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Competitive Binding of Ethylene, Water, and Carbon Monoxide in Metal-Organic Framework Materials with Open Cu Sites

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Abstract

Metal-organic frameworks (MOFs) with open metal sites (OMS) are known to have selectivity in olefin/paraffin separations because of pi-pi interactions between olefin double bonds and OMS. One challenge associated with these separations is that other species that potentially bind to OMS may also be present in feed streams, causing competition for these sites. We used Density Functional Theory (DFT) to assess the binding energy of ethylene, water, and carbon monoxide on a set of more than 60 MOFs with open Cu sites in the form of Cu dimers. One useful observation from our results is that the relative binding energies of pairs of molecules (e.g. ethylene and water) can be calculated accurately from calculations that hold the MOF structure rigid and only relax the positions of the adsorbing molecules. These kinds of calculations are far more numerically efficient than calculations that relax all degrees of freedom in the system, so this observation will be useful in future efforts to screen larger collections of materials. A second observation is that the binding energies of each molecule in the 60 MOFs are quite similar to the binding energies in CuBTC, an exemplar MOF with open Cu sites in the form of Cu dimers. Analysis of the variations that do exist in the binding energies among materials points to possible avenues for controlling either the absolute binding energies or the relative binding energies of species associated with OMS in these materials. The third observation is that two unusual MOFs can bind ethylene more strongly than water because of a dual-site binding mechanism in which an ethylene molecule can interact simultaneously with both dimers while the smaller water molecule interacts primarily with a single OMS. This observation suggests a possible avenue for developing other MOFs in which the binding energy of ethylene is higher than that of water.

1. INTRODUCTION

Ethylene is one of the world's largest chemical commodities. A key step in producing ethylene is the separation of ethylene from ethane, which is typically achieved industrially by high-pressure cryogenic distillation, a highly energy-intensive process.[1] One alternative process is to use nanoporous adsorbents such as metal-organic frameworks (MOFs) to separate olefins from paraffins.[2-4] Recently, the potential use of MOFs for this purpose has attracted considerable interest.[5-13] By assessing the rich functionality of organic linkers, metal nodes, and other physical properties in MOFs, high-performance materials for adsorption-based separations can potentially be developed.[14] One class of MOFs of particular importance for olefin/paraffin separation is materials with open metal sites (OMS). These sites allow pi-double-bond interactions with olefins, which leads to preferential interactions relative to paraffins.[3, 5-6, 15-16] As a result, MOFs with OMS offer opportunities for tuning the affinity of these materials towards certain adsorbates.

Bloch et al.[5] reported that a MOF with open Fe sites (Fe-MOF-74) exhibited an adsorption selectivity of 13 to 18 for an equimolar mixture of ethylene and ethane at 318 K.[17] Wang et al.[18] showed sorption isotherms for ethylene and ethane on CuBTC, a MOF with open copper sites, at 295 K that indicated preferential adsorption of ethylene over ethane. This finding was further supported by results from quantum mechanical calculations.[19] Kulkarni et al. evaluated the separation of the propylene/propane mixtures with MOFs with open copper sites using Grand Canonical Monte Carlo simulations.[6] Both experimental and computational results suggested that MOFs with OMS are strong candidates for the separation of olefins/paraffins.

The discussion above has highlighted examples of MOFs with OMS that have selectivity for olefins over paraffins. In considering practical separation processes, however, it is important to realize that these OMS may also bind other small molecules with high affinity. For example, water and carbon monoxide are both known to bind to the open Cu sites in CuBTC.[20-22] Although the levels of non-hydrocarbon species that are present will depend on the specific process used to generate a feed stream into a separation process, water, CO, and other species are very likely to be present with at least trace levels in any practical olefin/paraffin separation. For example, during the catalytic oxidative coupling of methane to ethylene process, byproducts can be CO, CO_2, C_2H_6, or H_2O based on O_2/CH_4 ratio, catalyst or other reaction conditions.[23-24] Thus, a potential challenge in the separation of ethylene from ethane using OMS MOFs is that water, carbon monoxide, or similar species may compete with ethylene for the open metal sites in MOFs. In this situation, the overall selectivity for ethylene over ethane could be significantly diminished. A key aim of this work is to quantify these effects in a range of MOFs.

