Computational identification of a metal organic framework for high selectivity membrane-based CO$_2$/CH$_4$ separations: Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$

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The identification of membrane materials with high selectivity for CO$_2$/CH$_4$ mixtures could revolutionize this industrially important separation. We predict using computational methods that a metal organic framework (MOF), Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$, has unprecedented selectivity for membrane-based separation of CO$_2$/CH$_4$ mixtures. Our calculations combine molecular dynamics, transition state theory, and plane wave DFT calculations to assess the importance of framework flexibility in the MOF during molecular diffusion. This combination of methods should also make it possible to identify other MOFs with attractive properties for kinetic separations.

Efficient separation of CO$_2$ from CH$_4$ is an important issue in natural gas processing$^{1,2}$ and landfill gas recovery.$^3$ Enormous reserves of natural gas with high levels of CO$_2$ are known.$^4,5$ Before these resources can be used, robust methods to purify CH$_4$ from CH$_4$/CO$_2$ mixtures with low cost are required. Membranes offer a powerful general approach to this challenge, provided that robust materials with high selectivities can be identified.$^6$

Metal organic frameworks (MOFs) are a class of crystalline nanoporous materials that have many potential advantages over traditional nanoporous materials for adsorption and chemical separations. An enormous number of different MOFs are known$^{7,8}$ and the physical and chemical structures of the pores in MOFs can be tuned with relative ease during synthesis. A range of experimental and modeling studies have examined MOFs in adsorption-based separations,$^9$-12 while a smaller group of studies has examined MOF membranes.$^{13,14}$ In MOFs, as in most nanoporous materials, CO$_2$ adsorbs more strongly than CH$_4$, although in general the selectivities that have been achieved based on adsorption are not dramatically different from those in other nanoporous materials such as zeolites. Because the pores of many MOFs are large relative to CO$_2$ and CH$_4$ molecules, diffusion of CO$_2$ is typically slower than CH$_4$. In MOFs of this kind, membrane-based separations, which rely on a combination of adsorption selectivity and diffusion selectivity, would have lower selectivity than an adsorption-based separation.$^{15}$

The conflicting trends in adsorption and diffusion selectivity noted above are not a universal property of all nanoporous materials. The silica zeolite DDR has been shown to have very high selectivity for CO$_2$ from CO$_2$/CH$_4$ mixtures when used as a membrane.$^{16}$ Molecular modeling of DDR demonstrated that this zeolite has two crucial properties that make this kinetic-based separation possible.$^{18}$ First, molecular diffusion of CO$_2$ is far more rapid than CH$_4$ in DDR because diffusion is controlled by narrow windows that restrict the motion of CH$_4$ to a much greater extent than the slightly smaller CO$_2$ molecules. Second, the pores between these windows are large relative to both molecules, so the presence of the slowly diffusing CH$_4$ does not significantly impede the motion of CO$_2$. The same two principles apply to a small number of other zeolites and aluminophosphates.$^{20,21}$

In this paper, we show using computational modeling that the structural features that make DDR and SAPO-34 appealing materials for CO$_2$/CH$_4$ separations are also shared by a microporous MOF, Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ (H$_2$hfipbb = 4,4’-(hexafluoroisopropylidene) bis(benzoic acid)). We use molecular simulations to examine the adsorption and diffusion of CO$_2$ and CH$_4$ in this MOF, both as single components and as mixtures. These simulations suggest that the CH$_4$ diffusion through Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ is strongly hindered by large energy barriers created by narrow windows in the MOF’s pores. Because the effects of structural relaxation in these windows could potentially be significant, we supplement our molecular simulations with quantum chemistry calculations using plane wave density functional theory (DFT). Our DFT calculations use the full periodic crystal structure of the MOF. Aside from the intrinsic significance of identifying a new material for this industrially important separation, the suite of methods we apply here will be applicable to a broad class of MOFs. They therefore open the possibility of efficiently identifying other MOFs among the thousands of known MOFs for use in high performance kinetic separations.

Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$ is a crystalline interpenetrating framework containing ordered microporous 1D channels, built on a Cu$_2$(hfipbb)$_2$(H$_2$hfipbb)$_2$ paddle-wheel building unit (see Fig. 1). Its synthesis, structure and room temperature adsorption properties for H$_2$ and selected alkanes have been examined experimentally.$^{22}$-24 We selected this MOF because it has cages that are moderate in size relative to small gas molecules ($\sim 5.1 \times 5.1$ Å) connected by small windows ($\sim 3.5 \times 3.2$ Å) based on atom to atom distances in the reported crystal structure.$^{22}$ Pan et al. examined propane, butane and pentane adsorption in Cu(hfipbb)(H$_2$hfipbb)$_{0.5}$, showing that this adsorption is size selective because of the favorable match between the larger of these alkanes and the material’s cages.$^{24}$ Similar effects are known for size selective adsorption in zeolites.$^{25}$ These experiments show that alkanes,
including CH₄, can adsorb in Cu(hfipbb)(H₂hfipbb)₀.₅, but no information is available regarding the diffusivities of these adsorbed molecules. We know of no previous reports of adsorption or diffusion of CO₂ in this material.

Molecular simulation methods for modeling gas adsorption and diffusion in MOFs are now quite well established, as described in a recent review.¹² We performed adsorption and diffusion simulations of CO₂/CH₄ mixtures in Cu(hfipbb)-(H₂hfipbb)₀.₅ using grand canonical Monte Carlo (GCMC) and equilibrium molecular dynamics (EMD), respectively. All simulations were performed at room temperature using a rigid MOF structure with atomic positions obtained from experimental data.²² A simulation volume of 2 × 2 × 2 crystallographic unit cells was used for all simulations. Assuming that the MOF is rigid greatly reduces the complexity of defining interatomic potentials for these simulations, as well as their computational efficiency. Later, we use plane wave DFT calculations to assess whether this assumption is justified.

Methane was modeled as a spherical Lennard-Jones (LJ) particle, while CO₂ was modeled as a rigid three-site molecule using the EPM2 model, an all atom model with LJ potentials and atomic charges to approximate the quadrupole moment of CO₂.²⁶,²⁷ The Lorentz-Berthelot mixing rules were employed to calculate the adsorbate-MOF LJ cross interaction parameters by using the universal force field (UFF)²⁸ for the framework atoms. LJ potentials were truncated at 13 Å and electrostatic interactions between CO₂ molecules were truncated at 25 Å. Framework–CO₂ electrostatic interactions were calculated by summation of the charge–charge interactions between each framework atom and each charge site of CO₂. These charge–charge interactions were pre-tabulated by direct calculation of the atomic charge–charge interactions.²⁹ The charges on atoms in the MOF framework were determined by DFT calculations with Accelrys DMol³, employing the PWC functional within the local density approximation and a double numerical basis set.³⁰,³¹ These partial charges depend upon the charge partitioning method that is applied, so we assigned charges with both the Mulliken³² and Hirshfeld³³ methods. The effect of these two sets of partial charges is discussed below.

A conventional GCMC technique was used to compute adsorption isotherms.³⁴ Simulations at the lowest fugacity for each system were started from an empty MOF. Each subsequent simulation at higher fugacity was started from the final configuration of the previous run. These simulations used 1.5 × 10⁷ moves for equilibration and 1.5 × 10⁷ moves for data collection at each state point. We report the adsorption isotherms as a function of fugacity. To convert fugacity into pressure, it would be necessary to use an equation of state to account for the non-ideality of CO₂ at the highest fugacities we simulated.

Fig. 2 shows the calculated single component and mixture adsorption isotherms of CH₄ and CO₂ in Cu(hfipbb)-(H₂hfipbb)₀.₅ at room temperature. As in most MOFs, CO₂ is more strongly adsorbed than CH₄ because of the strong quadrupole moment of CO₂. Because interactions between CO₂ and the MOF are dominant at low loadings, the isotherms calculated with charges assigned from the Mulliken and Hirshfeld methods differ at pressures less than 0.1 bar. At higher pressures, however, adsorbate–adsorbate interactions are more dominant and the isotherms with the two sets of partial charges are similar. The single component adsorption isotherm of CH₄ reaches saturation at fugacities less than 1 bar. At these conditions, CH₄ is essentially an ideal gas, so fugacity and pressure are equivalent.

