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Direct Calorimetric Measurement of Enthalpy of Adsorption of Carbon Dioxide on CD-MOF-2, a Green Metal–Organic Framework

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ABSTRACT: The enthalpy of adsorption of CO_2 on an environmentally friendly metal–organic framework, CD-MOF-2, has been determined directly for the first time using adsorption calorimetry at 25 °C. This calorimetric methodology provides a much more accurate and model-independent measurement of adsorption enthalpy than that obtained by calculation from the adsorption isotherms, especially for systems showing complex and strongly exothermic adsorption behavior. The differential enthalpy of CO_2 adsorption shows enthalpy values in line with chemisorption behavior. At near-zero coverage, an irreversible binding event with an enthalpy of −113.5 kJ/mol CO_2 is observed, which is followed by a reversible −65.4 kJ/mol binding event. These enthalpies are assigned to adsorption on more and less reactive hydroxyl groups, respectively. Further, a second plateau shows an enthalpy of −40.1 kJ/mol and is indicative of physisorbed CO_2. The calorimetric data confirm the presence of at least two energetically distinct binding sites for chemisorbed CO_2 on CD-MOF-2.

The rapidly increasing consumption of fossil fuels as a result of global industrialization has brought with it sharply rising CO_2 emissions, a topic that is becoming an urgent environmental and geopolitical issue.[1] The past few decades have seen various methodologies developed to engineer functional materials to remove CO_2 from combustion exhausts and other sources. The current materials being investigated for CO_2 capture include aqueous alkanolamine absorbents,[2,3] zeolitic structures,[4,5] and amine-functionalized porous media.[6−9] However, these current technologies depend upon a large amount of energy for regeneration, and many materials are derived from petrochemical sources and require intensive and costly synthetic preparation, or are themselves derived from toxic materials.[10,11] Therefore, there is a pressing need for energy-efficient and environmentally friendly materials with excellent CO_2 adsorption properties. This research has brought new challenges to familiar techniques, in particular, obtaining accurate and reproducible enthalpy measurements of room-temperature gas uptake which feature very high enthalpies of adsorption or hysteresis. In both cases, indirectly deriving accurate enthalpy of adsorption values from isothermal gas uptake measurements becomes problematic. In this Communication we present a direct calorimetric determination of enthalpy of CO_2 adsorption on a recently reported cyclodextrin-derived metal–organic framework (MOF), for which accurate indirectly determined enthalpies of adsorption are unobtainable as a result of a strong, initial chemisorptive process. We have applied a calorimetric methodology, which experimentally directly measures the enthalpy of gas uptake as a function of coverage, and, in doing so, have further elucidated the mechanism of CO_2 adsorption. MOFs are a relatively new class of highly porous materials with significant promise in gas adsorption owing to their high surface-to-volume ratio.[12] They are canonically constructed by connecting rigid organic linkers through coordinated metal cation clusters. Due to the nature of their unique synthesis processes, a major drawback for MOF materials is that, in their as-synthesized forms, they often possess petrochemicals, solvents, or potentially toxic chemicals. Recently, a series of MOFs have been synthesized from γ-cyclodextrin (γ-CD), a sugar-related natural product obtained from microbiological processes[13−15] and alkali metal salts. These MOFs are crystallized from water and alcohol (methanol or ethanol),[13,14] which are environment friendly and renewable. It was reported[14] that CD-MOF-2 (Figure 1) has a highly selective adsorption of CO_2 at low pressures. This strong CO_2

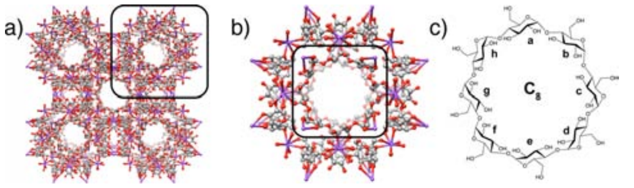

Figure 1. (a) Crystallographic packing of CD-MOF-2, showing multiple unit cells with a single unit cell highlighted by a black box and expanded. (b) Detail of the unit cell highlighted to the left, showing six cyclodextrin moieties, again highlighted by a black box, fixed by metal ions (rubidium) creating a cubic structure, the corners of which are γ-cyclodextrin. (c) γ-CD detail showing the cyclic arrangement of glucopyranose residues.