The binding affinity of small molecules in MOFs is affected by the electronegativity and binding geometry of molecules at the metal centers, which are further determined by the factors such as the topology and organic linker of MOFs, the number and species of atoms bonded to the metal, and the species of metal. The objective of this paper is to quantify the binding affinity of ethylene, water, and CO in a range of

MOFs with open Cu sites. Although MOFs with a range of OMS are available, materials with open Cu sites have been particularly widely studied, so they provide a useful basis from which to study the relative importance of linker identity and framework topology on molecular binding energies. These calculations are aided by previous work by Chung et al., who developed the Computation-Ready Experimental (CoRE) MOF database of roughly 5000 structures obtained from the Cambridge Structural Database[25] and the work of Nie et al.[26] and Kulkarni et al.[6], who identified a group of MOFs with open Cu sites among the materials in the CoRE MOF database. It is reasonable to suppose that the binding energy of small molecules on open metal sites in MOFs is dominated by the chemical nature of the open metal site. If this hypothesis is correct, all MOFs with Cu sites defined by Cu dimers should show similar binding characteristics for ethylene, water, and CO. To test this hypothesis, we first study one specific material (CuBTC) in detail and then compute molecular binding energies of numerous related materials. Through this study, we have built insight into how MOF structures influence binding affinities. CuBTC (Figure 1 left) is a useful material for this comparison because it has been studied extensively in prior calculations[6, 19] and experiments[18] and the paddlewheel unit (Figure 1 right) present in CuBTC is also present in a large number of other MOFs. In this paper, we first tested whether information from rigid MOF calculations can be a useful approximation of the calculation with all degrees of freedom in MOFs. Then we also probed the sensitivity of our results to the choice of exchange-correlation (XC) functional. To this end, we have established the relative binding affinity of H_2O, C_2H_4, and CO in 65 rigid Cu MOFs with Cu paddlewheel dimer OMS using the PBE-D3 XC functional. Finally, we identified two MOFs that are unusual in that they bind ethylene more favorably than water because of a dual-site binding mechanism.

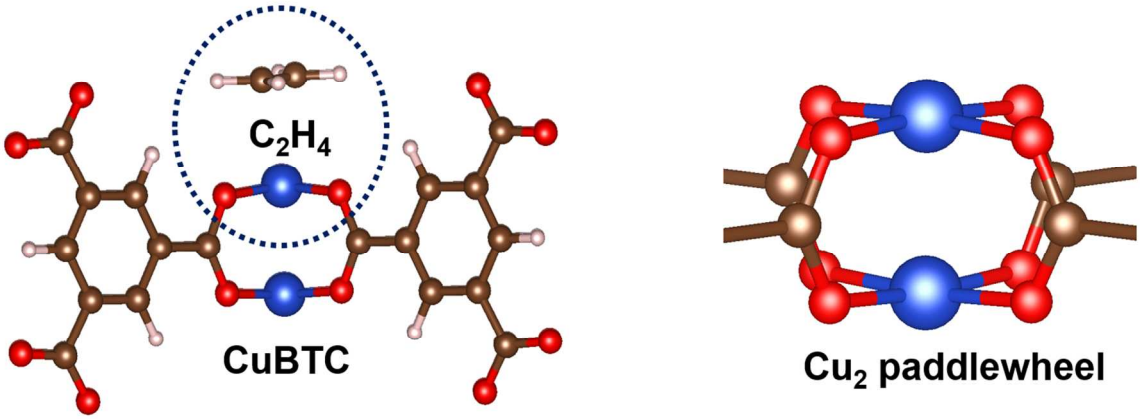

Figure 1: Left: Illustration of ethylene adsorbing on an open Cu site in CuBTC. Right: An expanded view of the Cu_2 paddlewheel unit in CuBTC. Cu, O, C, and H atoms are depicted in blue, red, brown, and white colors, respectively.

2. COMPUTATIONAL DETAILS

2.1 Density Functional Theory and Binding Energy Calculations

We calculate binding affinities using spatially periodic density functional theory (DFT) using the Vienna Ab Initio Simulation Package (VASP),[27] along with a plane-wave basis set and projected-augmented wave (PAW)[28] pseudopotentials. All calculations used the Perdew, Burke, and Ernzerhof (PBE)[29] GGA XC functional with D3 dispersion corrections (PBE-D3)[30] unless noted otherwise. During geometry relaxation of MOFs, we simultaneously optimized both the cell volume and ionic positions using a plane-wave cutoff energy of 520 eV and gamma-point sampling for Brillouin zone integration. Using a quasi-Newton method, we relaxed geometries until the force on each atom is smaller than 0.03 eV/Å. Conventional XC functionals, such as the local density approximation (LDA) or GGAs, can fail in describing localized d electrons of transition-metal ions because of errors in correlation and self-interaction errors.[31] Thus, we use Hubbard U corrections[32] for the localized d elections with a U value for copper of 4.0 eV.[33] We take into account spin ordering by including spin polarization and use locally antiferromagnetic ordering for Cu paddlewheels.[34-35]

