

Enhanced CO₂ Adsorption in Metal-Organic Frameworks via Occupation of Open-Metal Sites by Coordinated Water Molecules

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CO₂ is one of the most important greenhouse gases and its removal from flue gas and natural gas has become increasingly important. We report an interesting discovery in which the CO₂ uptake and its selectivity over N₂ and CH₄ in the metal-organic framework (MOF) Cu-BTC were significantly increased by the presence of water molecules coordinated to open-metal sites in the framework. This was first predicted by molecular simulations and later validated by experiments. A detailed analysis of simulation data revealed that interaction between the quadrupole moment of CO₂ and the electric field created by water molecules is responsible for the enhanced CO₂ uptake. These findings could open new possibilities for tuning the adsorption behavior of MOFs for CO₂ capture and other applications.

Introduction

Concerns about greenhouse gases in the atmosphere have led to significant interest in removing CO₂ from the exhaust streams of fossil fuel combustion as the first step in carbon sequestration.^{1,2} For flue gas, the high temperature and low CO₂ partial pressure make this separation particularly challenging. Separations involving CO₂ are also important in a variety of other applications such as upgrading of natural gas and hydrogen purification. Adsorption and membrane-based separation technologies hold many advantages for these problems, particularly because of their low energy requirements. Therefore, many materials have been investigated for CO₂ adsorption, including zeolites, other inorganic molecular sieves, and carbon-based materials.^{3–10}

Metal-organic frameworks (MOFs) are a new class of nanoporous materials that have potential applications in separation processes, catalysis, and gas storage. MOFs are synthesized using organic linker molecules and metal joints that self-assemble to form materials with well-defined pores,

high surface areas, and desired chemical functionalities.^{11–15} Because of these attractive properties, MOFs are promising candidates for CO₂ capture. In this work, we demonstrate that preadsorbing a small amount of water can increase the capacity and selectivity of the MOF Cu-BTC for CO₂. This unexpected result was first predicted by molecular simulation and then verified experimentally in our laboratory. This enhancement of the sorptive properties of Cu-BTC by coadsorbed water can be readily generalized to other guest molecules and other MOFs as a way to tune the properties of MOFs.

In many MOFs, the metal atoms are coordinatively saturated by the organic linkers that are connected to create the framework. However, in some MOFs, metal atoms are partially coordinated by solvent molecules from the synthesis procedure. It is common practice to activate MOFs at elevated temperature to remove the solvent and open the void space for desired guest molecules. If the evacuation temperature is high enough, all solvent molecules can be removed, including those that are coordinatively bound to framework metal atoms. Removing these coordinated solvent molecules leaves coordinatively unsaturated open-metal sites that have been shown to promote high gas uptake, especially for H₂ adsorption.^{16–24} Recently, for example, Bae et al.²⁵ showed that in a carborane-based MOF²³ removal of coordinated dimethylformamide (DMF) increased CO₂ and CH₄ adsorption and led to high selectivity for CO₂ over CH₄. The open-metal sites in MOFs are reminiscent of the extra-framework cations in zeolites, in that they are expected to

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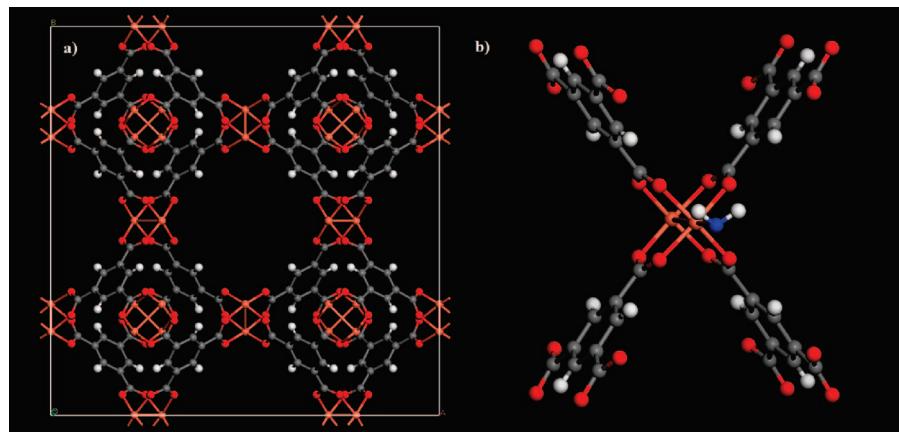