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adsorption was considered to be chemically reversible at 25 °C according to isothermal gas uptake measurements. The reactivity is attributed to CO_2 reacting with some of the numerous free hydroxyl groups within the MOF. Using cross-polarized solid-state NMR spectroscopy, the existence of carbonate resonances was confirmed.[14] In the present work, we utilize direct experimental enthalpy of adsorption measurements, for the first time on MOFs, to determine the strength of interaction quantitatively and directly by CO_2 adsorption calorimetry, test the reversibility of adsorption, and map the adsorption "hot spots" in CD-MOF-2 structure by relating the observed enthalpy plateaus as a function of coverage to the available hydroxyl sites in the structure.

The enthalpies of adsorption of CO_2 on MOFs have been studied extensively but indirectly[16] by isosteric heat of adsorption (Q_{st}) techniques. In this approach,[16] two or more CO_2 adsorption isotherms at different temperatures are collected and fitted to a polynomial equation to calculate Q_{st}. Further fitting is also needed to obtain the zero coverage isosteric heat of adsorption.[17] This method essentially differentiates a free energy curve (the isotherm) with respect to temperature (often over only a small range of about 10 K). This complicated and multistep calculation introduces considerable uncertainty, especially when the adsorption process is complex as a function of coverage and temperature, as is the case with CD-MOF-2. To this end, we have adapted a gas adsorption calorimetry method using a combination of a commercial Calvet-type microcalorimter and a commercial gas dosing system[18] (see Figure 2), developed in the Peter A. Rock Thermochemistry Laboratory at UC Davis, to obtain accurate experimental measurements. It has been used primarily for surface H_2O adsorption experiments,[18−23] but we show reliable efficacy in the measurement of CO_2 adsorption on CD-MOF-2.

CD-MOF-2, $[(C_{48}H_{80}O_{40}(RbOH)_2]_n$,[13−15] was used as synthesized.[13−15] Phase identification and component evaluation were performed by X-ray diffraction and thermogravimetric analysis and differential scanning calorimetry. BET surface area was measured by nitrogen adsorption analysis at −196 °C to be 1030 ± 5 m^2/g.[13−15] After degas, no detectable solvent was observed in the CD-MOF-2 crystals.

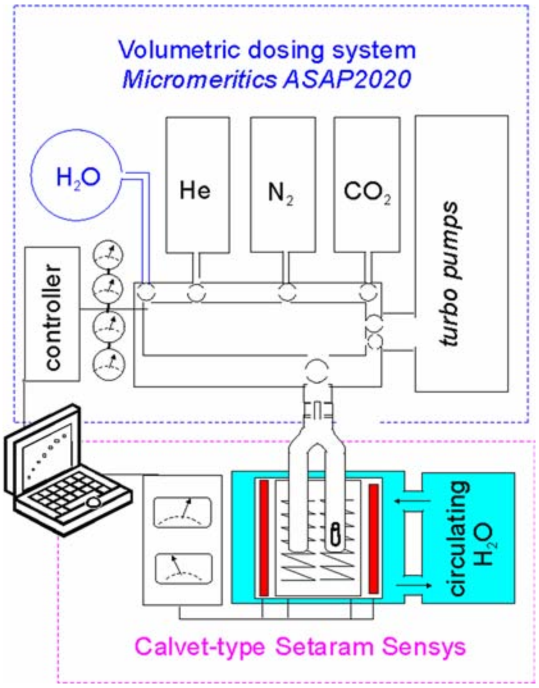

Figure 2. Experimental setup for CO_2 adsorption calorimetry on CD-MOF-2.