Initial coordinates for each MOF were taken from the CoRE MOF database. Each MOF was first energy minimized in the absence of adsorbed molecules. Nazarian et al. showed that this step is important to generate physically reliable structures, particularly for materials that contained solvent in the experimentally reported crystal structure.[36] After this initial geometry optimization, the cell shape and the volume was fixed in all subsequent calculations. We considered two approaches to calculating the binding energy of adsorbed molecules. One computationally efficient but approximate approach held all atoms in the MOF rigid and allowed only the coordinates of guest molecules to relax. A second approach allowed all atomic positions in the MOF and guest molecules to relax. Because calculations in the rigid system use far fewer computational resources than calculations in the fully flexible system, we test whether the more accurate flexible calculations can be approximated with useful precision with results from rigid calculations or not. The binding energies of adsorbed molecules were defined by

$$-\Delta E = E_{ads+MOF} - E_{MOF} - E_{ads}, \quad (1)$$

where $E_{ads+MOF}, E_{MOF},$ and E_{ads} represent the energy of a MOF with an adsorbed molecule, the energy of the empty MOF, and the energy of the adsorbate (guest molecule) in the gas phase, respectively. With this convention, ΔE is positive when adsorption is exothermic.

2.2 Adsorption Selectivity

Given the adsorbed- and gas-phase composition x_i and y_i, the selectivity of the adsorbent for component i relative to component j during mixture adsorption is

$$S_{i,j} = \frac{x_i/x_j}{y_i/y_j} \quad (2)$$

To interpret our computed binding energies, we establish a connection between binding energies and experimental isotherm loadings. Here, to compare the isotherm loading for ethylene/water or ethylene/carbon monoxide, we consider a Langmuir competitive adsorption model in which the molecules compete for the OMS sites. The loading ratio and selectivity for ethylene over water are then given by

$$\frac{\theta_{C_2H_4}}{\theta_{H_2O}} = e^{\frac{\Delta B.E._{ad}^{C_2H_4-H_2O}}{RT}} \frac{y_{C_2H_4}}{y_{H_2O}} \quad (3)$$

$$S_{C_2H_4/H_2O} = e^{\frac{\Delta B.E._{ad}^{C_2H_4-H_2O}}{RT}} \quad (4)$$

where $\frac{\theta_{C_2H_4}}{\theta_{H_2O}}$ is the loading ratio of ethylene to water, $\Delta B.E._{ad}^{C_2H_4-H_2O}$ is the difference between the binding energy of ethylene and that of water, $\frac{y_{C_2H_4}}{y_{H_2O}}$ is the mole ratio of ethylene to water in the gas phase, and T is the temperature. Expressions for other binary mixtures can be written that are entirely analogous to Eqs. (3) and (4). It is important to note that this description only includes adsorption at OMS rather than also including effects associated with physisorption of molecules in the MOF pores.[37-39] This description is therefore most accurate when the total loadings of the adsorbing molecules is low and when adsorption at the OMS primary adsorption site is strongly favorable when compared to other potential adsorption sites.

3. RESULTS AND DISCUSSION

The CoRE MOF database includes 129 MOF materials with unsaturated Cu sites.[26] Some MOF structures have duplicates in the database because multiple representations of the same MOF are reported in the Cambridge Structure Database. Notably, there are multiple entries for CuBTC in the CoRE MOF database. When duplicate materials were present, we performed calculations with only one initial structure.[36] Using an algorithm developed by Kulkarni et al.,[6] we detected a set of 100 dimer Cu MOFs with open metal sites. We

2.46 Å and 1.96 Å for the empty paddlewheel agree well with the experimental values of 2.50 Å and 1.94 Å.[40] The bond lengths of the framework showed deviations of less than 2% between the DFT and experimental structures. The initial orientations of guest molecules in CuBTC are taken from ref 21 for water, ref 6 for ethylene, and ref 22 for carbon monoxide. Table 1 shows binding energies of guest molecules with CuBTC calculated using various DFT XC functionals and with experimental data. Our calculations give binding energy that is ~6 kJ/mol more favorable for water than the earlier removed 32 MOF structures from further consideration because they had more than 600 atoms in their primitive cell, their initial geometry optimization did not proceed efficiently, or they had structural problems such as missing hydrogen atoms. As a result, our preliminary calculations focused on 65 MOFs with open metal sites defined by Cu dimers. The structure codes for the materials we considered are listed in Table S1. The previous work of Kulkarni et al.[6] showed that all of these materials are selective for olefins over paraffins, so in the results below we focus on the relative binding affinities of these materials for other small molecules relative to ethylene.

