Hydration Energetics of a Diamine-Appended Metal–Organic Framework Carbon Capture Sorbent

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ABSTRACT: mmen-Mg2(dobpdc) (mmen = N,N′-dimethyl-hethlyenediamine, dobpdc = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) is a diamine-appended metal–organic framework (MOF) material with promising future as an efficient CO2 capture sorbent for industry applications. Here, using adsorption calorimetry, the energetic landscape of mmen-Mg2(dobpdc) hydration has been revealed. Specifically, at near-zero water coverage, hydration results in the most exothermic differential enthalpy of adsorption of −110.9 ± 3.1 kJ/mol water. A differential enthalpy plateau at ∆65.8 ± 4.7 kJ/mol water is observed at the intermediate degree of hydration, which corresponds to water–diamine chemisorption through hydrogen bonding. Eventually, mmen-Mg2(dobpdc) hydration has been revealed. Specifically, at near-zero water coverage, hydration results in the most exothermic differential enthalpy of adsorption of −110.9 ± 3.1 kJ/mol water. A differential enthalpy plateau at ∆65.8 ± 4.7 kJ/mol water is observed at the intermediate degree of hydration, which corresponds to water–diamine chemisorption through hydrogen bonding. Eventually, mmen-Mg2(dobpdc) hydration is concluded at the second differential enthalpy plateau at ∆44.2 ± 1.8 kJ/mol water suggesting condensation of water within the internal channel space of mmen-Mg2(dobpdc). The position of the second plateau at about ∆44.0 kJ/mol water strongly suggests formation of liquid-like water clusters within the hydrophilic nanoconfinement environment. This comprehensive study energetically distinguishes the guest–host interfacial bonding and guest–guest intermolecular interactions for the water–mmen-Mg2(dobpdc) system, which provides fundamental thermodynamic data to enhance our understanding of the behavior of CO2 capture sorbents in the presence of moisture.

INTRODUCTION

Metal–organic frameworks (MOFs)-based materials have great potential to be applied as sorbents for adsorptive separation of gas1–4 or liquid mixtures5–8 such as carbon capture,9,10 alkane/alkene separation,11–13 organosulfur elimination,14 and noble gas mixtures separation.15–17 MOFs are a family of crystalline porous materials, constructed through coordination between metal nodes and organic linkers.17 Their open framework structures with large surface area feature accessible metal sites and tunable linkers, both of which can be further modified to introduce chemical functionalities. One example is a diamine-appended MOF, N,N′-dimethylthelyenediamine (mmen)-Mg2(dobpdc), (dobpdc = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate), which exhibits complex “first-order phase transition-like” metal site–amine cooperative insertion binding mechanism leading to step-shape CO2 sorption isotherms with high working capacity.18,19 Interestingly, the “step” of each isotherm right-shifts significantly as temperature increases.18,19 While its CO2 capture performance and adsorption energetics have been thoroughly investigated,19,20 the thermodynamics of water–mmen-Mg2(dobpdc) interactions remains undocumented. Moreover, considering the metastability of MOF-based materials under humid conditions, and potential applications of mmen-Mg2(dobpdc) in industrial settings, it is essential and critical to understand its hydration properties.

