Screening of Metal–Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach

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Received July 20, 2009; E-mail: snurr@northwestern.edu

It is an enormous challenge to capture and sequester CO_2 from the exhaust streams of fossil fuel combustion to reduce greenhouse gas emissions.[1] Coal-fired power plants generate about one-third of the CO_2 released to the atmosphere as a result of human activity, making them primary targets for CO_2 capture.[2] Typical flue gases from fossil fuel-fired plants contain 3 to 16% CO_2 by volume at ambient conditions.[3] The low partial pressure and high flow rates make this a challenging separations problem. Adsorption processes are attractive due to their low energy requirements, stimulating recent research to find suitable adsorbents for removing CO_2 from flue gas.[4]

Much attention has focused on metal–organic frameworks (MOFs), a new class of nanoporous materials that have potential applications in separation processes, catalysis, and gas storage. They are synthesized using organic linker molecules and metal joints that self-assemble to form crystalline materials with well-defined porous structures, high surface areas, and desired chemical functionalities.[5] These attractive properties make MOFs promising candidates for CO_2 capture.

Given the large number of possible MOF topologies, linkers, and metal nodes, there are an almost unlimited number of MOFs that could be synthesized. Screening and understanding of the fundamental structure/function relationships are, thus, very important for developing new processes based on MOFs. Most reports have focused on only a few MOFs at a time, often only one. In this work, we report screening of a diverse collection of 14 MOFs for CO_2 capture from flue gas. Synthesis, characterization, and adsorption measurements are reported for approximately half of the MOFs, and adsorption data are taken from the literature for the other half. The diversity of the chosen materials will help improve our understanding of CO_2 capture in MOFs.

In addition, we use these data to validate a generalized strategy for molecular modeling of CO_2 and other small molecules in MOFs. The strategy is fully predictive with no fitting of parameters. With the validation presented here, the approach can be used to rapidly screen additional MOFs, generating large savings in experimental time and cost. Briefly, grand canonical Monte Carlo (GCMC) simulations are performed for a model that includes electrostatic and Lennard–Jones interactions among the atoms in the system. The framework and the individual CO_2 molecules are considered to be rigid. Interactions among CO_2 molecules are modeled with the TraPPE force field,[6] and the Lennard–Jones parameters for the MOF atoms are taken from DREIDING[7] and (if not available in DREIDING) UFF[8] force fields. Partial charges on the MOF atoms are derived from DFT calculations. Further details are given in the Supporting Information (SI), along with the experimental details.

Figure 1 presents the experimental CO_2 uptake at 0.1 bar (the anticipated partial pressure of CO_2 in flue gas) and room temperature for the 14 MOFs. It is increasingly recognized that MOFs with a large
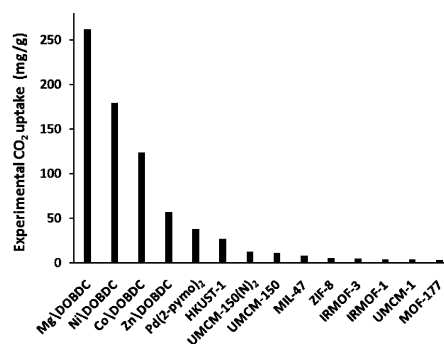

Figure 1. Experimental CO_2 uptake in screened MOFs at 0.1 bar. Data obtained at 293−298 K. See SI for exact temperature for each MOF.

capacity for CO_2 at high pressures often do not perform well at low pressures. Thus IRMOF-1 and MOF-177, which may be outstanding for other applications, are among the lowest performing materials here. Adding amine functionalities to the linkers of IRMOF-1 to produce IRMOF-3 provides only a small improvement in CO_2 uptake, as reported previously.[9] Yet, changing the metal from Zn in M\DOBDC to Mg, Co, or Ni provides big changes in CO_2 uptake.[10] M\DOBDC (where M = Zn, Mg, Ni, or Co and DOBDC = dioxybenzenedicarboxylate) MOFs have open metal sites that can interact with adsorbate molecules, and Mg\DOBDC performs particularly well. The lower atomic weight of Mg relative to Ni, Co, and Zn cannot completely explain the enhanced uptake of Mg\DOBDC (Figure 1). In order of increasing atomic weight of M, these uptakes are 0.721, 0.436, 0.638, and 0.213 molecules of CO_2 per metal atom for Mg, Co, Ni, and Zn, respectively. It is known that MgO exothermically chemisorbs CO_2 to form $MgCO_3$, and based on this Caskey et al.[10] suggested that the performance of Mg\DOBDC may be attributed to the relatively higher ionic character of the Mg−O bond. CO_2 is not chemisorbed by the Mg−O bonds in Mg/DOBDC, but the ionic character of this bond promotes higher CO_2 uptake. We find that, in M\DOBDC MOFs, CO_2 uptake increases with decreasing M−O bond length in the framework. The order of these bond lengths, which may be considered as an indication of the affinity of metals in this coordination state toward oxygen, is Mg−O (1.969 Å) < Ni−O (2.003 Å) < Co−O (2.031 Å) < Zn−O (2.083 Å).

The best performing materials in Figure 1 are the various forms of M\DOBDC, all of which have open metal sites. HKUST-1, UMCM-150, and UMCM-150(N)$_2$ also possess open metal sites, and it is interesting to ask why the M\DOBDC materials perform better. The identity of the metal, its accessibility, and the local environment may play a role and should be studied in the future. However, a simple explanation is that the M\DOBDC MOFs have a higher density of open metal sites (either per unit of surface area or per unit of free volume of material) (Table S35).

