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Thermodynamic Complexity of Carbon Capture in Alkylamine-Functionalized Metal-Organic Frameworks

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For coordinatively unsaturated metal-organic frameworks (MOFs), the metal centers can be functionalized as CO₂ capture/storage adsorbents by grafting species having specific active groups. We report direct measurement of enthalpy of adsorption of CO₂ on an alkylamine-appended MOF, mmen-Mg₂(dobpdc) employing gas adsorption calorimetry at 298, 323 and 348 K. This methodology provides, for the first time, the detailed dependence of energy and entropy of sorption as a function of coverage and temperature. The enthalpy data suggest three types of adsorption events: strongest exothermic initial chemisorption at low coverage, majority moderate chemisorption at intermediate loading and weakest physisorption at highest coverage. The partial molar properties and isotherms are consistent with the presence of two different potential chemisorption mechanisms: 2:1 (amine : CO₂) stoichiometry near zero coverage and 1:1 afterwards. Both chemical potential and differential enthalpy of adsorption become less negative with increasing temperature, implying increasing adsorbent entropy at elevated temperature. These observations are consistent with weaker CO₂ binding at higher temperature.

Introduction

To mitigate the effects of rising atmospheric CO₂ levels related to burning of fossil fuels, various strategies are being investigated to design and develop advanced materials to control and capture CO₂ emissions^{1, 2}. Current technologies emphasize CO₂ capture materials such as aqueous phase alkanolamine³ and solid framework materials⁴ including zeolite molecular sieves^{5, 6}, alkylamine-grafted silicas⁷⁻⁹ and metal-organic frameworks (MOFs). MOFs represent a class of highly porous, crystalline, metal-organic hybrid materials which have promising adsorption/separation properties due to their high surface areas, extremely open internal void space and chemical tunability. They are built through coordination between metal cations and rigid organic linkers¹⁰. Once the metal cation clusters are partially coordinated, leaving empty orbitals, further alkylamine functionalization is applicable, which may greatly enhance CO₂ adsorption¹¹⁻¹³. One model material is an alkylamine-appended MOF, mmen-Mg₂(dobpdc), (an expanded version of Mg-MOF-74 appended with *N,N'*-dimethylethylenediamine), developed by McDonald *et al.*¹⁴, which exhibits significantly improved carbon capture capability, steep gas uptake, unusual "S-shaped" isotherms¹⁴ and potential complicated reaction mechanisms¹⁵. The prospect of functionalized MOFs as gas sorbents brings up a challenging scientific issue, namely, to obtain accurate descriptions of the energetics of adsorption for multi-site, strong chemisorption possessing a steep initial stage and/or hysteresis. In such complex cases, the traditional isosteric heat calculation using adsorption

isotherms obtained at different temperatures can be problematic, in part because the functional form of equations used can not be constrained a priori and may indeed depend on temperature. In practical operation, energy efficient carbon capture from coal based power plants and natural gas streams requires adsorption at elevated temperature (usually above 313 K). Therefore, the energetic effects involved in these conditions are essential and crucial to understand and optimize an energy efficient CO₂ adsorption process. The calorimetric methodology in this study provides, for the first time, direct measurement of enthalpy of sorption as a function of coverage (including at very low gas loading) and temperature. Combining these calorimetric data and the adsorption isotherms enables accurate calculation of entropies of sorption. These thermodynamic parameters provide insight into binding mechanisms and their variation with coverage and temperature.

The gas adsorption calorimetry system developed in the Peter A. Rock Thermochemistry Laboratory at UC Davis includes a Calvet-type microcalorimeter combined with a commercial gas dosing system (Figure 1)¹⁶. Our earlier adsorption calorimetry studies mainly focused on H₂O vapor adsorption on surfaces of nanoparticles and nanoporous media confining different guest cations or molecules¹⁷⁻²⁰. Recently, we adapted this technique to explore the reaction mechanism of CO₂ adsorption on an environmental friendly sugar MOF (CD-MOF-2)²¹. Strong exothermic heat effects at near zero coverage were directly obtained and different active adsorption sites of the material were mapped and assigned to specific bonding geometries. In this work, we utilize this