The calorimetric system includes a commercial gas adsorption analyzer (Micromeritics ASAP 2020), which is coupled to a Calvet-type microcalorimeter (Setaram Sensys).[18] The CO_2 adsorption calorimetry was performed in three steps. First, ~30 mg of crystalline CD-MOF-2 (about 30 m^2) was placed into one side of a specially designed silica glass forked tube. The sample tube was then connected to the gas adsorption analyzer and degassed under vacuum (<10^{-3} Pa) overnight (12 h) at room temperature (25 °C) to maximize the removal of all adsorbed/confined species. Second, the free volume of the sample tube and the surface area were measured by five-point nitrogen adsorption BET analysis. Third, the silica glass forked tube was inserted into the twin chambers of the microcalorimetrer and connected to the analysis port of the ASAP 2020 analyzer. After another overnight evacuation at room temperature, the CD-MOF-2 sample was ready for CO_2 adsorption calorimetry at 25 °C. The ASAP 2020 analyzer was operated in incremental dosing mode. The amount of each dose (1 μmol) and the equilibration time (1.5 h) were preset with the software of the surface analyzer. The amount of adsorbed CO_2 was determined from the pressure drop. The adsorption isotherm and heat effects generated from adsorption were recorded simultaneously. Adsorption of each dose generated a distinct calorimetric peak. The integrated area of each peak is related to the enthalpy of adsorption of dosed CO_2. Actual adsorbed amounts from Micromeritics software were used to calculate enthalpies of adsorption per mole of CO_2. The reversibility of CO_2 adsorption was tested on the same sample. Right after the first round of CO_2 adsorption, the sample was kept in the same forked tube and submitted to 12 h vacuum treatment, followed by another two rounds of the same calorimetric measurements. Adsorption calorimetry experiments were repeated in triplicate on fresh CD-MOF-2 samples.

Figure 3a,b shows the adsorption isotherms and the associated calorimetric traces for the first and second rounds of CO_2 adsorption. Since CO_2 does not condense at room temperature, the steep gas uptake in the initial low-pressure region on the type I isotherm indicates a strong chemical interaction between CD-MOF-2 and CO_2 molecules. Along with the steep isotherm, the calorimetric peak area generated by adsorption of each dose decreases, showing that the differential enthalpy of CO_2 adsorption becomes less exothermic with increasing coverage. Figure 3c presents the differential enthalpy of CO_2 adsorption as a function of surface coverage (CO_2 per nm^2) for the first (black), second (red), and third (blue) rounds of adsorption.

For the first round of CO_2 adsorption, at near-zero coverage, the differential enthalpy of adsorption on a fresh CD-MOF-2 crystal is −113.5 kJ per mole of CO_2. The large magnitude of this exothermic heat effect strongly supports the previous conclusion[14] that CD-MOF-2 forms robust chemical bonds with absorbed CO_2. To the best of our knowledge, so far this is the strongest interaction measured between CO_2 and any MOF or amine or zeolitic sorbent at room temperature. As surface coverage increases, the enthalpy of CO_2 adsorption becomes less exothermic, reaching a first plateau (−65.4 kJ/mol CO_2) when the coverage is between 0.1 and 0.3 CO_2 per nm^2. Considering the molecular structure of CD-MOF-2 (Figure 1),