The mixture isotherm in Fig. 2 corresponds to equimolar bulk phase mixtures. As implied by the single component isotherms, CO₂ is favored over CH₄ in mixture adsorption. The adsorption selectivity for the equimolar bulk gas mixture is around 4 for the pressure range shown in Fig. 2. The observation that CO₂ is preferentially adsorbed in a MOF relative to CH₄ is not novel, and previous studies have shown that the adsorption selectivity is typically only weakly dependent on the bulk phase composition.¹³,¹⁴,¹⁷,³⁵

Initial MD simulations of adsorbed CH₄ in Cu(hfipbb)-(H₂hfipbb)₀.₅ indicated that CH₄ could not move between adjacent cages on the nanosecond time scales accessible using MD. The reasons for this behavior are clear from the potential energy surface for adsorbed CH₄. Fig. 3 shows that the minimum potential energy of CH₄ as the molecule is moved along a pore in the MOF. The minimum energy occurs in the
center of the MOF’s cages, and these locations dominate adsorption of CH₄. A large energy barrier exists to moving CH₄ through the narrow windows connecting cages along the [010] direction; our calculations based on a rigid MOF structure give a barrier of $\Delta E \approx 72$ kJ mol⁻¹. This corresponds to a diffusion coefficient that is far too slow to be directly observed with MD. We note that this approach could significantly underestimate the mobility of CH₄ if flexibility of the MOF’s windows can lower the activation energy for diffusion. We examine this possibility later using quantum chemical calculations.

Unlike CH₄, CO₂ diffusion in Cu(hfipbb)(H₂hfipbb)₀.₅ is rapid enough that it can readily be characterized using MD. We used EMD to compute the self diffusion coefficient of CO₂, both as a single component adsorbate and in adsorbed mixtures with CH₄. All MD calculations for CO₂ were performed using Hirschfeld charges; the results below are not sensitive to this choice. MD was performed in the canonical ensemble with a Nose-Hoover thermostat for 20 independent MD simulations of length 20 ns for each loading and/or composition we considered. Initial states were created using GCMC, then equilibrated using a short EMD trajectory.

The computed self-diffusivities of CO₂ in Cu(hfipbb)(H₂hfipbb)₀.₅ are shown in Fig. 4. When CO₂ is adsorbed as a pure component, the self diffusivity is $\approx 10^{-6}$ cm² s⁻¹ and decreases slightly as the adsorbate loading increases. As a benchmark, the diffusion coefficients of molecular solvents in liquids are typically $\approx 10^{-5}$ cm² s⁻¹. This result indicates that Cu(hfipbb)(H₂hfipbb)₀.₅ satisfies the first property we listed above that is required for an effective kinetic separation because the diffusivity of one species (CO₂) is orders of magnitude larger than the other (CH₄).

The second requirement for an effective kinetic separation is that the presence of the slowly diffusing species must not significantly retard the rapidly diffusing species. There are many examples of nanoporous materials in which this undesirable slowing of motion is known, so a general expectation is that this requirement will not be met. Fig. 4 shows the computed self diffusivity of CO₂ in 50/50 adsorbed CO₂/CH₄ mixtures. In every case, the diffusivity of CO₂ is reduced by less than a factor of 2 relative to pure CO₂. The origin of this desirable effect is easy to understand; CO₂ and CH₄ molecules can readily pass one another in the cages of the MOF. The presence of the slowly moving CH₄ molecules has at most a weak impact on the net diffusion of CO₂.

A complication with the binary data discussed above is that it is defined in terms of the adsorbed mixture concentration, which obscures the diffusion properties of mixtures that are relevant for typical gas compositions. Fig. 4 also shows results for the adsorbed mixture associated with an equimolar bulk mixture. Because of the adsorption selectivity of the MOF.

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Fig. 2 Single component and mixture adsorption isotherms of CH₄ and CO₂ at 298 K in Cu(hfipbb)(H₂hfipbb)₀.₅. Mixture isotherms are for an equimolar bulk phase mixture. For CO₂, results are shown with two different methods for assigning partial charges to the MOF framework atoms.

Fig. 3 Minimum potential energy of CH₄ as a function of position along the pore axis in Cu(hfipbb)(H₂hfipbb)₀.₅, calculated using the methods described in the text.

Fig. 4 Self diffusivities of CO₂ at 298 K in CO₂/CH₄ mixtures as a function of CO₂ loading at various compositions with single component diffusivity of CO₂ in Cu(hfipbb)(H₂hfipbb)₀.₅.
(cf. Fig. 1), the adsorbed mixture in this case is ~80% CO2. The diffusivity of CO2 in these adsorbed mixtures is only slightly smaller than the result for pure CO2.