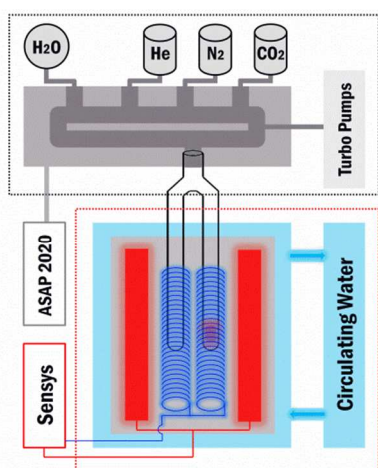


Figure 1. Experimental apparatus for CO₂ adsorption calorimetry.

methodology to investigate the enthalpy of CO₂ adsorption on an alkylamine-functionalized MOF, mmen-Mg₂(dobpdc). By performing direct enthalpy of adsorption measurements, we determine the enthalpy of gas adsorption as a function of CO₂ loading (mmol/g sorbent), the magnitude of the strong, initial binding at near zero gas coverage, adsorption reversibility, the proportion of major chemisorbed CO₂, and the enthalpy of adsorption at several temperatures. In light of these direct experimental observations, we interpret the mechanism of CO₂ adsorption and discuss the change of partial molar properties in the CO₂-mmen-Mg₂(dobpdc) system as a function of gas loading and of temperature. We conclude that CO₂ adsorption in mmen-functionalized Mg₂(dobpdc) is a complex process involving multiple thermodynamic factors reflecting changes in structure and bonding as temperature and gas loading vary.

Experimental methods

The detailed chemical and structural analyses of mmen-Mg₂(dobpdc), including both detailed crystallographic information and powder X-ray diffraction patterns, have been published elsewhere¹⁴ by some of the coauthors in the present work. So we do not repeat them here.

Small-angle X-ray scattering (SAXS) measurement of mmen-Mg₂(dobpdc) was conducted at B1 station of Cornell High Energy Synchrotron Source (CHESS) using an angle dispersive synchrotron X-ray technique to determine the material structure. Using a double crystal monochromator, the white X-rays were collimated into monochromatic beam at a wavelength of 0.485946 Å for SAXS measurement²². A large MAR345 detector was used to record the X-ray scattered signals from the sample. Using a Fit2D software, the two-dimensional (2D) images were integrated into one-dimensional (1D) patterns with intensity as a function of 2θ (degree) for structural analysis.

The enthalpies of CO₂ adsorption were measured by gas adsorption calorimetry (see Figure 1) at 298, 323 and 348 K using a gas adsorption analyzer (Micromeritics ASAP 2020) coupled to a Calvet-type microcalorimeter (Setaram Sensys)¹⁶. About 30 mg of mmen-Mg₂(dobpdc) was placed in one side of a custom-made silica glass forked tube, and the other side of the tube was left empty as a reference. This sample tube was placed into the twin chambers of the microcalorimeter, connected to the analysis port of ASAP 2020 and subjected to degas under vacuum (< 10⁻³ Pa) for 36 hours at 373 K to maximize the desorption of any initial adsorbates. The gas adsorption analyzer was set in incremental dosing mode (1 μmol per

dose). To ensure equilibration, the time between each dose was 1.0–1.5 hour. In each experiment, the isotherm and associated heat effect were recorded simultaneously. Each dose of CO₂ resulted in a distinct calorimetric peak representing the heat effect generated by the adsorption of that dose. Volumetric detection of the amount of adsorbed CO₂ was recorded by the gas adsorption analyzer. Calisto Processing software (AKTS, Switzerland) was used to obtain enthalpies of adsorption (kJ per mole of CO₂). Between each set of adsorption measurements, the sample was regenerated at 373 K under vacuum overnight.