Figure 1. (a) Dry Cu-BTC unit cell, (b) hydrated Cu-BTC (4 wt %) with coordinated water molecule from DFT. Copper atoms are orange, oxygens red, carbons gray, and hydrogens white. The oxygen atom of the coordinated water molecule is shown in blue.

create large electric fields and to bind polar molecules. In zeolites, it is well-known that the presence of water significantly decreases the adsorption of CO_2 because water competitively adsorbs on the cations, blocking access for CO_2 . In this work, the opposite effect is found: water bound to open-metal sites substantially increases CO_2 adsorption.

Methodology

Computational. Cu-BTC (also known as HKUST-1) is a well-studied MOF first synthesized by Chui *et al.*²⁶ For our simulations, we took the structure reported by them. The structure (Figure 1a) is composed of large central cavities (diameter 9.0 Å) surrounded by small pockets (diameter 5.0 Å), connected through triangular-shaped apertures (diameter 3.5 Å). The Cu-BTC framework has paddlewheel type metal corners connected by benzene-1,3,5-tricarboxylate (BTC) linkers. Each metal corner has two copper atoms bonded to the oxygens of four BTC linkers. In the as-synthesized material, each copper atom is also coordinated to one water molecule (not shown in Figure 1a), that is, two water molecules for each paddlewheel metal corner, corresponding to 8 wt % water loading.

We did grand canonical Monte Carlo (GCMC) simulations to predict the adsorption isotherms in Cu-BTC. All simulations were

performed with the Monte Carlo simulation suite of the MUSIC²⁷ code and included a 2×10^7 step equilibration period followed by a 2×10^7 step production run. A cutoff distance of 12.8 Å was used for Lennard-Jones interactions. The Ewald sum technique was used to compute the electrostatic interactions. All simulations were performed at 298.0 K and included random insertion, deletion and translation moves with equal probabilities. One Cu-BTC unit cell was used during all simulations and Cu-BTC atoms including the water molecules coordinated with the Cu-BTC framework were kept fixed.

Prior to GCMC simulations, density functional theory (DFT) calculations were performed for two purposes: first, to optimize the position of the hydrogen atoms of the water molecules (the reason for the optimization calculations will be explained in the next section) and second, to calculate the partial charges of the Cu-BTC framework atoms that were used later in the GCMC simulations. All DFT calculations were performed with the Gaussian03²⁸ software using the PBEPBE level of theory and 6-31+G* basis set. More simulation details and force field parameters can be found in the Supporting Information.

Experimental. Cu-BTC was synthesized according to the recipe given by Rowsell *et al.*²⁹ The as-synthesized crystals were activated at a temperature of 448 K for complete removal of solvent molecules. See Figure S12 in the Supporting Information for TGA analysis. Three different samples were prepared from the activated crystals. The first sample was the completely dehydrated Cu-BTC, which was not exposed to any further treatment. The other two samples were hydrated to varying degrees by exposing them to different levels of humidity. The first hydrated sample was fully saturated with water, and the second one had a 4 wt % loading of water. Note that 4 wt % water loading corresponds to one water molecule per two copper atoms. CO_2 adsorption isotherms were measured volumetrically. See the Supporting Information for experimental details.