Degradation of MOFs under humid conditions21 and decreased CO2 adsorption capacity in the presence of moisture have been reported.22,23 On the other hand, in numerous studies, it has been observed that hydration affected CO2
capture capacity. For example, Liu et al. reported a significantly decreased CO$_2$ adsorption capacity for Mg$_2$(dobdc) (1,4-dioxido-2,5-benzenedicarboxylate) when it was exposed to steam. Chen et al. examined the role of water in CO$_2$ capture on both hydrated and dehydrated MIL-101 (Cr). Interestingly, they found that the water molecules in hydrated MIL-101 (Cr) acted as additional CO$_2$ adsorption sites, which led to increased CO$_2$ uptake at low pressure. Moreover, it has been reported that a 5-fold increase in CO$_2$ adsorption capacity on MIL-100 (Fe) was seen at 40% of relative humidity. For mmen-Mg$_2$(dobpdc), Long and his colleagues thoroughly investigated its CO$_2$ capture performance in the presence of moisture. Specifically, Fourier transform infrared (FTIR) results suggested that water did not impact the cooperative insertion mechanism of CO$_2$ capture. Surprisingly, they also found that for mmen-Ni$_2$(dobpdc), one member of the mmen-M$_2$(dobpdc) family did not adsorb CO$_2$ through cooperative insertion, attributed "hydration-boosted" CO$_2$ capture capacity. They attributed such enhancement to the formation of bicarbonates and/or alkyl ammonium carbamate species. They also found that for mmen-Mg$_2$(dobpdc), one member of the mmen-M$_2$(dobpdc) family did not adsorb CO$_2$ through cooperative insertion, attributed "hydration-boosted" CO$_2$ capture capacity. They attributed such enhancement to the formation of bicarbonates and/or alkyl ammonium carbamate species. This phenomenon was highlighted by Jones and colleagues.27 These studies point out the critical role of water in governing CO$_2$ capture performance and mechanisms. However, experimental thermodynamic studies on sorbent hydration energetics and mechanisms using calorimetry are rarely reported.

Adsorption calorimetry has been primarily applied to study the surface energetics of nanoparticles and nuclear materials and binding site distribution within porous materials and on catalyst surface. A typical setup includes a Calvet microcalorimeter coupled with a commercial gas adsorption analyzer (see Figure 1a). Recently, we applied this method-
the calorimeter from high vacuum. About 20 mg of mmen-Mg₂(dobpdc) was loaded on one side of a home-made silica glass forked tube. The other side of the tube remained empty serving as a reference. This sample tube was introduced into the calorimeter, connected with the gas dosing port, and degassed under vacuum (<10⁻⁶ mmHg) at 100 °C for 24 h to remove any presorbed species. During the calorimetry measurements, 3Flex, the gas dosing system, dosed water vapor incrementally. Each dose introduced ~1 μmol of water vapor with at least 2 h gap to ensure that the adsorption reached thermodynamic equilibrium, which was evidenced by a horizontally flat baseline. Each adsorption equilibrium led to a corresponding calorimetric signal (peak). The adsorption isotherm and associated heat effects were monitored and recorded simultaneously. Integration of the area under the calorimetric peak returned the total heat effect (k) of a particular dose (mole of adsorbate). We used a Calisto Processing software (AKTS, Switzerland) for peak area integration and data analysis.

**Thermogravimetry—Differential Scanning Calorimetry—Mass Spectrometry (TG—DSC—MS).** TG—DSC—MS analysis was performed using a STA 449 F3 Jupiter (Netzsch Instrument) coupled with a quadrupole mass spectrometer QMS 403 D (Aéolos) to elucidate the dehydration and decomposition processes of hydrated mmen-Mg₂(dobpdc) in air. A sample pellet, ~10 mg, was placed in aPt crucible and heated from 35 to 600 °C at 10 °C per min under air flow (20 cm³/min). The evolved gases were analyzed simultaneously at both MS, in which signals of water (m/z = 18) and CO₂ (m/z = 44) were recorded.

### RESULTS AND DISCUSSION

The 1D SAXS pattern of mmen-Mg₂(dobpdc) is presented in Figure 1c, in which three major peaks are identified with d-spacings of 1.86 nm (d₁), 1.07 nm (d₂), and 0.93 nm (d₃). Their corresponding d₁/d₂ ratios are approximately 1, √3, and 2. Such geometry strongly suggests a 2D hexagonal superstructure.36 Considering the mesoporosity of mmen-Mg₂(dobpdc), the first three peaks in Figure 1c are indexed as (10), (11), and (20). Further, we calculated the lattice constant of mmen-Mg₂(dobpdc) (2.15 nm) using the following equation.36

\[
\frac{1}{d_{hk}^2} = \frac{4h^2 + hk + k^2}{3a^2}
\]