Three sets of calorimetric experiments were designed to investigate CO₂ adsorption mechanisms. First, reversibility of CO₂ adsorption was tested by performing the enthalpy of CO₂ adsorption measurements a second time after regeneration under vacuum at 373 K for 12 hours between the two sets of measurements. Then the following procedure was used to separate chemisorption from the whole adsorption event. Right after the second round of CO₂ adsorption (up to saturation) on fresh mmen-Mg₂(dobpdc) at 298 K, the same sample was degassed without heat treatment in the same forked tube, followed by a third round of adsorption calorimetry at 298 K. The purpose was to retain the chemisorbed CO₂ but remove the physisorbed CO₂ so that this round of calorimetry could not access the strong binding sites since they remained filled. Finally, enthalpies of CO₂ adsorption were measured at 298, 323 and 348 K. The absence of heat effects from dosing of CO₂ in calorimeter above 298 K was verified with experiment using silica glass in place of the sample. All the measurements were triplicated for reproducibility.

Results

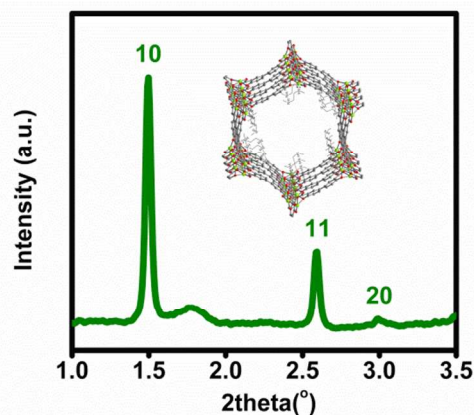


Figure 2. Small-angle X-ray scattering (SAXS) pattern for mmen-Mg₂(dobpdc) and structure of mmen-Mg₂(dobpdc), green, red, and gray spheres denote Mg, O, and C atoms, respectively.

The 1D integrated SAXS pattern is shown in Figure 2. There are three detectable peaks with d-spacings of 1.86 nm (d₁), 1.07 nm (d₂), and 0.93 (d₃) nm, respectively. Therefore, the corresponding ratios (d₁/d_n) are close to 1, √3, and 2, indicating a typical hexagonal superstructure. Combined with the nature of this mesoporous sample, the first three peaks are therefore indexed as (10), (11), and (20), respectively. It should be noted that this unique labeling is derived from the 2D hexagonal structure²³. Therefore, the constant of the 2D hexagonal meso-structure lattice (a) was calculated to be 2.15 nm using the equation below²³:

$$\frac{1}{d_{(hk)}^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2}$$

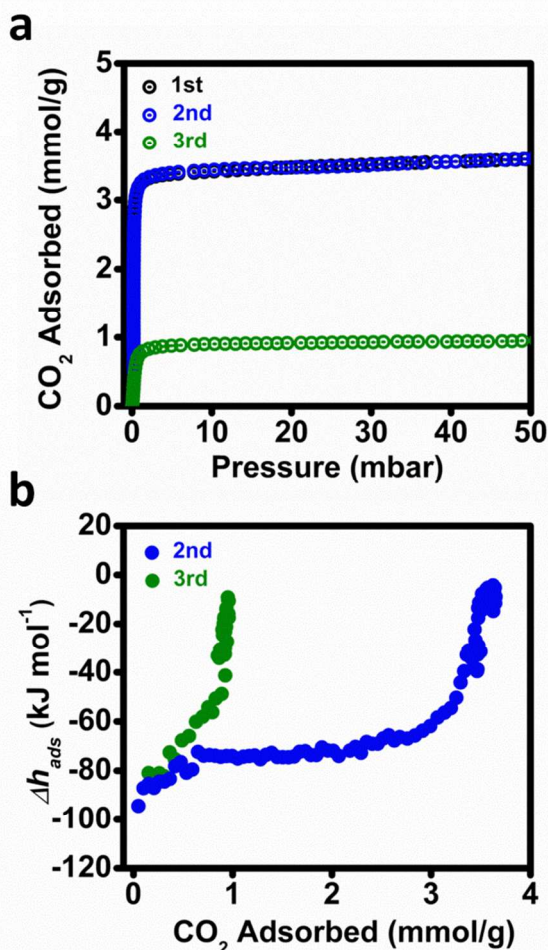


Figure 3. a) CO₂ adsorption isotherms at 298 K for the first (black) and second (blue) CO₂ adsorption round on the same mmen-Mg₂(dobpdc) sample (degassed at 373 K for 12 h after the first round). After the second round of CO₂ adsorption, the sample was subjected to degas without heating for 12 h at 298 K. Then the third round (green) CO₂ adsorption experiment was performed; and b) differential enthalpies of CO₂ adsorption at 298 K for fresh mmen-Mg₂(dobpdc) (blue) and the same sample with major chemisorption on the plateau range inhibited (green).