Results and Discussion

There have been many prior molecular simulation studies of adsorption in Cu-BTC.^{30–38} None of them investigated

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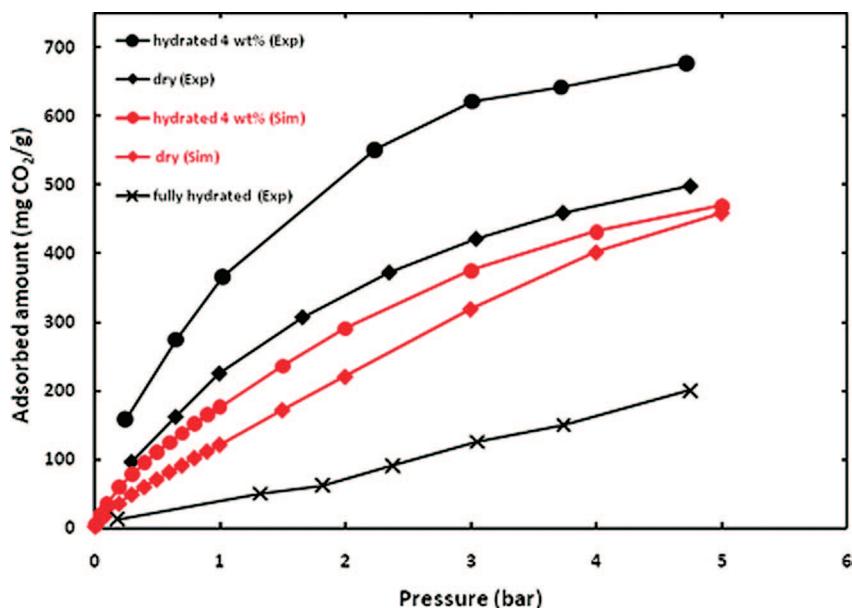


Figure 2. Simulated and experimental adsorption isotherms for CO_2 at 298 K in Cu-BTC with different water contents.

the effect of coordinated water molecules on the adsorption of gases. To include the coordinated water molecules in our simulations, the oxygens of the water molecules were located at the positions reported in the crystal structure of Chui et al.²⁶ We considered a water loading of 4 wt % by deleting one of the coordinated water molecules from each paddlewheel corner leaving only one copper atom coordinated. The crystal structure does not report the positions of the water hydrogen atoms. Therefore, we placed the hydrogen atoms manually using the Materials Studio Visualizer³⁹ and then optimized their positions with DFT calculations. In the optimized structure, the hydrogen atoms lean toward the carboxylate oxygens. See Figure 1b. GCMC simulations were performed to calculate CO_2 adsorption isotherms for the completely dehydrated Cu-BTC and the hydrated (4 wt %) Cu-BTC at 298 K. The predicted isotherms are shown in Figure 2 (red). Over the pressure range considered, the presence of coordinated water molecules increases the adsorption of CO_2 . At the lowest pressures, the increase is substantial. For example, at 0.1 bar, the hydrated Cu-BTC adsorbs 71% more CO_2 than the dry Cu-BTC. At 1 bar, the increase is around 45%, and at 2 bar 32%.

To test our prediction, we performed experimental adsorption measurements of CO_2 in Cu-BTC with different levels of hydration. The experimental isotherms are shown in Figure 2 (black) along with the simulated results. Over the entire pressure range examined, the experimental sample loaded with 4 wt % water adsorbs more CO_2 than the dry sample,

confirming the trend predicted by simulation. In addition, a fully hydrated Cu-BTC sample adsorbs very little CO_2 at all pressures, which is not surprising because the pores are full of water molecules.

The experiments validate the simulation prediction qualitatively, but there is not quantitative agreement of the isotherms, with the simulations consistently underestimating the experimental results. It should be emphasized, however, that there is some disagreement among experimental CO_2 adsorption isotherms for Cu-BTC in the literature, as shown in Figure 3.^{40–42} Differences in the isotherms may be due to different MOF synthesis and activation methods. At least six different synthesis routes have been reported for Cu-BTC,^{29,42–44} and the resulting Langmuir surface areas range from 918 to 2257 m^2/g .^{26,29,40–43,45} For example, Cu-BTC originally reported by Chui et al. was prepared at 180 °C in an autoclave in water/ethanol. This Cu-BTC product had a Langmuir surface area of 918 m^2/g . At the other extreme, Wong-Foy et al.⁴⁵ report a Langmuir surface area of 2257 m^2/g for a Cu-BTC prepared at 85 °C in DMF/water/ethanol. After solvent exchange, the latter sample was handled in an environment free from air and moisture.