DRIFTS data were collected to ensure the success of mmen—metal coordination (see Figure 2). After heating at 100 °C, two well-resolved peaks are observed between 3400 and 3200 cm⁻¹, which correspond to the stretching vibration modes of grafted (3259 cm⁻¹) and free (3328 cm⁻¹) N—H groups37 of the mmen molecule. The bands between 2800 and 3000 cm⁻¹ are assigned to the stretching vibration of the mmen molecule.18,35 The peaks found at about 1630 and 1590 cm⁻¹ are probably due to the carbamate C=O stretching modes.38 There is also a well-resolved IR band at about 1334 cm⁻¹ owing to the vibrational mode of C—N within carbamate,38,39 which is the product of CO₂ cooperative insertion in mmen-Mg₂(dobpdc). This set of data is a strong evidence suggesting the success in grafting of mmen molecules at the metal sites of Mg₂(dobpdc). Moreover, it also details the adsorption isotherm at 25 °C and corresponding thermodynamic data for comparison.20 The triplicated water adsorption isotherms are overlapped, which suggests good reproducibility. The most exothermic near-zero coverage differential enthalpy of hydration is −110.9 ± 3.1 kJ/mol water, which is more exothermic than that of CO₂ adsorption, −94.4 ± 2.8 kJ/mol CO₂.20 Subsequently, the differential enthalpy of hydration curve tends to be less exothermic and switches to a plateau at −65.8 ± 4.7 kJ/mol water. This plateau starting from ~0.2 mmol/g suggests strong hydrogen bonding between water and the amine groups of mmen-Mg₂(dobpdc). Notably, at an uptake of 3.5 mmol/g, CO₂ adsorption becomes energetically less favorable (less exothermic) compared with hydration. At about 4.0 mmol/g, the differential enthalpy of the hydration
curve gently reaches its second plateau at $-44.2 \pm 1.8$ kJ/mol water. The magnitude of this heat effect strongly suggests condensation of water within the hydrophilic confinement environment of mmen-Mg$_2$(dobpdc).

To further reveal the thermodynamic insights into mmen-Mg$_2$(dobpdc) hydration as a function of water loading, we derive other partial molar properties of water adsorption, including chemical potential (differential free energy) and differential entropy of hydration (see Figure 3c,d). In our earlier study, we choose pure CO$_2$ at 1 atm and 25 °C as the standard state. In this study, the chemical potential (partial molar free energy) is derived from the water adsorption isotherm using the equation $\Delta \mu = RT \ln(p/p^o)$, in which $p/p^o$ is the relative pressure of water vapor. The choice of the standard state for a particular adsorption system does not impact the results of our analysis because what we obtain is the difference between the initial state (pseudosorption of a specific dose) and the final state (postadsorption equilibrium of that dose). We use the chemical potential and directly measured differential enthalpy of hydration data to calculate the partial molar hydration entropy using the following relation: $\Delta h_{ads} = \Delta h_{ads} - T \Delta s_{ads}$.

The chemical potential mimics the fashion of differential enthalpy of hydration profile. Specifically, $\Delta h_{ads}$ appears to be less negative as more water is loaded. At near-zero coverage, the steep increase in both differential enthalpy and chemical potential of hydration highlights the strong thermodynamic driving force of initial water–mmen-Mg$_2$(dobpdc) binding. Meanwhile, the partial molar hydration entropy tends to be less negative as water loading increases. This indicates that the dynamics of water confined within mmen-Mg$_2$(dobpdc) channels appears to be bulk water-like. Such a phenomenon has not been observed in our earlier study on thermodynamics of Cu-HKUST-1 hydration, which has much more hydrophobic surfaces.