Table 1. Differential enthalpies of CO₂ adsorption at near zero coverage and major chemisorption only at 298, 323 and 348 K.

Temperature (K)	$\Delta h_{ads-zero\ coverage}$ (kJ per mole CO ₂)	$\Delta h_{ads-chemi}$ (kJ per mole CO ₂)
298	-94.4 ± 2.8	-75.0 ± 2.2
323	-82.3 ± 4.1	-61.8 ± 3.6
348	-71.8 ± 4.0	-52.0 ± 5.4

Figure 3 presents the adsorption isotherms and associated differential enthalpy of adsorption curve for the first, second and third round of CO₂ adsorption. The measured enthalpies of adsorption are listed in Table 1. The isotherms and differential enthalpy of adsorption curves of the first and second round of adsorption overlap entirely. This reproducibility strongly suggests that, after regeneration, mmen-Mg₂(dobpdc) maintains its CO₂ adsorption capacity without decreasing selectivity, keeping the same number of strong adsorption sites. The most exothermic differential enthalpy of CO₂ adsorption at near zero coverage is -94.4 ± 2.8 kJ per mole of CO₂. This strongly exothermic heat effect complements previous work of McDonald *et al.*¹⁴ by providing enthalpy of CO₂

adsorption at near zero coverage, which could not be calculated by fitting isotherms. The differential enthalpy of adsorption becomes less exothermic as more CO₂ is adsorbed. It reaches a plateau of -75.0 ± 2.2 kJ per mole CO₂, which is the enthalpy of adsorption for the majority of chemisorption sites. The current data on this plateau, which represents most of the adsorption, are in good agreement with both the calculated adsorption energy from simulation¹⁵ (-69 kJ/mole CO₂) and the isosteric heat effect¹⁴ (-71 kJ/mole CO₂). The data at lower and higher coverage capture detail not seen in any earlier experiments or calculations.

The isotherm and enthalpies for the third round of adsorption represent readsorption of CO₂ which can be removed by strong vacuum at 298 K. The energetics suggests that this is mostly physisorption, with a possible small fraction of chemisorbed CO₂. Difference between this isotherm and those of fresh mmen-Mg₂(dobpdc) (first and second round) represents CO₂ bound on the major chemisorption sites (the plateau). When the pressure is 1.0 mbar, the amount of this chemisorbed CO₂ is about five times that of CO₂, which can be removed by vacuum. The differential enthalpy of adsorption curve in the third round (see Figure 3b) shows no plateau representing the major chemisorption because the chemisorbed CO₂ is already present. As soon as the adsorption passes the stage of very small amounts of added CO₂, the curve directly passes into physisorption behavior.

To further elucidate complex CO₂ adsorption mechanisms, the partial molar properties of CO₂ adsorption and the isotherm at 298, 323 and 348 K are plotted versus the amount of CO₂ adsorbed per gram of mmen-Mg₂(dobpdc) in Figure 4 (also see Figure S1). Pure gas phase CO₂ at 1 atm is selected as the standard state at each temperature. Chemical potential (partial molar free energy) curves are obtained directly from the adsorption isotherm, $\Delta\mu_{CO_2}(gas\ phase) = RT\ln(p/p^o)$, $p^o = 1\ atm$. In the pressure and temperature range investigated, the fugacity coefficient of CO₂ is very close to 1, so CO₂ can be considered to be an ideal gas whose enthalpy does not depend on pressure at constant temperature, so the only enthalpy term is that arising from adsorption. The partial molar entropy of adsorption is derived by using the relation $\Delta\mu = \Delta h - T\Delta s$. Specifically, all the isotherms exhibit signature steps with the switch points shifting to higher pressure as temperature increases (Figure 4a). Chemisorption of CO₂ at higher temperatures yields less exothermic differential enthalpies, also supported by the upward shifted plateaus shown in Figure 4b. Similar trends are also found on the $\Delta\mu_{ads}$ plots (Figure 4c). For a given temperature, the chemical potential change becomes less negative as adsorption proceeds, reflecting the change in enthalpy and entropy, and indicating decreasing sorbent binding (less favorable reaction). The chemical potential curves exhibit similar temperature dependence as the differential enthalpy, with $\Delta\mu_{ads}$ showing less negative values at higher temperature for a fixed CO₂ loading. The temperature dependence of chemical potential and partial molar enthalpy is a strong indication of energetically less favorable adsorption at higher temperature. The entropy of adsorption becomes less negative with increasing temperature (Figure 4d), also consistent with weaker binding at higher temperature. In addition, the standard state partial molar entropy of adsorption can be separated into terms arising from the pressure change and from adsorption. Each point of the isotherm (chemical potential curve) corresponds to adsorption equilibrium of CO₂ on mmen-Mg₂(dobpdc) at a specific temperature and pressure, in which the chemical potential of gas phase CO₂ is equal to that of the adsorbed molecules on the surface. Since in the experimental conditions investigated CO₂ can be treated as ideal gas, the chemical potential relations for adsorption equilibrium is represented by the equations below, where the reference state for CO₂ is taken as the ideal gas at 1 atm and the given temperature.