We calculated an accessible surface area of 2137 m^2/g for a perfect Cu-BTC crystal using a geometric method reported previously.^{46,47} Our Cu-BTC sample was prepared similarly

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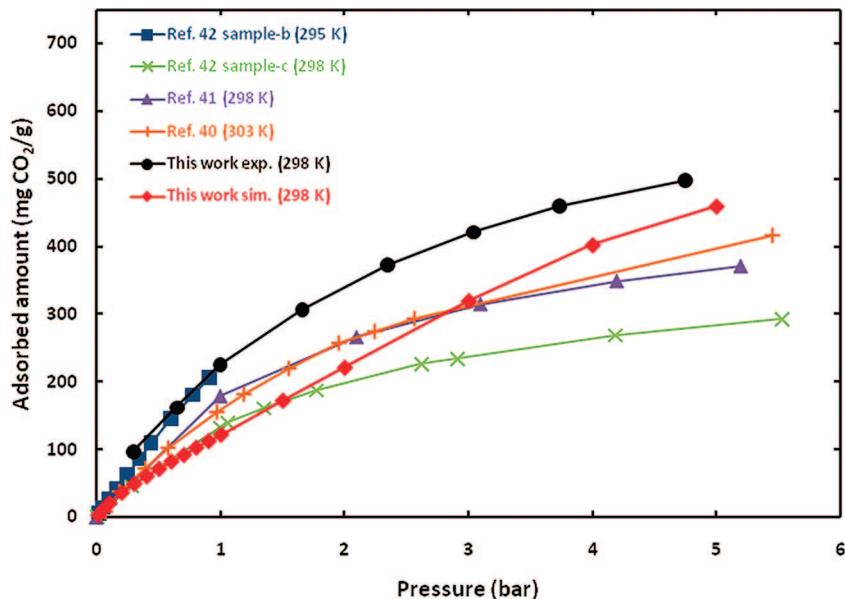


Figure 3. Experimental adsorption isotherms of CO_2 in Cu-BTC obtained from different resources.

to Wong-Foy *et al.* and had a Langmuir surface area of $1492 \text{ m}^2/\text{g}$. This is about 70% of the calculated value, which can be viewed as an upper limit for a perfect crystal. A water loading of 4 wt % corresponds to titrating half the copper atoms in a pristine sample of Cu-BTC with water molecules. However, because the surface area for our Cu-BTC sample is only $1492 \text{ m}^2/\text{g}$, we might conclude that fewer copper atoms are available for adsorbing water, and hence the 4 wt % water loading will, in fact, titrate more than half of the available copper open-metal sites. To confirm this hypothesis, a sample was also loaded with 8 wt % water. If our hypothesis is correct, this sample should adsorb less CO_2 adsorption than the 4 wt % sample because it contains uncoordinated water molecules that simply block pore space (similar to the fully hydrated sample). Note that simulation of CO_2 adsorption in Cu-BTC with 8 wt % water loading shows more CO_2 uptake than in the 4 wt % water sample (see Figure S8 in the Supporting Information). Consistent with our hypothesis, the experimental sample with 8 wt % water adsorbs less CO_2 than the 4 wt % sample. In fact, it even adsorbs less CO_2 than the dry sample. From these results, it can be argued that quantitative differences between simulation and experiment can be explained by deviations of the experimental MOF sample from the perfect crystal used in the simulations. Even with these differences, the experiments validate the qualitative prediction that preadsorption of water can be used to tune the affinity of Cu-BTC for CO_2 .