3.1 Comparison with Literature Data for CuBTC

We verified our calculation procedures by focusing on CuBTC. We obtained the coordinates for CuBTC from the CoRE MOF database (structure code FIQCEN) and optimized the empty framework using the PBE-D3 XC functional allowing both the unit

cell shape and volume and the positions of atoms to relax. Our computed Cu-Cu and Cu-O bond lengths of calculations of Grajciar et al.[21] with the same XC functional. This difference appears to be due to small differences in the optimized structures and calculation protocols.

Table 1. Binding Energies (in kJ/mol) of Guest Molecules with the CuBTC Evaluated with Various XC Functionals and Heat of Adsorption from Experiment

Guest molecules	PBE-D3 (This work)	Other XC functionals	Experimental
Water	46.3	40.3 (PBE-D3)[21]	50.7±2.9 (313 K)[41]
Ethylene	40.4	31.1 (vdw-DF2)[6]	32.5[42]
Carbon monoxide	27.9	32.3 (B3LYP)[22]	29.0[43]

3.2 Comparison of Rigid and Flexible MOF Binding Energies

Compared to the calculations of binding energies in a MOF where all degrees of freedom are allowed to relax, using a rigid MOF greatly reduces the computational burden. To understand whether information from rigid MOF calculations can be useful, we calculated the binding energy of water, ethylene, and carbon monoxide for 12 MOFs in the flexible and rigid systems. All degrees of freedom of the adsorbing molecules were energy minimized in each set of calculations. These 12 MOF materials were chosen because they were already geometry optimized (without adsorbates present) by Nazarian et al.[36] The resulting binding energies are shown in Figure 2(a) and more details are given in Table S2 and S3. As expected, the rigid system underestimates the binding energy because the flexible system has more degrees of freedom. Some binding energies are underestimated by as much as 12 kJ/mol, but the variation between the rigid and flexible results is smaller than this for the majority of cases. The mean average deviation (MAD) between the flexible and rigid calculations for these 12 materials is 4.3, 4.0, and 3.8 kJ/mol for ethylene, water, and CO, respectively.

As shown in Eqs. (3) and (4), the differences between molecular binding energies are more important than the absolute binding energies in understanding adsorption selectivity. Figure 2(b) replots the results from Figure 2(a) in terms of the relative binding energies for pairs of molecules in each MOF. As might be expected, the variation between the rigid and flexible calculations is considerably less when the relative binding energies are considered rather than the absolute binding energies. Figure 2(b) shows that almost all of the relative binding energies are given by results from rigid MOF calculations within a precision of ±4 kJ/mol. The MAD between the flexible and rigid calculations for these 12 materials is 1.0, 1.4, and 0.6 kJ/mol for ethylene-water, ethylene-CO, and water-CO, respectively. This observation is likely to be useful in future efforts to assess molecular binding energies in larger collections of OMS MOFs using DFT calculations.