Our molecular simulations predict that Cu(hfipbb)- (H2hfipbb)0.5 has excellent properties for a membrane-based separation of CO2 from CO2/CH4 mixtures, since adsorption favors CO2 by a moderate factor and diffusion favors CO2 by orders of magnitude. Because this desirable outcome rests heavily on the large activation barrier that was calculated for CH4 diffusion using a rigid MOF structure, it is important to understand whether allowing flexibility in the MOF structure will significantly reduce this barrier. Because the development of accurate classical force fields for the internal degrees of freedom in MOFs is challenging,12,39 addressing this topic with molecular simulations is problematic. As in small pore zeolites,18 the large barrier that exists for CH4 diffusion through the windows of Cu(hfipbb)(H2hfipbb)0.5 is dominated by short-range repulsive interactions, not long range dispersion forces. This means that DFT calculations can be used to reliably probe these interactions. We have therefore used plane wave DFT calculations to examine the effect of MOF flexibility on the diffusion of CH4 in Cu(hfipbb)(H2hfipbb)0.5.

We used the Vienna ab initio Simulation Package (VASP)40 for our DFT calculations. The computational supercell is fully periodic in all directions, and represents the full crystal structure of the MOF. The PW91 GGA functional31 was used to describe electron exchange-correlation with a kinetic energy cutoff of 500 eV and a 1 × 2 × 1 Monkhorst-Pack sampling of k-space.41 Geometry optimizations were performed until the maximum force on each atom was <3 × 10−2 eV Å−1. Spin polarization was included to consider the MOF’s magnetic ground state; we determined that the Cu dimers are antiferromagnetically coupled as they are in other MOFs such as CuBTC.42,43 The experimental crystal structure of Cu(hfipbb)-(H2hfipbb)0.5 from Pan et al.24 was used in all DFT calculations, holding the cell parameters fixed. This choice is appropriate because the rare event associated with CH4 moving through a window is unlikely to affect the net lattice parameters. Only the 6 C and 4 H atoms in each ring associated with the pore window were allowed to relax during our calculations; all other atoms in the MOF were constrained in their crystallographic positions. The degrees of freedom of the adsorbate molecules were chosen depending on the type of the calculation as described below.

Adsorption energies of CO2 and CH4 in the pore of Cu(hfipbb)-(H2hfipbb)0.5 were calculated after relaxation of each molecule in the cage of the MOF. All degrees of freedom in the adsorbates and the aromatic rings in the MOF mentioned above were allowed to relax in these calculations. The adsorption energy is given by

$$E_{ads} = E(\text{MOF + adsorbate}) - E(\text{MOF}) - E(\text{adsorbate})$$

where $E(\text{MOF + adsorbate})$, $E(\text{MOF})$, and $E(\text{adsorbate})$ are the total energies of the MOF with an adsorbate molecule, the MOF with no adsorbate, and an isolated adsorbate molecule, respectively. The results are shown in Table 1. We anticipate that our DFT calculations strongly underestimate the attractive dispersion forces that exist for each molecule inside the MOF.44,45 When the molecules are adsorbed in the MOF’s cage, they each give DFT adsorption energies that are slightly negative (see Table 1). Within the caveat above regarding dispersive interactions, this result is qualitatively consistent with the experimental observation of Pan et al. that alkanes adsorb readily in the MOF.24

<table>
<thead>
<tr>
<th></th>
<th>CO2</th>
<th>CH4</th>
<th>C2H6</th>
</tr>
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<tbody>
<tr>
<td>$E_{ads}$ (kJ mol−1)</td>
<td>−9.7</td>
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</tr>
<tr>
<td>$E_{trans}$ (kJ mol−1)</td>
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<td>45</td>
<td>45</td>
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<td>Mean rotation angle (deg.)</td>
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<td>4.3</td>
<td>5.8</td>
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The activation energies for CO2 and CH4 diffusion were estimated by constraining the C atom in each molecule in the center of the MOF’s window and allowing the remaining adsorbate degrees of freedom and the aromatic rings described above to relax. This is a rather crude way to determine the transition barrier but because of the simple geometry of the system it is sufficient to distinguish differences in the activation barrier between these adsorbates. Repeating this calculation with the positions of the adsorbate’s C atoms shifted by ±1.0 Å along the pore axis support the identification of the window as a transition state. The diffusion activation energy is defined as the difference in the total energies of a molecule in the window and in the pore, $E_{trans} = E_{\text{window}} - E_{\text{pore}}$. As shown in Table 1, the activation energy for CH4 is computed to be 45 kJ mol−1, compared with 16 kJ mol−1 for CO2. In the estimated transition states, the aromatic rings of the framework rotate by a small amount (2.4° for CO2 and 4.3° for CH4) relative to the rigid structure. Using DFT without relaxation of these rings gave a CH4 activation energy of 57 kJ mol−1. This value is smaller than the 72 kJ mol−1 predicted by our molecular simulation, but it is clear that the activation energy for CH4 diffusion in this MOF is much larger than for CO2, and that including flexibility in the MOF does not change this qualitative conclusion.