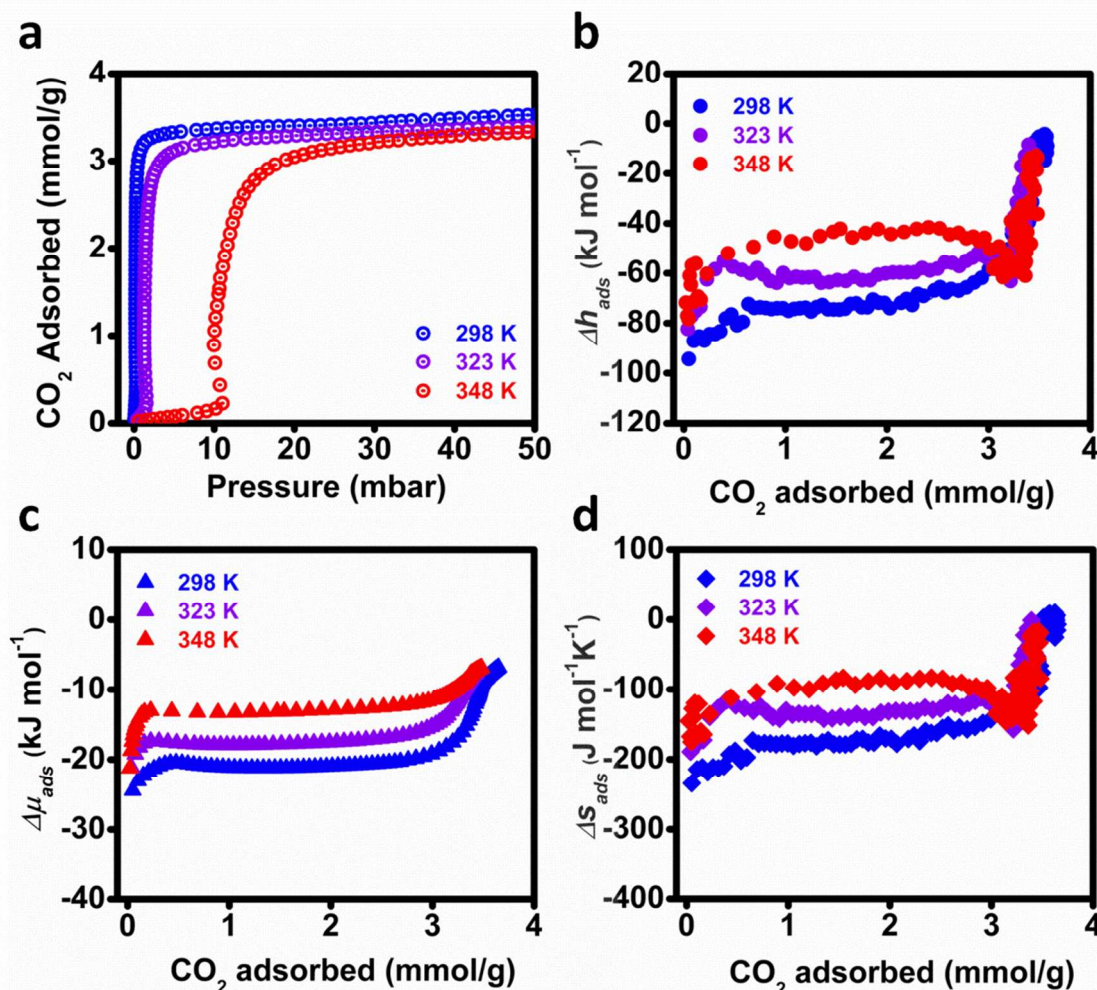


Figure 4. a) CO₂ adsorption isotherms and b) corresponding differential enthalpies c) free energies and d) differential entropies of CO₂ adsorption curves at 298 (blue), 323 (purple) and 348 (red) K on the same mmen-Mg₂(dobpdc) sample.

$$\Delta\mu_{\text{CO}_2}(\text{gas phase}) = RT\ln(p/p^\circ), (p^\circ = 1 \text{ atm}) \quad (1)$$

$$\Delta\mu_{\text{CO}_2}(\text{adsorbed}) = \Delta h_{\text{CO}_2}(\text{adsorbed}) - T \Delta s_{\text{CO}_2}(\text{adsorbed}) \quad (2)$$

$$\Delta\mu_{\text{CO}_2}(\text{gas phase}) = \Delta\mu_{\text{CO}_2}(\text{adsorbed}) \quad (3)$$

$$RT\ln p = \Delta h_{\text{CO}_2}(\text{adsorbed}) - T \Delta s_{\text{CO}_2}(\text{adsorbed}) \quad (4)$$

$$\Delta s_{\text{CO}_2}(\text{adsorbed}) = \frac{\Delta h_{\text{CO}_2}(\text{adsorbed})}{T} - R\ln p \quad (5)$$

Therefore, the partial molar entropy change associated only with the binding of CO₂, can be derived as $\Delta s_{\text{adsorption}} = \Delta h_{\text{CO}_2}(\text{adsorbed})/T$, (see Figure 5a), and $\Delta s_{\text{adsorption}}$ shows the same trend as the differential adsorption enthalpy. On the other hand, the entropy contribution from pressure variation ($\Delta s_{\text{pressure}} = -R\ln p$) is shown in Figure 5b. It becomes less positive at a given loading as temperature increases because at higher temperature a higher pressure is needed for a given coverage. Both chemisorption and physisorption of CO₂ are reproducible with regeneration at 373 K; adsorption is reversible and the MOF does not degrade upon regeneration.

Discussion

The enthalpies of sorption at room temperature in the plateau region, representing chemisorption, which accounts for most of the adsorption, are in the same range as previous values from both isosteric heat calculated from the temperature dependence of adsorption isotherms¹⁴ and quantum-chemical calculations¹⁵. Direct gas adsorption calorimetry provides additional resolution in describing chemisorption of CO₂ on fresh, zero coverage material at various temperatures and at low and high coverage. Such sensitivity and resolution is not provided by the prior studies and indeed those methods can not readily discern the dependence of adsorption on coverage and temperature.