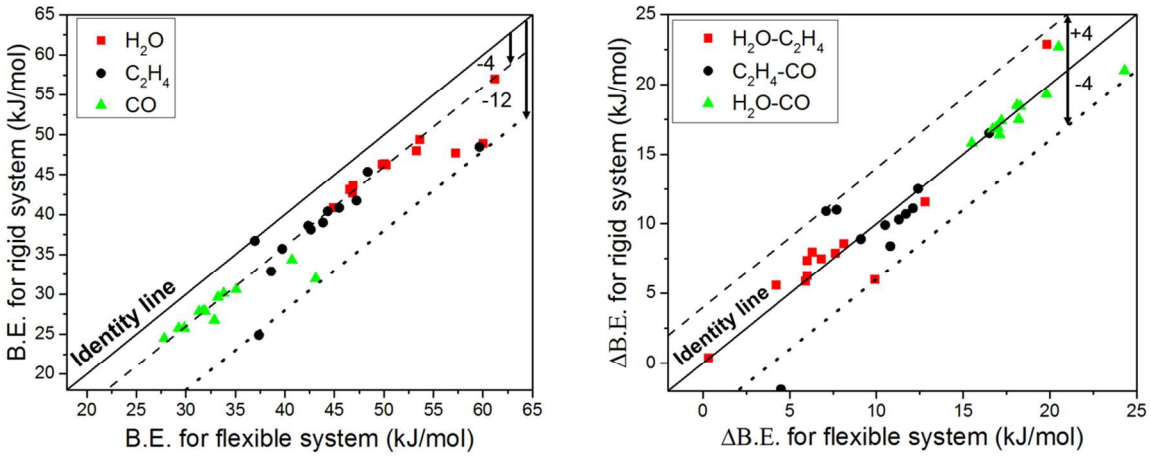

Figure 2: (a) A comparison of the binding energies (B.E.) of water, ethylene, and carbon monoxide in 12 dimer Cu MOFs between the flexible and rigid system and (b) a comparison of the differences of binding energies (water-ethylene, ethylene-CO, and water-CO) in 12 dimer Cu MOFs between the flexible and rigid system.

3.3 Comparison of Two Dispersion Corrected DFT XC Functionals

An accurate description of adsorbate interactions with open copper sites is significant for the study of binding energies of MOFs and the choice of an appropriate XC functional is important for the reproduction of material properties.[44-47] Grajciar et al.[44] evaluated the accuracy of nine XC functionals for the description of adsorption in MOFs and they found the accuracy of individual functionals depends on a particular adsorbate and adsorbent and even on the model size and geometry. Additionally, they reported PBE-D2 and -D3 performed the best among the functionals tested on the periodic model of CuBTC with respect to DFT/CC. To probe the sensitivity of our results to the choice of functional, we compared the performance of two dispersion corrected DFT methods, PBE-D3 and vdW-DF2 for 12 Cu MOFs with OMS.

We calculated the binding energy of water, ethylene, and carbon monoxide for 12 MOFs with PBE-D3 and vdW-DF2 XC functionals using rigid MOF structures. All degrees of freedom of the adsorbing molecules were energy minimized in each set of calculations. These 12 MOF materials were chosen from the above calculations. The resulting binding energies are shown in Figure 3(a) and more details are given in Table S4 and S5. Figure 3(a) shows PBE-D3 has stronger binding energies than vdW-DF2, consistent with Grajciar's work.[44] The mean average deviation (MAD) between the PBE-D3 and vdW-DF2 XC functionals for these 12 materials is 6.3, 4.8, and 4.1 kJ/mol for ethylene, water, and CO, respectively. Figure 3(b) replots the results from Figure 3(a) in terms of the relative binding energies for pairs of molecules in each MOF. Similar to the comparison of the rigid and flexible calculation, the variation between the PBE-D3 and vdW-DF2 calculations is considerably less when the relative binding energies are considered rather than the absolute binding energies. Figure 3(b) shows that almost all of

the relative binding energies are given by results from PBE-D3 MOF calculations within a precision of ±4 kJ/mol. The MAD between the PBE-D3 and vdW-DF2 calculations for these 12 materials is 1.9, 2.2, and 1.2 kJ/mol for ethylene-water, ethylene-CO, and water-CO, respectively. These results show that the relative binding energies of molecular pairs on the OMS in CuBTC are not highly sensitive to the choice of functional. For this reason, we focus on results from calculations using PBE-D3 in the remainder of the paper.