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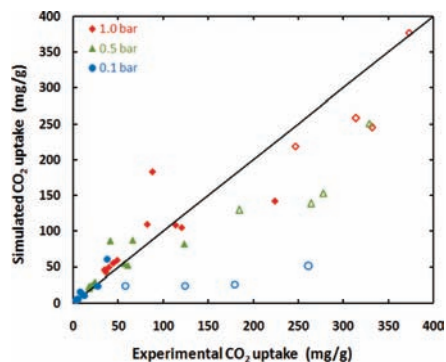[‡] University of Michigan.
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Figure 2. Comparison of simulated and experimental CO_2 uptake in screened MOFs at 0.1, 0.5, and 1 bar. Data for M\DOBDC samples shown as open symbols. If M\DOBDC data at 0.1 bar (open blue circles) are excluded, $R^2 = 0.87$; with all data included, $R^2 = 0.74$. Data were obtained at 293−298 K (SI).

A comparison of the simulated and experimental uptake of CO_2 is shown in Figure 2 at 0.1, 0.5, and 1 bar. There is generally good agreement between predicted and measured adsorption, with the exception of the M\DOBDC samples at 0.1 bar (open blue circles). Our force field is not expected to perform well for strong interactions between open metal sites and CO_2. However, the predictions for the other MOFs with open metal sites (HKUST-1, UMCM-150, and UMCM-150(N)$_2$) are very good, as shown in the SI. This may be due to the lower density of open metal sites (Table S35) compared to M\DOBDC, thus lessening their overall contribution to adsorption. With this one exception, trends are predicted correctly, and for this diverse group of MOFs, the simulations perform well. The model correctly predicts the top 5 MOFs in this group as Pd(2-pymo)$_2$, Mg\DOBDC, Ni\DOBDC, Zn\DOBDC, and Co\DOBDC in agreement with the experiments (Table S32). Identifying the best candidates is the most important task in screening, and the model is quite successful by this standard. Once the top candidates are identified, they can be studied in more detail computationally and experimentally. Given this validation, the model presented here could be used for ranking other materials, providing insights and suggesting the most promising materials for experimental study. Note that new and even hypothetical MOFs can easily be screened using modeling.

As noted, the model could be improved in several ways. For example, framework flexibility could be included. Greathouse et al.[11] recently demonstrated that including framework flexibility has little effect on adsorption of small gases in IRMOF-1. It might be expected to be more important for molecules that fit very tightly in the pores, but including framework flexibility would make the simulations significantly slower and force fields are not available for a wide variety of MOFs. Also, the model does not include polarization or orbital interactions. These effects are expected to play a role in the interaction of CO_2 with the open metal sites. Using X-ray diffraction and IR spectroscopy, Dietzel et al.[12] showed that at low pressures CO_2 molecules coordinate to Ni^{2+} ions in the Ni\DOBDC framework, forming $Ni^{2+}\cdots O=C=O$ adducts with an end-on configuration. The oxygen lone pair orbitals of CO_2 interact with the cations,[13] and the distance measured between the oxygen atom of CO_2 and the Ni atom (2.29 Å) is shorter than the sum of their van der Waals radii (3.1 Å).

The MOFs studied provide a good set for obtaining additional insights into what MOF properties correlate with high CO_2 uptake at low pressures. Frost et al.[14] showed that hydrogen uptake in MOFs falls into three regimes. At low pressures, uptake in different MOFs correlates with the heat of adsorption; at intermediate pressures, uptake correlates with the MOF surface area; and at the highest pressures, uptake correlates with the free volume available within the MOFs. Such correlations were also reported for CO_2 adsorption in MOFs.[15] Figure 3 shows that, for the MOFs studied here, there is an excellent correlation between the CO_2 uptake and heat of adsorption at $P < 1$ bar. Also, there is no correlation with the surface area or the free
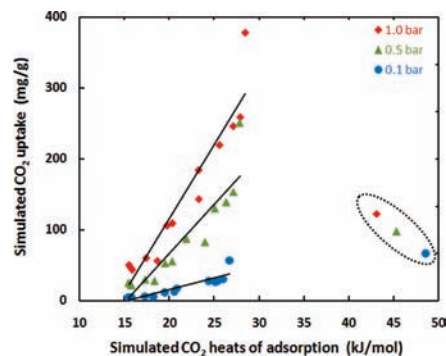

Figure 3. CO_2 uptake and heats of adsorption for the screened MOFs at 0.1, 0.5, and 1 bar from simulation. Data were obtained at 293−298 K (SI). The points in the dotted circle are for Pd(2-pymo)$_2$.

volume (Figures S35 and S36). An interesting exception to the trend in Figure 3 is the Pd(2-pymo)$_2$ MOF, which has a lower free volume and smaller pores than those of other materials. Thus, even at low pressures, the pores are essentially filled, shifting this MOF into the free volume regime.[14]

In conclusion, we have screened a diverse set of 14 MOFs for low-pressure CO_2 uptake using experiments and a consistent, predictive molecular modeling approach. Below 1 bar, CO_2 uptake correlates well with the heat of adsorption; thus MOFs having a high density of open metal sites are promising. Molecular modeling can aid in selection of adsorbents for flue gas separation by screening a large number of materials and providing insight into the mechanism of CO_2 adsorption.

Supporting Information Available: Molecular model and simulation details; experimental procedures; full funding agency acknowledgment and disclaimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA9057234