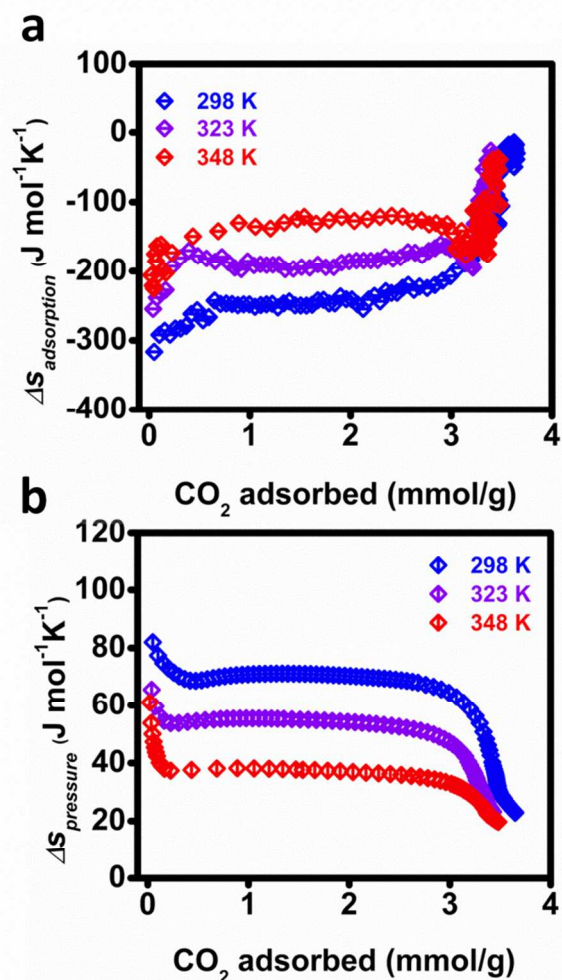


Figure 5. Entropies of CO₂ adsorption at 298 (blue), 323 (purple) and 348 (red) K on the same mmen-Mg₂(dobpdc) sample, a) contribution from CO₂ adsorption, b) contribution from CO₂ expansion from 1 atm to the pressure in the adsorption isotherm.

The partial molar properties (Δh_{ads} , $\Delta \mu_{\text{ads}}$, Δs_{ads}) and their corresponding isotherms at all three temperatures show clear evidence of discontinuity or at least of very rapid change over a small interval of coverage when plotted against the loading of CO₂ (Figure 4). The sharp changes and plateaus on these curves divide each adsorption event into three distinct stages, the strongest exothermic initial adsorption, the majority moderate chemisorption at intermediate coverage and the weakest physisorption at highest coverage. Indeed, these discontinuous steps are strong indication of changing adsorption mechanisms, perhaps representing the occupation of distinct families of adsorption sites. Most previous reports suggest a 2:1 (amine : CO₂) reaction stoichiometry^{8, 15, 24}. More recently, quantum-chemical calculations¹⁵ demonstrate a 1:1 amine: CO₂ stoichiometry with a higher adsorption capacity as well as weaker adsorption energy than that of the 2:1 stoichiometry. In light of the current calorimetric observations, a multi-step reaction mechanism as a function of amount of CO₂ adsorbed is proposed. When the first dose is introduced, the local pressure of CO₂ in the pores of mmen-Mg₂(dobpdc) is extremely low. In other words, the population of amine groups on the pore surfaces is significantly higher than the very few CO₂ molecules inside the pores. Therefore, at this initial stage of chemisorption, a 2:1 stoichiometry is very likely to be favored, producing the most exothermic heat effect,

supported by the S-shape step observed on the isotherm. Later on the isotherm, as more CO₂ molecules are deposited into the channels and adsorbed, fewer amine groups are available. Subsequently, when about 0.5 mmol/g CO₂ is loaded, the chemisorption appears to change sharply, probably to a 1:1 stoichiometry representing the lowest free energy (see the free energy plateau in Figure 4c). Such evolution is reflected in both the enthalpy curves and isotherms. Therefore, it is reasonable to have an S-shaped isotherm with stronger initial binding that fades with increasing coverage as the mechanism of binding changes. Furthermore the most exothermic heat effects at low concentration with the 2:1 mechanism also have the most negative binding entropy, so the switch in mechanism reflects a competition between energetic and entropic factors. The calorimetric data support a sharp change in adsorption mechanism with loading but do not of themselves identify the microscopic structural details. Further structural and spectroscopic evidence is necessary to reveal and describe the reaction pathway on the molecular level²⁵. Interestingly, for CO₂ adsorption at 323 and 348 K, the enthalpy of adsorption tends to be slightly more exothermic near the end of the plateau, before the start of physisorption. Although there is not clear spectroscopic evidence, it is possible that at high coverage and elevated temperatures the surface structure may undergo some rearrangement. This has not been investigated in detail as the overall effect is small.