To compare our DFT calculations more directly with the experiments of Pan et al. with adsorbed alkanes, we performed similar calculations for C2H6. To estimate the transition state for C2H6 diffusion, both C atom positions were fixed with the C-C bond along the pore axis, while all adsorbate H atoms were allowed to move. The calculated diffusion activation energy for C2H6 is identical to that of CH4 within the accuracy of our calculations. This is reasonable considering that passage of C2H6 through the window is dominated by the energy required to place a single methyl group in the pore window. This implies that the activation energy for propane and butane to diffuse in Cu(hfipbb)(H2hfipbb)0.5 is likely to be similar to that of CH4.

We can use a simple transition state expression to estimate the diffusivity of CH4 in Cu(hfipbb)(H2hfipbb)0.5 by assuming that the CH4 hopping rate between cages is $k = n \exp(-E_{\text{trans}}/kT)$. Taking the pre-exponential to be $n = 10^{12}$−$10^{13}$ s−1 implies that the average time between cage-to-cage jumps is 0.7−7 µs, using our DFT result for the activation energy. This gives

[Table 1 Adsorption energies in the cage, diffusion activation energy and rotation angles of aromatic rings in the window for CO2, CH4, and C2H6]
a one-dimensional diffusivity, \( D = \frac{1}{2} D_i a^2 \), of \( 0.4-4 \times 10^{-10} \ \text{cm}^2 \ \text{s}^{-1} \), where \( a = 0.727 \ \text{nm} \) is the cage-to-cage distance along the pore. This value is comparable to the diffusion coefficient of many bulky molecules in zeolites; the self diffusivity of benzene in Na-X, for example, is \( \sim 10^{-10} \ \text{cm}^2 \ \text{s}^{-1} \).\(^{46}\) Even though this diffusion is slow relative to CO\(_2\), it is easily high enough that well equilibrated samples could be observed in the alkane adsorption experiments of Pan et al. We can therefore conclude that our calculations are consistent with all features of these experiments.

A simple estimate of the selectivity of a membrane for a binary mixture of CO\(_2\) and CH\(_4\) is given by \( S_{\text{CO}_2/\text{CH}_4} = \frac{c_{\text{CO}_2}}{c_{\text{CH}_4}} \), where \( c_i \) is the adsorbed amount (diffusivity) of species \( i \) in the adsorbed mixture of interest. Our calculations predict that \( c_{\text{CO}_2} / c_{\text{CH}_4} \sim 4 \) for a broad range of bulk phase compositions. Our MD simulations indicate that the diffusivities of the two species in adsorbed mixtures are quite similar to the diffusivities of the pure adsorbed components, so it is reasonable to estimate \( D_{\text{CO}_2} / D_{\text{CH}_4} \) using pure component values. Using our MD results for the rapidly diffusing CO\(_2\) and the transition state theory (TST) estimate with a DFT-based activation energy for CH\(_4\), we predict that \( D_{\text{CO}_2} / D_{\text{CH}_4} \sim 2400-24000 \). That is, our calculations predict that a membrane based on this MOF would have a net selectivity for CO\(_2\) of \( 10^4-10^5 \). This selectivity is higher than any known polymeric membrane for this separation\(^{47}\) or the any known a polymeric membrane. These so-called mixed matrix membranes (MMs) offer a useful avenue for tuning the properties of polymeric membranes, thus leveraging the commercial technologies that already exist for making high surface area membranes. Initial studies of MMs with large pore MOFs\(^{16,51}\) have indicated that MOFs are relatively straightforward to incorporate into these membranes.

In addition to identifying a specific MOF predicted to have extraordinary properties as a membrane for an industrially important separation, our results hint that multiple other MOFs with excellent properties for kinetic separations also exist. We have demonstrated that a well developed suite of computational methods can be used to examine molecular adsorption and diffusion in MOFs in a way that should open exciting opportunities for developing materials for these kinds of applications.

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References