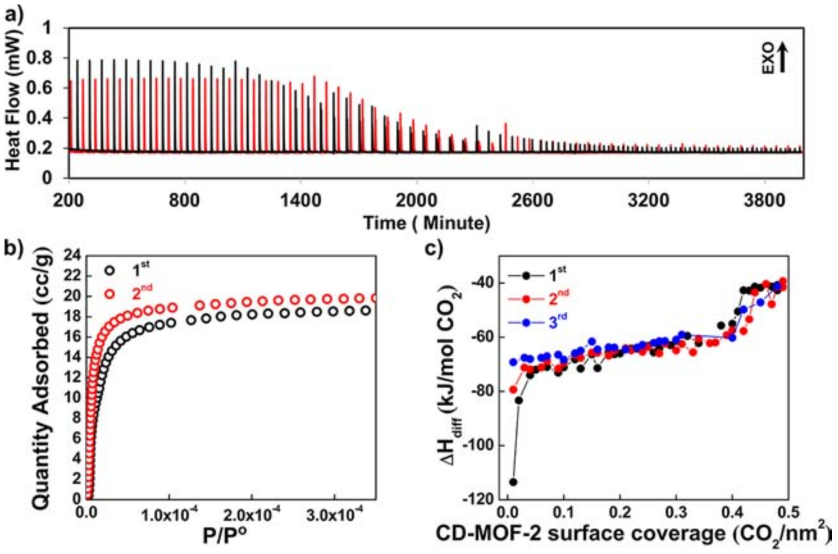

Figure 3. (a) CO_2 adsorption isotherms and (b) corresponding calorimetric traces (at 25 °C) for the first (black) and second (red) CO_2 adsorption on the same CD-MOF-2 sample (after degassing at 25 °C for 12 h). (c) Differential enthalpies of CO_2 adsorption (at 25 °C) for the first (black), second (red), and third (blue) rounds of adsorption on the same CD-MOF-2 sample.

the CO_2 adsorbed at near-zero coverage can be classified as chemisorbed CO_2 interacting with the most reactive primary hydroxyl groups, in turn producing the most exothermic interaction energy. The CO_2 adsorption between 0.1 and 0.3 CO_2 per nm^2, though less exothermic, is still within the range for chemisorption. It can be assigned to adsorption of CO_2 onto the majority of less reactive hydroxyl groups, which may include both primary and secondary hydroxyls. As the coverage of CD-MOF-2 increases to above 0.3 CO_2 per nm^2, the first plateau of the differential enthalpy curve ends with a sharp change to the second plateau at about −40.1 kJ/mol CO_2. The CO_2 adsorbed after this point is considered to be physisorbed. Tables 1 and 2 summarize the calorimetric data of CO_2 adsorption on fresh CD-MOF-2 at very low coverage. Integral enthalpy of CO_2 adsorption is defined as the sum of differential enthalpies of CO_2 adsorption divided by the total moles of CO_2 adsorbed up to this coverage. In each round of adsorption, the integral enthalpy of adsorption tends to be less exothermic as the surface coverage of CD-MOF-2 increases (Table 2).

Table 1. Differential Enthalpies of Adsorption for CO_2 Adsorption on Fresh CD-MOF-2

	differential enthalpy of adsorption of CO_2 (kJ/mol CO_2)		
coverage of CO_2/nm^2	round 1	round 2	round 3
∼0.0	−113.5 ± 0.9	−77.7 ± 1.1	−71.0 ± 0.8
0.1−0.3	−65.4 ± 1.6	−65.4 ± 0.7	−65.5 ± 1.0
>0.4	−40.0 ± 1.8	−41.4 ± 0.6	−43.5 ± 1.9

Table 2. Integral Enthalpies of Adsorption for CO_2 Adsorption on Fresh CD-MOF-2

	integral enthalpy of adsorption of CO_2 (kJ/mol CO_2)		
coverage of CO_2/nm^2	round 1	round 2	round 3
∼0.0	−113.5 ± 0.9	−77.7 ± 1.1	−71.1 ± 0.8
0.1−0.3	−73.0 ± 0.8	−68.8 ± 1.5	−65.9 ± 1.2
>0.4	−67.5 ± 1.1	−66.0 ± 0.8	−63.7 ± 1.2