Although a less exothermic enthalpy of adsorption with significant change of magnitude as temperature increases is not commonly observed for typical inorganic materials, the observed trend of chemisorption enthalpy for this MOF is entirely possible, since the organic functional groups of hybrid materials have additional degrees of freedom from vibration, rotation, and/or changing hydrogen bonding environments. In addition, the inherent flexibility of MOF type hybrid materials may contribute to the entropy term. Moreover, upon heating, the adsorption and desorption rates tend to increase dramatically approaching a point, at which the CO₂ mass transfer at gas/solid interface reaches dynamic equilibrium, with a significant number of molecules moving on the surface (Figure 5). The above factors may make the energy of adsorption less favorable but increase the entropy of the system, as observed in this work.

The present thermodynamic study highlights several outstanding features of mmen-functionalized Mg₂(dobpdc) compared with traditional amine based MOF CO₂ sorbents. First, its unique “S-shaped” isotherm followed by steep uptake endows it with a large adsorption capacity at room temperature, a high chemisorption to physisorption ratio, and considerable binding strength. This enhances the capacity, selectivity, and stability during storage and transportation of a CO₂ loaded MOF. In addition, the decreased magnitude of heat effects at higher operating temperature may make desorption easier and reduce energy cost in sorbent regeneration. Furthermore, this study also implies that the entropic contribution at elevated temperature is significant and hence may have to be considered for optimization of applications. The present study is a first step and emphasizes the fundamental physical chemistry of interaction between the mmen-Mg₂(dobpdc) and CO₂, without overcomplicating the system with additional components. In future optimization of the industrial application of CO₂ capture sorbents, H₂O vapor, SO_x, and NO_x, should also be considered.

Conclusions

Direct gas adsorption calorimetry of CO₂ on mmen-Mg₂(dobpdc) determined the binding energies as a function of loading, tested the capture reproducibility and reversibility, separated and quantified the different types of binding sites, and suggested reaction mechanisms in different loadings at different temperature. These

detailed findings are a crucial first step to design and optimize new carbon capture materials. Future research will focus on expanding thermodynamic study of carbon dioxide adsorption at various temperatures, and on hydrated functionalized MOF surfaces, providing essential information for MOF-based CO₂ adsorbents in real operating conditions.

Acknowledgements

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Notes

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†D.W. and A.N. designed the research. T.M.M. and J.R.L. provide the material. D.W., Z.Q. and P.Z. performed the experiments. D.W., S.V.U. and A.N. analyzed the data. D.W. and A.N. wrote the paper.

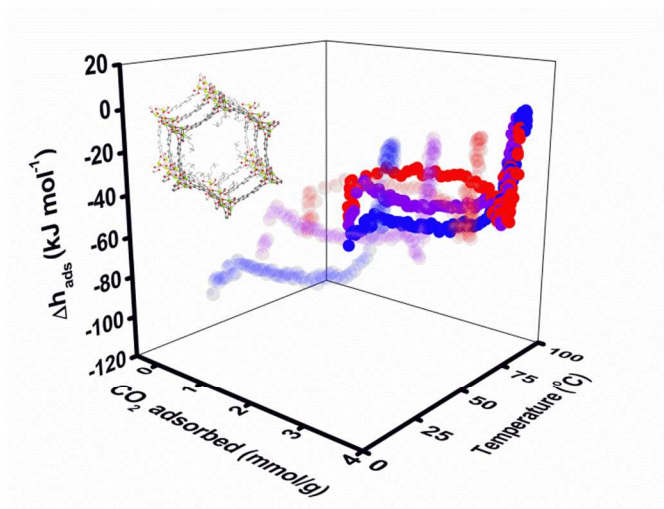
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- 25 Spectroscopic and structural studies, which support our thermodynamic conclusions, have been carried out parallelly by some of the coauthors in this work. A separated paper has been submitted to elsewhere.

Graphical Abstract



The CO_2 adsorption enthalpy on an alkylamine-appended MOF, $\text{mmen-Mg}_2(\text{dobpdc})$, was directly identified by adsorption calorimetry at 298, 323 and 348 K. The data suggest three adsorption events as function of coverage: two types of strong chemisorption and one weak physisorption. A multistage reaction mechanism was proposed. Moreover, both $\Delta\mu_{ads}$ and Δh_{ads} become less negative with increasing temperature. Thus, the unusual increasing adsorbent surface entropy and weakening CO_2 binding are suggested at elevated temperature.