CO_2 adsorbed is thought to be physisorbed as the coverage of CD-MOF-2 rises over 0.3 CO_2 per nm^2. According to the authors, the predominant adsorption mechanism is CO_2 adsorption on the structural sugar alcohol groups rather than interaction with accidental OH^- in the pores. They also demonstrated that, whereas all other adsorbed CO_2 is reversible, the CO_2 attached to the most reactive primary hydroxyl groups is bound irreversibly at about 0% coverage, even under a strong vacuum throughout the desorption process.

It was recently reported [4] that 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 CO_2 adsorption is completely reversible based on matching isotherms. The CD-MOF's free hydroxyl groups interact with CO_2 in NMR tests, increasing the CO_2 absorption capacity (44 mg g^{-1}) at pressures below 1.32 mbar and temperatures between 273 and 298 K. This was subsequently supported by microcalorimetry experiments, which revealed that the adsorption energy recorded at zero-coverage is comparable to the enthalpy of reaction between aqueous hydroxide and gaseous CO_2 (66.4 kJ mol^{-1} at 25 °C) and that the adsorption energy decreases with coverage, indicating that the interaction between CO_2 and KOH is not the primary adsorption mechanism. Finally, it was demonstrated that CO_2 uptake rises with pressure and falls with temperature. At 303 and 323 K, the 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 CO_2 adsorption in CD-MOFs. While CO_2 adsorption on negatively charged alkoxide groups happens spontaneously, it is thermodynamically impossible for CO_2 to bind with neutral alcohol groups on CD-MOF-2 -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 the CO_2 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, CO_2 molecules bind to primary and secondary sites. Additionally, it was shown that the previously identified physisorption of weak CO_2 binding could 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 NH_2-CD-MOF-2 is lower (963 m^2 g^{-1}) than that of CD-MOF-2 (1030 m^2 g^{-1}). At low pressures, there is a significant affinity between the framework and CO_2, indicating chemisorption, which forms carbonic acid functionalities on the primary face's free hydroxyl groups. At high pressures, physisorption occurs, with a point of inflection of 16 cm^3 g^{-1}. Additionally, they discovered that it can permanently store CO_2 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 Me_2CO vapor to recreate the NH_2-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-NH_2-β-CD through a substitution process with ammonia. According to their method, the sonic cavitation brought on by ultrasonication raised the temperature, quickened the cooling rate, and sped up the fabrication of NH_2-γ-CD-MOF, cutting the synthesis time in half to 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 m. Additionally, utilizing the vapor diffusion approach and empirical formula of $[C_{42}H_{70}NO_{34}K]_n$, they were able to create the NH_2-β-CD-MOF, which crystallized on the P_{21} space group by coordinating potassium cations with hydroxyl and amino groups on the -CD. The maximal adsorption capacity of NH_2-β-CD-MOF (12.3 cm^3/g) is 10 times greater than that of β-CD-MOF (1.2 cm^3/g), according to their CO_2 adsorption/desorption studies. Because carbon dioxide and the amino-group in NH_2-β-CD-MOF have such a great affinity for one another at lower pressures (0–200 mmHg), they were able to permanently fix CO_2 and increase the CO_2 gas uptake by the chemisorption process to 7.8 cm^3/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 improves the water stability of NH_2-β-CD-MOF because they can more successfully compete with foreign water molecules than hydroxyl groups, preventing water molecules from attacking metal sites (–OH···K+···O). The 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.
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]
CD-MOF-1	Vapor-diffusion	KOH	γ-CD	Completely evacuated CD-MOF reached 24 mg CO_2 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 is 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 to CO_2	[8]
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 applied 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 employed 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 is stable after heating to 100 °C. At 77 K, CD-HF-1 cannot absorb N_2 gas molecules because the channels' size is similar to the kinetic size of N_2, which prevents 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 m^2 g^{-1}) at 195 K demonstrated a greater CO_2 uptake than CD-MOF-1 (BET surface area of 306 m^2 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, which indicates 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 cm^3 g^{-1}, more than CD-MOF-2's (100 cm^3 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 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 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 possibility of research ranging from synthesizing new CD-MOFs, modifying existing CD-MOFs to improve their properties and enable 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 that the high affinity between CO_2 molecules and the CD-MOFs was demonstrated by the fact that CD-MOF-1 and CD-MOF-2 displayed extremely steep adsorption isotherms for CO_2 at low pressure 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 of CO_2/C_2H_2 (1:2, v/v) on CD-MOF-1 and CD-MOF-2 at 100 kPa and 298 K is 6.6 and 16.0, respectively, based on the Ideal Adsorbed Solution Theory (IAST). This outperforms previously reported porous materials that exhibit inverse adsorption during CO_2/C_2H_2 separation. The fourth type of porous materials to date with inverse CO_2/C_2H_2 adsorption at ambient settings are CD-MOF-1 and CD-MOF-2. 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. 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 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. Higher filler loading of more than 1 wt.% led to higher methane permeability and decreased CO_2/CH_4 selectivity because filler in the polymeric matrix did not disperse well, formed holes, and accumulated. As the filler loading in PU increased, the permeability of both gases dropped. The permeability for CO_2 and CH_4 at optimal CD-MOF loading of 0.2 wt.% was attained at 5 bar, 214 and 7.49 barrer pressures, respectively. All membrane samples displayed a decrease in permeability with increased CO2/CH4 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 CO_2 permeability and CO_2/CH_4 selectivity in PU/γ-CD-MOF (0.2 wt.%) were discovered [13].

For the separation of CO_2/CH_4 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 CO_2 and CH_4 in the CA matrix decreased gradually. These results are consistent with the Maxwell model. The ideal CO_2/CH_4 selectivity values are 36.79 and 38.49, respectively, at 0.2 and 0.4 wt.% CA/γ-CD-MOF. As with other membranes, CO_2 and CH_4's permeability reduced as pressure rose. Raising the input pressure improves CO_2/CH_4 selectivity for all CA/γ-CD-MOF membrane samples in single gas permeation testing. In the CA/γ-CD-MOF (0.4 wt.%) sample, the highest selectivity is reached at 5 bars. 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 CO_2 capture, numerous hurdles must be overcome before these materials can be deployed on a big scale. CD-MOFs' 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 time-consuming and costly. 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 understand CD-MOFs' structure and behavior better. Techniques including X-ray diffraction (XRD), nuclear magnetic resonance (NMR) spectroscopy, and electron microscopy can be used to get detailed information about the structure and stability of CD-MOFs. Researchers could develop new characterization techniques or use existing ones to understand better CD-MOFs and how they might be modified for CO_2 capture.

Most of the studies on CD-MOFs focused on synthesizing and characterizing their structures. Studies that include applications of CD-MOFs are so far 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, which shall be discussed in the next section. 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 CO_2 capture. This involves optimizing the framework's pore size and surface area to improve CO_2 adsorption and selectivity. Researchers also examine how varied operating variables, such as temperature and pressure, affect CD-MOF efficacy for CO_2 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 CO_2 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 CO_2 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 CO_2 capture is required to grasp their potential fully. 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 CO_2 capture systems.

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