Heats of Adsorption for Seven Gases in Three Metal–Organic Frameworks: Systematic Comparison of Experiment and Simulation

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The heat of adsorption is an important parameter for gas separation and storage applications in porous materials such as metal–organic frameworks (MOFs). There are, however, few systematic studies available in the MOF literature. Many papers report results for only one MOF and often only for a single gas. In this work, systematic experimental measurements by TAP-2 are reported for the heats of adsorption of seven gases in three MOFs. The gases are Kr, Xe, N₂, CO₂, CH₂, n-C₄H₁₀, and i-C₄H₁₀. The MOFs studied are IRMOF-1, IRMOF-3, and HKUST-1. The data set provides a valuable test for molecular simulation. The simulation results suggest that structural differences in HKUST-1 experimental samples may lead to differing heats of adsorption.

Introduction

Metal–organic frameworks (MOFs) are promising materials for gas separation and storage applications due to their exceptional pore volume in the micro- to mesopore range and their tailorable.1-4 Hence, there is an increasing number of studies dealing with gas adsorption in MOF materials including H₂, CH₄, N₂, and CO₂, among others.5 However, various authors have pointed out discrepancies for reported pore volumes, adsorption isotherms, and heats of adsorption among different groups.6,7 These differences can arise due to differences in MOF synthesis or solvent removal, as well as problems in performing the adsorption measurements with small amounts of sample. Another difficulty is that many papers report results for a single material and often only for one or two gases. To make meaningful comparisons, there is a need for systematic studies of multiple gases on the same MOF sample and for studies of a particular gas on multiple MOFs.

Systematic studies of this sort would also provide a stringent test of predictions from molecular simulation for adsorption in MOFs. Molecular simulation is becoming an important tool in MOF chemistry and material science in general, because it can provide useful insights about the relation between molecular-level structure and observed macroscopic properties, including adsorption. If simulations are sufficiently accurate, they can also be used to screen hypothetical MOFs before they are synthesized. Several reviews of molecular modeling in MOFs have appeared recently, highlighting the rapid growth of this field.8-10

In this work, we report low-loading heats of adsorption for Kr, Xe, N₂, CO₂, CH₂, n-C₄H₁₀, and i-C₄H₁₀ in IRMOF-1 (also known as MOF-5), IRMOF-3, and HKUST-1 (also known as Cu-BTC). The IRMOF structure is made of Zn₆O tetrani clusters connected by rigid dicarboxylic linkers such as benzene 1,4-dicarboxylate (IRMOF-1) to generate a cubic framework. The resulting compounds show square channels, which are connected in the three dimensions. IRMOF-3 differs from IRMOF-1 by the functional amino group on the benzene 1,4-dicarboxylate linker. They have a cage size of about 15 Å at channel intersections with pore openings of about 7.5 Å. The HKUST-1 structure of formula Cu₇(BTC)₃(H₂O) comprises a binuclear Cu₃ paddywelled,11 The Cu²⁺ ions are connected through a weak bond, and the second axial coordination site is filled by a weakly bonded water molecule which can be easily removed with a heating treatment at 383 K, rendering the Cu Lewis acid center directly accessible. HKUST-1 structure consists of two types of “cages” and two types of “windows” separating these cages.12,13 Large cages (13.2 and 11.1 Å in diameter) are interconnected by 9 Å windows of square cross section. The large cages are also connected to tetrahedral shaped side pockets of roughly 6 Å through triangular shaped windows of about 4.6 Å (3.5 Å in the hydrated form). The data set provides a valuable test for molecular simulation. Good agreement between simulation and experiment is obtained for the IRMOFs but not for

Table 1. Simulation Parameters for HKUST-1

<table>
<thead>
<tr>
<th>atom</th>
<th>q [e]</th>
<th>ε/k</th>
<th>σ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.0</td>
<td>2.158</td>
<td>3.114</td>
</tr>
<tr>
<td>O</td>
<td>-0.6</td>
<td>48.19</td>
<td>3.03</td>
</tr>
<tr>
<td>Ca</td>
<td>0.7</td>
<td>47.86</td>
<td>3.47</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0</td>
<td>47.86</td>
<td>3.47</td>
</tr>
<tr>
<td>Cc</td>
<td>-0.15</td>
<td>47.86</td>
<td>3.47</td>
</tr>
<tr>
<td>H</td>
<td>0.15</td>
<td>7.65</td>
<td>2.85</td>
</tr>
</tbody>
</table>

HKUST-1. The simulations suggest that the discrepancy may be explained by blockage of the small pockets in the HKUST-1 experimental sample.

