Strong and Reversible Binding of Carbon Dioxide in a Green Metal−Organic Framework

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S *Supporting Information*

ABSTRACT: The efficient capture and storage of gaseous CO_2 is a pressing environmental problem. Although porous metal−organic frameworks (MOFs) have been shown to be very effective at adsorbing CO_2 selectively by dint of dipole−quadruple interactions and/or ligation to open metal sites, the gas is not usually trapped covalently. Furthermore, the vast majority of these MOFs are fabricated from nonrenewable materials, often in the presence of harmful solvents, most of which are derived from petrochemical sources. Herein we report the highly selective adsorption of CO_2 by CD-MOF-2, a recently described green MOF consisting of the renewable cyclic oligosaccharide γ-cyclodextrin and RbOH, by what is believed to be reversible carbon fixation involving carbonate formation and decomposition at room temperature. The process was monitored by solid-state ^{13}C NMR spectroscopy as well as colorimetrically after a pH indicator was incorporated into CD-MOF-2 to signal the formation of carbonic acid functions within the nanoporous extended framework.

Figure 1. (a) Structural formula of γ-cyclodextrin (γ-CD) with the primary hydroxyl groups colored red. (b) Stick representation of a single cubic $(γ-CD)_6$ unit of the extended framework of activated CD-MOF-2. The primary faces of the six γ-CD tori point inward, while the secondary faces are oriented outward and are coordinated by 24 Rb^+ cations to another six $(γ-CD)_6$ units, forming a 3D extended bcc structure wherein gases may pass through portals defined by (i) cylindrical channels of aligned CD tori with diameters of ∼0.9 nm and (ii) smaller aligned triangular-shaped windows. The spherical inner cavities of the $(γ-CD)_6$ cubes have a diameter of ∼1.7 nm and are lined with 24 primary hydroxyl groups, whose O atoms are shown as red spheres. (c) Space-filling representation of the $(γ-CD)_6$ unit in which the six γ-CD rings forming the sides of the cube are shown in different colors.

In view of the predicted detrimental effects of CO_2 emission, capture of CO_2 from gaseous waste streams has become an urgent scientific objective.[1] Recently, several approaches toward the capture of CO_2 have employed porous metal−organic frameworks (MOFs)[2] assembled by linking organic and inorganic building blocks. While these advances in the technology of CO_2 capture are noteworthy[3] for their high storage capacity, the vast majority of these MOFs are fabricated from nonrenewable materials in harmful solvents, many of which are derived from petrochemical sources.[4] We recently reported[5] the discovery of a series of MOFs composed of γ-cyclodextrin (γ-CD) (Figure 1a), a product prepared[6] microbiologically from starch (amylose) and thus obtained from atmospheric carbon and fixed by photosynthesis. The γ-CD tori are coordinated to each other by alkali metal cations in units of six, i.e., $(γ-CD)_6$ (Figure 1b), forming three-dimensional (3D) body-centered-cubic (bcc) extended structures. These CD-MOFs, which are crystallized from water and either methanol or
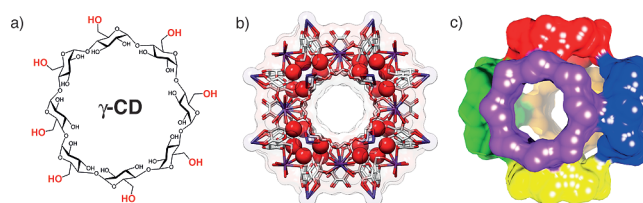
ethanol, are inexpensive and, importantly, "green" in the sense that they can be synthesized from renewable sources that are themselves derived from water, CO_2, and nontoxic metal salts. We seek to apply this green material in the international green initiative to find methodologies for trapping CO_2 in exhaust gases produced by combustion of organic matter. MOFs have been considered for this task, and there are broadly two distinct mechanisms by which reversible CO_2 capture occurs within these frameworks. One method is binding of CO_2 to vacant coordination sites on metal atoms.[7] While this approach has led to materials with high selectivity for CO_2, the effect of water (a combustion product) on binding is yet to be determined. Another method uses weakly nucleophilic or polar functional groups that bind CO_2 in a physisorptive manner by means of dipole interactions.[8] While this method is likely to be far less
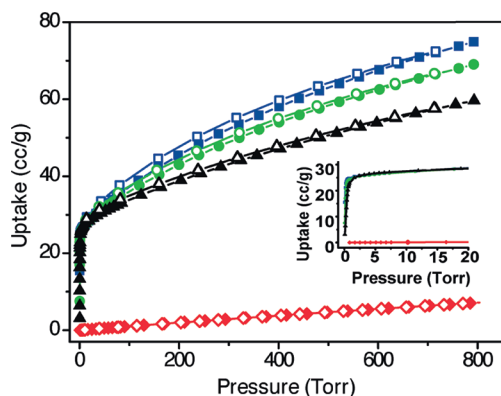
Figure 2. Gas adsorption isotherms for activated CD-MOF-2, illustrating the uptake of CO_2 measured consecutively at 273 K (blue squares), 283 K (green circles), and 298 K (black triangles) to be contrasted with the uptake of CH_4 at 298 K (red diamonds). Solid symbols indicate gas sorption and open symbols gas desorption. The initial steep rises observed at very low CO_2 pressures reach the same value of ~23 cc/g regardless of temperature and are believed to be characteristic of a chemisorption process.[11]