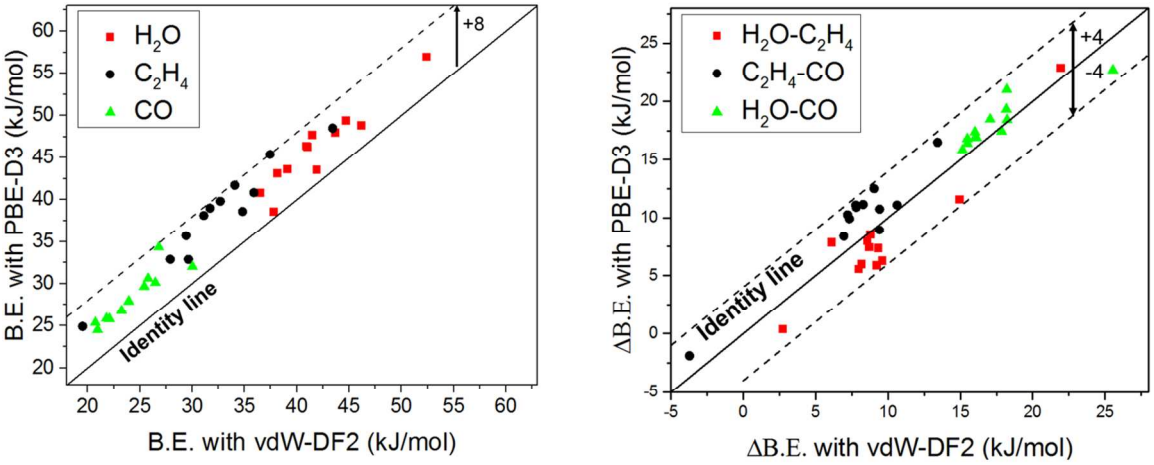

Figure 3: (a) A comparison of the binding energies (B.E.) of water, ethylene, and carbon monoxide in 12 dimer Cu MOFs between the PBE-D3 and vdW-DF2 functionals and (b) a comparison of the differences of binding energies (water-ethylene, ethylene-CO, and water-CO) in 12 dimer Cu MOFs between the PBE-D3 and vdW-DF2 functionals.

3.4 Molecular binding energies for 65 dimer Cu MOFs

Motivated by the results above, the binding energies for water, ethylene, and carbon monoxide were calculated and given in Table S6 for 65 rigid Cu MOFs. The average binding energy is 45.2 kJ/mol for water, 38.8 kJ/mol for ethylene, and 28.2 kJ/mol for carbon monoxide. The average difference between the binding energies of water and ethylene (ethylene and carbon monoxide) is 6.4 (10.6) kJ/mol. The MAD of the binding energy difference for these 65 materials is 2.5, 2.3, and 1.9 kJ/mol for ethylene-water, ethylene-CO, and water-CO, respectively. **Error! Reference source not found.** plots the differences in binding energies as a function of the binding energy of ethylene for the 65 MOFs. The main information we obtain from **Error! Reference source not found.** is that (1) the majority of materials are water selective relative to ethylene or CO; (2) 24 of the 65 MOFs have higher selectivity of ethylene to water than CuBTC; (3) only two of the 65 MOFs have higher binding energies of ethylene than for

water; and (4) for a given MOF, the selectivity of ethylene to carbon monoxide is always greater than the selectivity of ethylene to water.

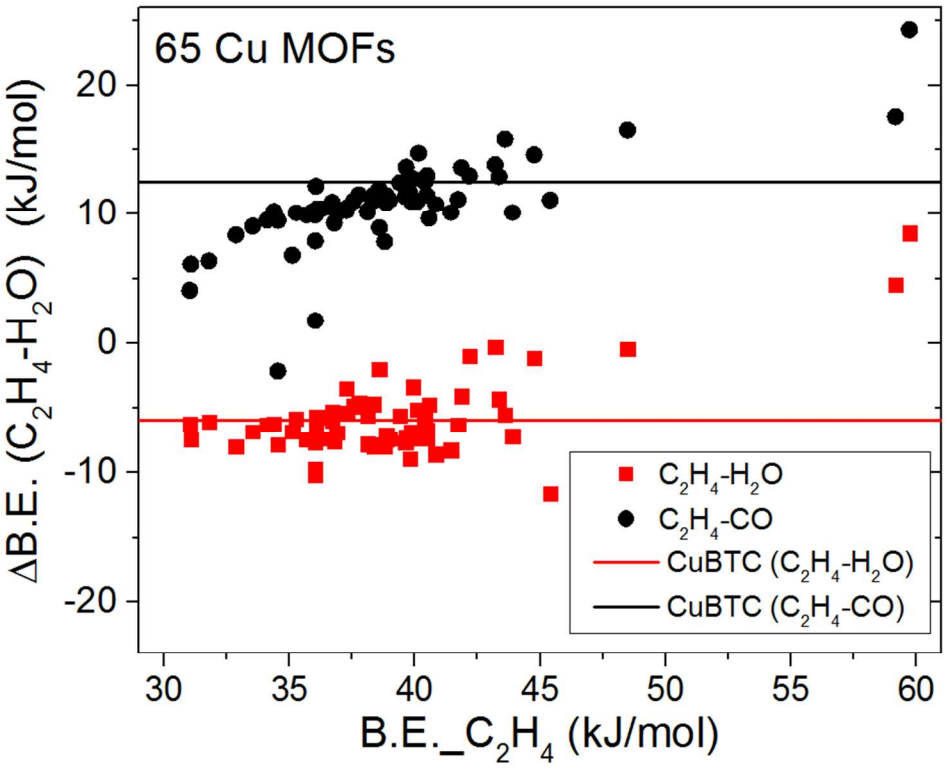

Figure 4: The difference of binding energies (ethylene-water and ethylene-CO) as a function of the binding energy of ethylene in 65 rigid dimer-Cu MOFs with OMS. The results for CuBTC are indicated with horizontal lines.