To gain some insight into why coordinated water molecules increase CO_2 adsorption, we examined the interaction energies from the GCMC simulations. Figure 4 shows the interaction energies between CO_2 and dry Cu-BTC and hydrated (4 wt %) Cu-BTC broken into Coulombic and non-Coulombic (Lennard-Jones) components. With the introduction of coordinated water molecules to the Cu-BTC structure, the non-Coulombic energy increases by 4–11% within the loading range reported in Figure 4. On the other hand, the Coulombic energy increases by a factor of 2.1–4. Thus

the Coulombic interactions between water and CO_2 are mostly responsible for the increase in CO_2 adsorption. The electrostatic interaction arises from the quadrupole moment of CO_2 interacting with the electric field gradient of the sorbent, which is increased when water occupies the copper open-metal site.

We also simulated adsorption of CH_4 and N_2 in the dry and hydrated Cu-BTC structures. In contrast to CO_2 , adsorption of CH_4 was not significantly affected and adsorption of N_2 was reduced by the coordinated water molecules (see Figures S9 and S10 in the Supporting Information). This is consistent with CO_2 having a larger quadrupole moment than N_2 . (CH_4 has no quadrupole moment.) In addition, we simulated equimolar mixtures of CO_2/CH_4 and CO_2/N_2 in dry Cu-BTC and hydrated Cu-BTC at 298 K. The predicted selectivities are presented in Figure 5. The coordinated water molecules significantly improve the selectivity of CO_2 over CH_4 and N_2 , which is a promising outcome for the separation of CO_2 from natural gas and flue gas, respectively. An increase in CO_2 selectivity over CH_4 with hydration was previously reported for the MOF MIL-53.⁴⁸ The mechanism in that system involves an almost complete blockage of pores for nonpolar CH_4 by water molecules and a breathing effect⁴⁹ that takes place around 11 bar as water is progressively displaced by CO_2 , causing a structural shift in the MOF that opens the pores in favor of CO_2 . This is obviously a completely different mechanism than what we observe in Cu-BTC.

In our simulations, we have modeled the Cu-BTC framework as rigid and used the same unit cell for the dry and hydrated structures. One might ask whether removing the coordinated water molecules could cause a structural change in the unit cell of Cu-BTC that is neglected in our simulations. Prestipino *et al.*¹⁶ studied the structure of Cu-BTC with spectroscopic and

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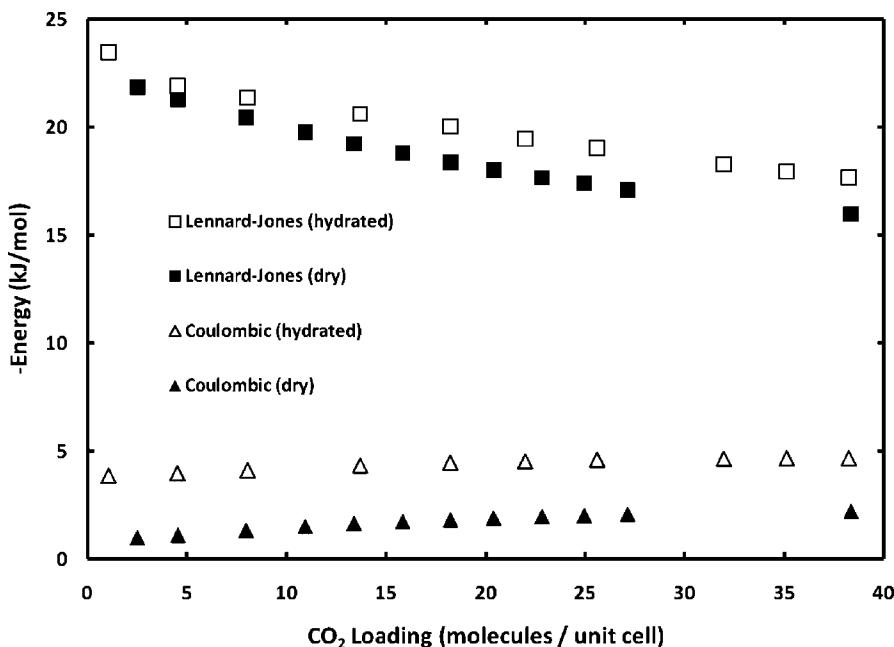


Figure 4. Interaction energies between CO_2 and dry Cu-BTC and hydrated Cu-BTC (4 wt %) from GCMC simulations at 298 K. To convert molecules per unit cell to mg/g, multiply by 4.3557.