Furthermore, we separate the differential entropy of hydration into two terms, one corresponding to (1) the entropy change due to pressure increase, $\Delta S_{pressure} = -R \ln(p)$, the other (2) purely originates from hydration, $\Delta S_{hydration} = \Delta h_{adsorption}/T$. The results are plotted in Figure 4, in which pressure increase leads to entropy increases, while adsorption results in more ordered, liquid-like water adsorbed on the sorbent surface and confined within the pore space of mmen-Mg$_2$(dobpdc), leading to entropy decrease. The TG–DSC–MS results of hydrated mmen-Mg$_2$(dobpdc) in air flow are presented in Figure 5. There appears to be a four-stage weight loss mechanism. Specifically, in stage 1, between 35 and 150 °C, the sample loses about 15% of its weight, resulting in a broad endothermic peak due to dehydration and desorption of CO$_2$ picked up once exposed to ambient conditions (see Figure 5, m/z = 18 and 44). In stage 2, further dehydration between 150 and 295 °C accounts for another ~15% weight loss leading to an endothermic heat event. Subsequently, in stages 3 and 4, the sample experiences a two-step highly exothermic combustion accompanied with simultaneous liberation of water and CO$_2$. Particularly, stage 3 decomposition ranges from 295 to 450 °C showing a sharp exothermic peak centered at 397 °C, which is very likely due to combustion of mmen. After 450 °C, all organic species, primarily the organic linkers of Mg$_2$(dobpdc), are fully oxidized to water and CO$_2$ in stage 4. The TG–DSC–MS results synchronize well with the water adsorption calorimetry data, both of which highlight the presence of two groups of energetically distinctive water in hydrated mmen-Mg$_2$(dobpdc), including chemisorbed water and loosely confined physisorbed water. The populations of these two types of water are approximately the same, according to the isotherm and TG–DSC–MS data. The delayed presence of the first two water peaks in the MS profiles is due to the dynamic nature of TG–DSC–MS thermal analysis and diffusion resistance from the sorbent.

In light of the calorimetric results, we are able to interpret the hydration mechanism of mmen-Mg$_2$(dobpdc). First, the differential enthalpy, entropy, and chemical potential of water adsorption all point out that the hydration of mmen-Mg$_2$(dobpdc) has three distinctive steps, including (i) near-zero coverage water binding on the most favorable sites, (ii) water adsorption at the majority amine groups through hydrogen bonding (the first plateau), and (iii) water–water intermolecular interactions under pore confinement. In general, (i) and (ii) are classified as guest–host interfacial interactions, while (iii) is categorized as guest–guest intermolecular interactions under nanoco confinement. This is distinctly different from what we have found for CO$_2$ capture on mmen-Mg$_2$(dobpdc), in which only adsorbate–adsorbent binding was detected. This is because at near-room temperature and pressure below 1 bar, CO$_2$ does not have significant intermolecular interactions, whereas water molecules tend to bind themselves through hydrogen bonding. As a result, water–water interactions (clustering and/or condensation) are particularly severe under nanoco confinement in materials with mesoporosity and hydrophilic surfaces. In sharp contrast, hydration of hydrophobic MOFs and solid-state oxides usually...
returns differential enthalpy of hydration much less exothermic than $-44.0 \text{ kJ/mol water}$. In other words, water molecules tend to fill channels or pores with hydrophilic surfaces, yet they form highly dynamic metastable clusters within hydrophobic environments.

This calorimetric study highlights a few unique hydration properties of mmen-Mg$_2$(dobpdc). The condensation is very likely to result in pore blockage leading to poor gas transport and sorbent degradation. In summary, the fundamental calorimetric study provides comprehensive thermodynamic insights governing the complex interactions among water, CO$_2$, and mmen-Mg$_2$(dobpdc).

### CONCLUSIONS

In this study, we applied water adsorption calorimetry as a fundamental tool to study the thermodynamics of mmen-Mg$_2$(dobpdc) hydration. We found that beyond the near-zero coverage binding (110.9 ± 3.1 kJ/mol water), mmen-Mg$_2$(dobpdc) hydration is stepwise featuring two distinctive stages representing water–amine interfacial binding (65.8 ± 4.7 kJ/mol water) and water–water intermolecular interactions (condensation) in pores (44.2 ± 1.8 kJ/mol water). Further, the chemical potential and partial molar entropy evolutions of mmen-Mg$_2$(dobpdc) hydration were derived from the calorimetry results and discussed, which mirror favorable hydration on a hydrophilic sorbent. This set ofhydration thermodynamics data is complementary to the existing CO$_2$ capture studies on mmen-Mg$_2$(dobpdc), which aids our fundamental understanding of the energetics of hydration related to CO$_2$ capture on mmen-Mg$_2$(dobpdc) (M: metal) sorbents.

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**Notes**
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### REFERENCES


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