The calculation described above identified two MOFs that bind ethylene more strongly than water: BIMDIL (MOF-11) and BIMDEF.[48] We calculated the binding energies for these two MOFs in fully flexible MOFs and find that they are consistent with those calculated by the rigid system. Table 2 shows the differences of binding energies calculated by the rigid and flexible systems. These two MOFs were reported by the same research group[48] and the materials are polymorphs, i.e. they have the same stoichiometry but different crystal structure. Although the relative binding energies of water and ethylene in these materials are interesting, the absolute binding energies (> 70 kJ/mol for ethylene) are large. This observation is likely to make these materials unsuitable in many practical applications, since moderate heats of adsorption are favored to allow cost-effective desorption of adsorbed molecules and regeneration of sorbents.

Table 2. Binding energies in MOF-11 and BIMDEF. Capital R stands for calculations in rigid system and F stands for flexible system.

B.E.(kJ/mol)	H_2O	C_2H_4	CO	C_2H_4 - H_2O	C_2H_4 - CO
MOF-11_R	51.2	59.7	35.4	8.5	24.3
MOF-11_F	62.9	71.1	47.3	8.2	23.8
BIMDEF_R	54.6	59.2	41.6	4.6	17.6

BIMDEF_F	71.1	75.1	53.4	4.0	21.7

Taking MOF-11 as an example, we analyzed the origins of these unusual relative binding energies. From adsorption in CuBTC, we know that for water adsorption, the optimal distance between Cu and the O atom in water is ~2.3 Å and the water binding energy is negligible (~5-8 kJ/mol) when this distance is increased to 3.7 Å.[21] For ethylene adsorption, however, the optimal distance between Cu and a C atom in ethylene is 2.7 Å and this binding energy is still considerable (~25 kJ/mol) when this distance is 3.3 Å.[6] Figure 5 shows that MOF-11 has a narrow pore in which the distance between two Cu atoms in different dimers is ~6 Å. As a result, MOF-11 defines a "dual-binding" site for ethylene that interacts favorably with two Cu atoms on separate Cu dimers. This situation is conceptually similar to the "dual cation" sites that can allow very strong binding of CO_2 in cationic zeolites.[49] This mechanism does not apply, however, to water, which is too small to interact favorably with the two Cu dimers at the same time. These observations explain the unusual relative binding energies of ethylene and water in MOF-11. The other MOF (BIMDEF), which has a similar structure with BIMDIL, also has a narrow pore in which the distance between two Cu atoms in different dimers is 6.02 Å. As a result, it also gives the same atypical preferential binding of ethylene over water. This observation suggests a possible avenue for developing other MOFs in which the binding energy of ethylene is higher than the binding energy of water.