affected by water, the constituent materials are typically toxic and the selectivity for CO_2 over other gases is smaller than for methods using open metal sites. Fixing CO_2 as carbamates by using pools of amines[9] has been explored extensively, but the carbamate end product is thermodynamically very stable, making recycling impractical because heat (and thus more energy) is needed to liberate the CO_2 and regenerate the free amine. Nevertheless, inspired by the notion of using weakly nucleophilic functional groups to fix CO_2 chemically and reversibly, we found in CD-MOF-2 a surfeit of free alcohol groups (Figure 1a) and anions[10] to help sustain carbonic acid formation.

Initial CO_2 gas-uptake experiments with CD-MOF-2 revealed an atypically strong affinity between CO_2 and the MOF at low pressures, an observation that is indicative of a chemisorptive process.[11] To determine the role a chemisorptive process might have on gas adsorption, isotherms were measured for both CO_2 and CH_4 with CD-MOF-2 at incremental temperatures (Figure 2). The total uptake of CO_2 in the low-pressure region (<1 Torr) was clearly unaffected by temperature over the range 273−298 K, with a notable inflection point at ~23 cm^3/g regardless of the sample temperature. At these low pressures, the selectivity (as the ratio of the initial slopes) for CO_2 over CH_4 was nearly 3000-fold, a considerable difference that is unmatched in the literature as far as we can tell.[12]

Additionally, the steep slopes of the isotherms in this region (Figure 2 inset) suggest a strong binding event that would equate with the formation of a covalent bond. Notably, the abrupt transition in higher-pressure regimes (>1 Torr) becomes much more dependent upon temperature, as indicated by the 30% greater uptake of CO_2 at 273 K than at 298 K. These observations are consistent with covalent bond formation occurring preferentially at low pressures and giving way to physisorption at elevated pressures, with the change in uptake mechanism occurring when the CO_2 content of the MOF is ~23 cm^3/g. We were able to obtain these isotherms repeatedly on the same sample, showing the process to be fully reversible at room temperature.

Alkylcarbonic acids are known[13] to form as a result of the reaction between CO_2 and free primary alcohol groups. Although it has been pointed out[14] that the addition of nucleophilic groups,[15] specifically primary amines, to MOFs through the rational design of struts[16] or by way of postsynthetic modification improves CO_2 capture, to our knowledge no spectroscopic evidence has been provided for the formation of the