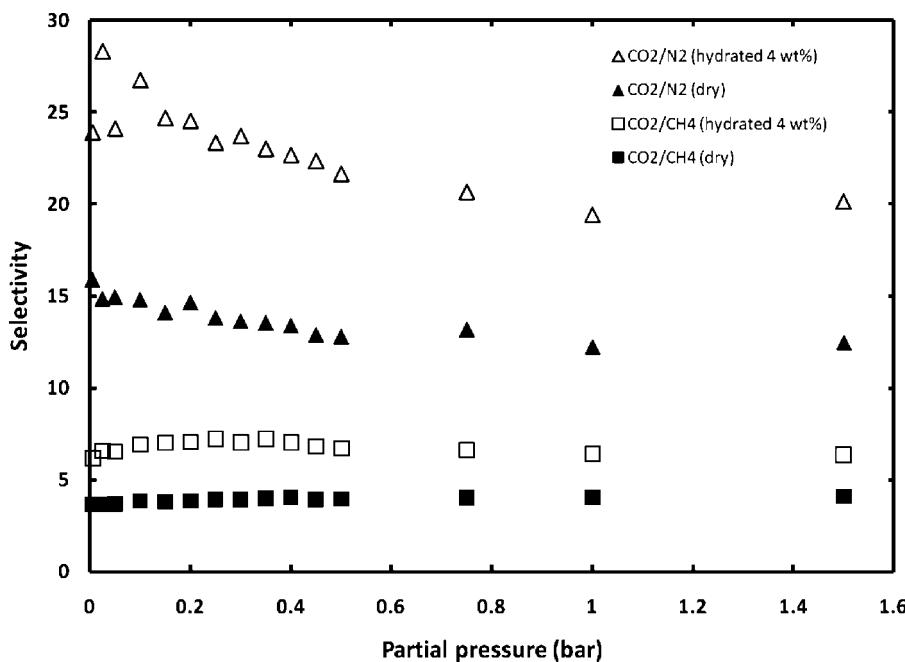


Figure 5. CO_2 selectivities from the simulations of equimolar mixtures of CO_2/CH_4 and CO_2/N_2 at 298 K.

X-ray diffraction methods after the coordinated water molecules were removed by activation at 453 K. They reported that the distances in the hydrated structure between the two copper atoms (2.628 Å) and between the copper and oxygen atoms (1.952 Å) were shortened by 0.14 and 0.02 Å, respectively, upon dehydration. In addition, the unit-cell length decreased from 26.342 to 26.2243 Å, which corresponds to a 1.3% volume reduction. Note, however, that the unit-cell lengths were not measured at the same temperature, so part of the unit-cell shrinkage could also be due to negative thermal expansion, which has been reported for other MOFs.⁵⁰ These structural

changes are very small and were neglected in our work. Prestipino et al. did not report the dehydrated Cu-BTC crystal structure.

Conclusion

We have shown that water molecules coordinated to open-metal sites significantly increase CO_2 adsorption in Cu-BTC. This result was first discovered using molecular simulation and then verified experimentally, showing the power of molecular modeling. Axial ligation of coordinatively unsaturated metal sites by various molecules could open new possibilities for tuning the adsorption behavior of MOFs for CO_2 capture and other applications.

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Supporting Information Available: Details of DFT calculations, GCMC simulations, force field information, and experimental setup and procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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