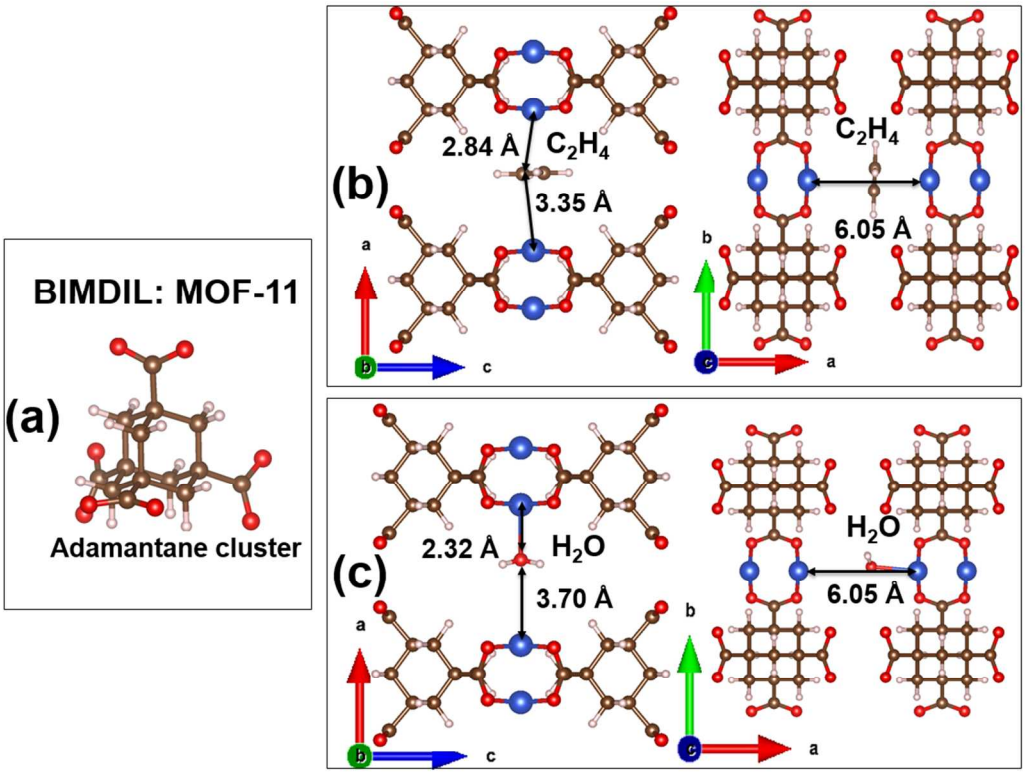

Figure 5: (a) The linker of MOF-11 and (b, c) the orientation of C_2H_4 and H_2O inside the pore of MOF-11 viewed from two directions

4. SUMMARY

In this work, DFT calculations have been performed to investigate the influence of MOF structure on binding affinity by establishing the relative binding affinity of H_2O, C_2H_4, and CO in 65 dimer-Cu MOFs with open metal sites. Although DFT calculations that allow all degrees of freedom in a material to relax are necessary to most accurately calculate binding energies of adsorbed molecules, we found that calculations using rigid MOF structures give relative binding energy differences for these small molecules that differ by ±4 kJ/mol from the much more computationally demanding fully flexible calculations. This observation will be useful in future efforts to examine relative binding energies in larger libraries of materials. The binding energies of each molecule in the 65 MOFs we examined are quite similar to the binding energies in CuBTC, an exemplar MOF with open Cu sites. This is not necessarily surprising, as the interaction between adsorbates and open metal sites are localized within 2~3 Å. As a result, the influence of the organic linker and MOF topology is secondary in determining the binding energies of small molecules on these OMS. In the future, we will extend this work to study the influence of the metal identity on the binding affinities for MOFs with OMS.

A key aim of this work was to quantify the relative binding energy of ethylene, water, and carbon monoxide on open Cu sites in MOFs, since the latter two species may potentially compete with ethylene for these sites during adsorption of gas mixtures. CO binds less strongly than ethylene in these materials, suggesting that the presence of trace levels of CO is likely to not be critical in separations that aim to take advantage of the binding of ethylene. Almost all of the materials, however, bind water more favorably than ethylene. This suggests that the presence of water in feed streams could potentially reduce the ability of these OMS MOFs to selectively adsorb ethylene. Although there are examples such as the binding of CO_2 by amines where the presence of water can enhance binding,[50] adsorption of ethylene and water on OMS in MOFs is likely to be a more straightforward competitive process. Our calculations identified two materials that are unusual because they bind ethylene more strongly than water. This situation is possible when two separate Cu dimers are sufficiently close to one another that an ethylene molecule can interact simultaneously with both dimers while the smaller water molecule interacts primarily with a single OMS.

Our results have focused on potential competition for selective binding sites in MOFs by small molecules that may be present in feed streams containing ethylene. Throughout this paper we have described calculations for defect-free crystalline materials. A potential barrier to using MOFs with open Cu sites is limitations on the stability of these materials. A recent meta-analysis of adsorption experiments for CO_2 and N_2 in CuBTC[51] supports the widespread observation that this material is at best marginally stable.[52] Degradation of this material due to exposure to water has been most carefully studied, although there is mounting evidence that trace levels of acid gases (including CO_2) can accelerate degradation of some MOFs.[53] Because the specific mechanisms of materials degradation are poorly understood, it is not clear that this kind of instability is intrinsic to all MOFs with open metal sites. Development of MOF-based sorbents for practical separations applications must consider issues associated with long-term stability of these materials in addition to the potential role of competitive adsorption.

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