resultant organic acids. The free hydroxyl groups[17] located on each individual γ-CD torus seem to be capable of serving as reactive functional groups for reversible carbonic acid formation (Figure 3a). Spectroscopic evidence showing the solid-state reactivity of γ-CD with CO_2 was obtained by cross-polarization magic-angle-spinning (CP/MAS) ^{13}C NMR spectroscopy. For the solid-state NMR spectroscopic experiments, crystalline samples were activated by exchanging the aqueous methanolic solution with dichloromethane before being evacuated and dried at low pressure (<2.0 × 10^{-3} Torr) for 2 days to remove all of the remaining water. The activated CD-MOF was exposed to an atmosphere of dry CO_2 for 10 min and transferred into an airtight zirconium solid-state NMR rotor. The ^{13}C NMR spectrum of a crystalline sample of activated CD-MOF-2 (Figure 3b, bottom) shows separate peaks for C1 and C1′ as well as for C4 and C4′ as a result of the commuted symmetry induced by the alternating Rb$^+$ cations on the primary and secondary faces of the γ-CD tori. Upon exposure to CO_2, a new peak[18] centered at 158 ppm emerged (Figure 3b, top), consistent with formation of a carbonate.[19] To rule out the possibility that OH$^-$ counterions of CD-MOF-2 are the reactive agents, forming carbonate anions[20] by reaction with CO_2, we examined CD-MOFs prepared from RbF or potassium benzoate that are isostructural with CD-MOF-2 but contain non-nucleophilic and weakly basic counterions. The CP/MAS spectra of both MOFs showed identical resonances at 158 ppm, precisely the chemical shift found in CD-MOF-2 upon exposure to CO_2.
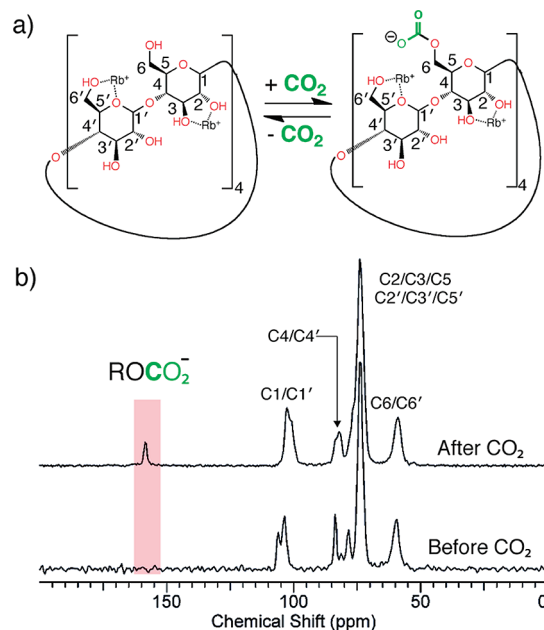

Figure 3. (a) Schematic diagram illustrating the equilibrium proposed to exist during the chemisorption of CO_2 by CD-MOF-2, expressed in the context of the structural formula of one of the four repeating maltosyl units present in a single γ-CD torus. (b) CP/MAS ^{13}C NMR spectra (400 MHz, room temperature) of activated CD-MOF-2 before (bottom) and after (top) exposure to CO_2. Upon exposure to CO_2, CD-MOF-2 shows a new peak at 158 ppm due to the formation of carbonic acid functions. This additional resonance is accompanied by changes in the chemical shifts of other peaks in the spectrum, supporting the observation that a chemical reaction between the gaseous CO_2 and the framework of activated CD-MOF-2 has occurred. Gaseous CO_2 is not detected by this CP/MAS NMR method but is usually observed as a very sharp singlet at 126 ppm in direct-polarization experiments.

We speculate that this favorable reactivity arises because the γ-CD units of CD-MOF-2 possess a significant number of accessible hydroxyl groups that define the circumference of a large (1.7 nm diameter) pore and have a high capacity for CO_2 relative to ambient pressures. These large local reactant concentrations facilitate the formation of bound CO_2 molecules in ways reminiscent[21] of the enhanced reactivity observed within supramolecular host/guest complexes that arises from the greater local concentration within a supramolecular ensemble, which can increase the reactivity by orders of magnitude in some cases.