Even though the initial −113.5 kJ/mol value of CO_2 adsorption enthalpy on CD-MOF-2 at near-zero coverage is similar to that of CO_2 adsorption on some oxides with basic surfaces,[24] it is highly unlikely for an analogous acid−base reaction, producing bicarbonate or carbonate ions, to involve any significant concentration of free OH^- counterions randomly and loosely associated with the framework.[13−15] As a crystalline solid, CD-MOF-2 has a unique structure with a very high concentration of hydroxyl groups from the sugar moieties located in specific crystallographic sites in its structure. Their number and charge make it unlikely that much other "free hydroxyl" is present. Furthermore, the enthalpy of reaction between aqueous hydroxide and gaseous CO_2 to form bicarbonate is approximately −66.4 kJ/mol[25] at 25 °C, which could not explain the much larger exothermic effect of CO_2 adsorption on CD-MOF-2. Moreover, theoretical calculations have shown that bicarbonate formation in aqueous media has an energetic barrier of 33.5−54.4 kJ/mol[26] and is therefore unlikely to be rapid and reversible at ambient conditions. Thus, we conclude that CO_2 adsorption on the structural sugar alcohol groups, rather than reaction with adventitious OH^- in the pores, is the main adsorption mechanism.

The differential enthalpies of adsorption data also allow us to investigate the reversibility of CO_2 adsorption on CD-MOF-2 (Figure 3c). While the isothermal gas uptake analysis suggests ideal reversible behavior over a wide temperature range,[9] the enthalpies of adsorption at near-zero coverage differ distinctly for the first adsorption and the subsequent ones. The near-zero coverage enthalpy of adsorption on fresh CD-MOF-2 (−113.5 kJ/mol CO_2) is much more exothermic than those of the second and third adsorption series (average −75.6 kJ/mol CO_2). However, the differential enthalpies of adsorption values merge onto the plateau between coverages of 0.1 and 0.3 CO_2 per nm^2, and the rest of the plots of the differential enthalpies of the second and third adsorption series entirely overlap the first series. These observations strongly suggest that the CO_2 adsorbed onto the most reactive primary hydroxyl groups cannot be desorbed even under strong vacuum for 12 h, but the adsorption on the less reactive hydroxyls and the physisorption of CO_2 are reversible. In the second and third rounds of adsorption experiments, CD-MOF-2 exhibits the same or even slightly higher CO_2 adsorption capacity. Therefore, the calorimetric data suggest that the strong but mainly reversible CO_2 sorption in environmentally friendly sugar-based MOFs like CD-MOF-2 could be harnessed for CO_2 scrubbing applications.

The conditions for accurate enthalpy measurements from indirect methods based upon gas isotherm data are frequently narrow in temperature and rely heavily on an ideal Type I isotherm featuring no hysteresis and a single mechanism of adsorption. In the case of CD-MOF-2, two mechanisms of adsorption have been identified, and correct determination of enthalpy of adsorption by calculation from the gas isotherm proved impossible due to the single averaged enthalpy value returned by the traditional approaches, and the problematic calculation for steep uptakes. Thus, adaptation of a direct calorimetric technique initially used to determine enthalpies of adsorption of water vapor on nanoparticles was used to derive experimental values of enthalpy of CO_2 adsorption as a function of coverage. This method provides direct and accurate enthalpy of adsorption measurements for the ever-increasing number of MOF architectures designed for catalysis and CO_2 sequestration at room temperature. The enthalpy of CO_2 adsorption on an environmentally friendly metal−organic framework, CD-MOF-2, possessing both chemisorption and physisorption characteristics, provided an excellent proof-of-principle in addition to elucidating the chemical nature of the interactions and guest molecules. The enthalpies of adsorption of CO_2 are −113.5 kJ/mol CO_2 at near-zero surface coverage, likely on the most reactive primary hydroxyl groups, −65.4 kJ/mol CO_2 on less reactive hydroxyl groups, and −40.1 kJ/mol for physisorbed CO_2. The vast majority of chemisorption on hydroxyl groups and all physisorption of CO_2 are reversible, but the most reactive primary hydroxyls appear to sorb CO_2 irreversibly at near-zero coverage. In addition, repeated adsorptions using the same sample of CD-MOF-2 maintain its adsorption capacity and energetic characteristics, showing the robust nature of the material.

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Notes

The authors declare no competing financial interests.

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