If we are correct in assuming that formation of a carbonate ester by reaction with a hydroxyl group of a γ-CD occurs as the primary mechanism, it should be possible to detect the CO_2 uptake using an inexpensive and readily available pH indicator. Thus, methyl red, a zwitterionic azobenzene-based pH indicator, was diffused into the pores of CD-MOF-2 by suspension in a CH_2Cl_2 solution of the dye. The red solution was decanted, and brilliant yellow crystals were obtained after washing and drying in vacuo (Figure 4a). The yellow color arises from the incorporated methyl red, which undergoes partial anion metathesis (and thus deprotonation) with the counterions in the pore structure, an observation consistent with previous findings.[5a] The dried crystals were transferred to a scintillation vial, which was then exposed to both dry (from a tank) and humid (from sublimed dry ice) CO_2. The initial color change from yellow to orange/red occurred quickly (Figure 4b), regardless of the CO_2 source, and after 5 min, no further color change could be discerned by the naked eye. When the source of CO_2 was removed, the crystals reverted to a yellow color (Figure 4c), indicating that the transient carbonic acid function had returned to the alcohol, liberating CO_2. This Le Châtelier-like process was repeated more than 10 times with no apparent fatigue observed on the material.
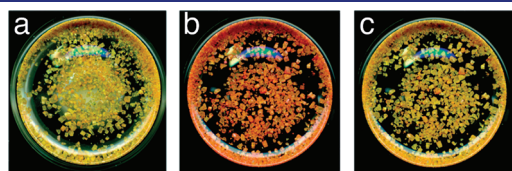

Figure 4. Photographs of crystalline activated CD-MOF-2 samples with incorporated methyl red at selected time intervals during CO_2 sorption and desorption processes. (a) Yellow crystals of activated CD-MOF-2 prior to CO_2 exposure. It is postulated that interstitial OH^- counterions (CD-MOF-2 is prepared from γ-CD and RbOH) maintain a basic environment within the framework, leading to deprotonation of the methyl red dye. (b) Red crystals obtained after exposure of the yellow crystals from (a) to CO_2 over the course of 5 min. It is proposed that chemisorption of CO_2 at the many OH groups facing into the cavities of the $(\gamma\text{-CD})_6$ units results in the formation of carbonic acid functions throughout the extended framework, producing an acidic environment that protonates the dye, turning it red. (c) Crystals that reverted back to yellow following removal of the CO_2 atmosphere, allowing ambient air to enter the vial over the course of 5 min. It is hypothesized that the metastable carbonic acid species dissociate and release CO_2, returning the interior of the framework to a basic environment.

This strong uptake of CO_2 occurs only when the γ-CD tori are arranged in the solid state as CD-MOF.[22] Pulverizing the crystals of this MOF turned it into an amorphous powder, as determined by powder X-ray diffraction (PXRD) measurements (Figure 5a),[23] and quelled the carbonate formation, as determined by solid-state NMR spectroscopy. The surface accessibility of these hydroxyl groups in the crystalline state far exceeds
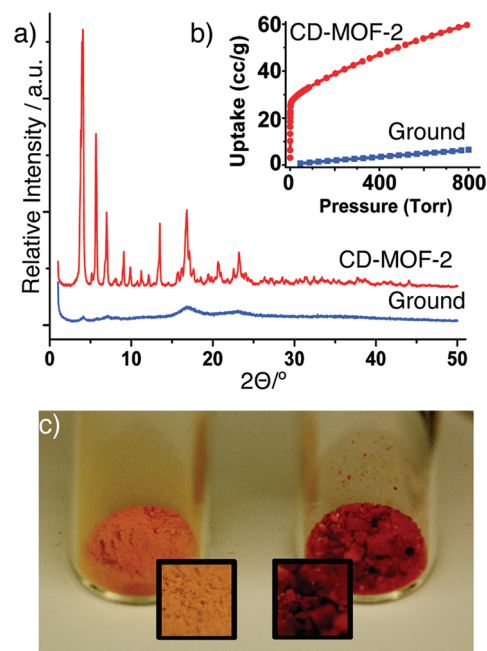

Figure 5. (a) PXRD analysis of pristine CD-MOF-2 (red, top) and a sample ground in a mortar and pestle for 7 min (blue, bottom). The grinding process reduced CD-MOF-2 into an amorphous powder, as reflected in the diffraction pattern. (b) CO_2 uptake isotherms (298 K) for crystalline CD-MOF-2 (red circles) and a sample ground into an amorphous powder (blue squares). The powdered sample exhibited very little CO_2 sorption and no steep rise in the low-pressure region. (c) Photograph of activated CD-MOF-2 with incorporated methyl red that was (left) ground to an amorphous powder or (right) allowed to remain pristine and then exposed to CO_2 for 5 min. The insets show magnified images. No color change was evident in the amorphous sample, while the crystalline material underwent the expected change to a red color.

that in the amorphous state, as determined (Figure 5b) by Langmuir and BET analysis [see Figure S3 in the Supporting Information (SI)]. Additionally, no evidence of carbonate formation was observed by CP/MAS NMR spectroscopy of pure γ-CD after exposure to CO_2. We repeated the CO_2 uptake color-change experiments (Figure 5c) on pulverized CD-MOF-2 and found that the amorphous material did not change color upon exposure to CO_2, in contrast to a pristine crystalline sample.

In conclusion, we have established that CD-MOF-2 is highly selective for the absorption of CO_2 at low pressures.[24] This selectivity is believed to be the result of chemisorption and to rely upon the free hydroxyl groups present in CD-MOF-2, which act as reactive hotspots for the formation of carbonic acid groups when CO_2 diffuses into the framework. Furthermore, the formation of an inherently acidic product as a result of this chemisorption allowed for the detection of CO_2 colorimetrically by swapping anions with a small-molecule pH indicator within the MOF structure. We have also shown that the strong and selective uptake of CO_2 is a property unique to nanoporous crystalline CD-MOF-2 and is not observed for other CD-based mixtures with amorphous morphologies. The fact that CD-MOFs can be made from environmentally benign materials whose synthesis is essentially carbon-neutral and have the demonstrated ability to absorb CO_2 from the atmosphere makes them promising materials for carbon fixation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Synthesis and characterization of all compounds and additional experimental results. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(4) While most reported MOFs utilize struts derived from petrochemical sources, there is a recent trend in research in which biologically relevant and naturally-derived materials are being incorporated into frameworks, although they very often have toxic transition metals serving as their secondary building units. For a review of these new "MBioFs", see: Imaz, I.; Rubio-Martínez, M.; An, J.; Solé-Font, I.; Rosi, N. L.; Maspoch, D. *Chem. Commun.* **2011**, *47*, 7287.

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(10) The counterions associated with the alkali metal cations that hold the γ-CD units together in CD-MOFs are retained within the framework.[5a] In the case of CD-MOF-2 obtained from RbOH, it was not possible to detect the presence of the counterions by X-ray crystallography, and the fact that the OH^- anions are not bound to the Rb^+ cations suggests that the metal centers are coordinatively saturated and unable to bind guests. However, for CD-MOFs prepared from ^{1}H NMR-active alkali metal salts such as potassium benzoate, the counterions were clearly visible in the ^{1}H NMR spectra of redissolved samples in D_2O as well as in the solid-state ^{13}C CP/MAS NMR spectra described in this communication (see the SI).

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(20) The reversibility of CO_2 uptake is further evidence that the OH^- counterions do not react with CO_2 to form bicarbonate anions, as it is highly unlikely and thermodynamically unfavorable for the reverse process (dissociation of a bicarbonate anion into a gaseous CO_2 molecule and a OH^- ion) to occur.

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(22) As a control, the same experiment was performed on crystals of MOF-5 that were loaded with methyl red and exposed to NH_3 gas to form the (deprotonated) ammonium azo dye salt. MOF-5 is free of hydroxyl groups capable of forming an acid moiety to elicit a pH-based color change and thus would not be expected to demonstrate chemisorption. The presence of CO_2 had no effect on the crystal color.

(23) The effect of grinding on the crystallinity of CD-MOF-2 was determined by pulverizing a dry sample with a mortar and pestle and recording PXRD patterns at differing time intervals (see the SI). Seven minutes of grinding reduced CD-MOF-2 to an amorphous powder.

(24) There is a strong correlation between the amount of pure CO_2 adsorbed at low total pressure and the amount of CO_2 adsorbed at low partial pressure under atmospheric conditions. See: Yang, R. T. *Adsorbents: Fundamentals and Applications*; Wiley: Hoboken, NJ, 2003.