Experimental Section

IRMOF samples were prepared by a method reported elsewhere.\(^6\) In brief, benzene 1,4-dicarboxylic acid (H\(_2\)BDC, Aldrich, 2.5 g, 15 mmol) and Zn(NO\(_3\))\(_2\)\(\cdot\)4H\(_2\)O (Merck, Pro Analysis, 5.8 g, 20 mmol) are dissolved in 500 mL of DMF (Aldrich, anhydrous). The solution is heated at reflux for 18 h. The white precipitate is filtered under inert atmosphere at room temperature and washed three times with DMF. The samples were kept under inert atmosphere. Samples were characterized by XRD, \(^1\)H and \(^13\)C NMR, IR, and N\(_2\) physisorption at 77 K. The BET surface areas are very large (1540 m\(^2\)/g) and pore volume (0.8 cc/g) in good agreement with the highest values reported elsewhere.\(^6\)

Heats of adsorption were measured by using pulse–response experiments in an ultrahigh-vacuum reactor system referred to as a TAP reactor (temporal analysis of products).\(^14\) The experiments are carried out by pulsing a small amount of gas (10 nmol 50 vol % in argon) over a fixed bed of adsorbent placed in a microtubular reactor and measuring the pulse responses of the gas by a mass spectrometer at the reactor exit. By modeling these pulse responses, heats of adsorption at very low coverage can be calculated. Advantages of operating in ultrahigh vacuum are (i) external mass-transfer limitations are completely absent, (ii) molecule–wall interactions dominate, and (iii) the strongest adsorption sites are probed. This technique has been used to quantify adsorption parameters including heats of adsorption and diffusion of gases over various adsorbents such as zeolites\(^15\) and activated carbon.\(^16\) Prior to adsorption experiments, samples were desorbed at 550 K at 100 Pa. Measurements and modeling were performed using “best of practice” procedures.\(^17\) Adsorption experiments were carried out with Kr, Xe, N\(_2\), CH\(_4\), CO\(_2\), n-C\(_{4}\)H\(_{10}\), and i-C\(_{4}\)H\(_{10}\).

Adsorption isotherms for CO\(_2\) were also obtained by gravimetric measurements with a Rupprecht & Patashnick TEOM 1500 pulse mass analyzer. It consists of a microreactor with a high-resolution microbalance that generates real-time measurements of mass changes during gas–solid reactions.\(^18–20\)

The TEOM measures mass changes based on inertial forces, ...
The monitoring of the CO2 partial pressure from 0.2 to 133 kPa using an equation of state (here Peng–Robinson). Simulations are random translation of a molecule, rotation, and random reinsertion, insertion of a new molecule, and deletion of a randomly chosen existing molecule. We used 10^5 cycles. Henry coefficients and heats of adsorption at infinite dilution are obtained from NVT simulations using a single molecule. MC moves used are translation, rotation, and random reinsertion. During the simulation, the average potential energy is monitored, which is related to the heat of adsorption as \( \Delta H = \langle U_{\text{gas}} \rangle - \langle U_{\text{eq}} \rangle - RT \), where \( U_{\text{gas}} \) is the potential energy of the guest molecule inside the host framework, \( U_{\text{eq}} \) is the potential energy of the adsorbate in the ideal gas reference state, and \( R \) is the gas constant. For the NVT simulations, we also used 10^5 cycles. Henry coefficient information is retrieved from the reinsertion MC move.23

The frameworks were kept rigid during the simulations with the positions taken from the crystallographic data in the literature.11,24,25 The interactions of the adsorbates with the framework were modeled using Lennard-Jones potentials and static partial charges. The parameters for the framework were taken from the CHELPG method in Gaussian03.27 Note that it has been found by several authors that simulation results for adsorption in IRMOFs are not very sensitive to precise values of the charges at room temperature.9,10 The CO2 molecule was modeled as a rigid molecule using Lennard-Jones parameters and charges from the TriPPE model.28 Charge interaction was computed with the Ewald summation29 using a relative precision of 10^-6. The number of unit cells was 1 x 1 x 1. The Lenard-Jones interactions were truncated at 12.8 Å and tail corrections were omitted. Lorentz–Berthelot mixing rules were used to calculate mixed Lennard-Jones parameters. The charges for the framework and HKUST-1 are listed in Table 1. Similar charges for HKUST-1 were reported by Yang et al.29 More details can be found in refs 30–33. For future investigations, we also determined the framework charges for a variety of other IRMOF structures.

**Simulation Methods and Model**

Adsorption isotherms were obtained using grand canonical Monte Carlo (GCMC) simulations.21,22 The volume \( V \), the temperature \( T \), and the chemical potential \( \mu \) are kept fixed; and at these conditions, the average number of molecules is computed. The chemical potential can be derived from the gas-phase pressure by using an equation of state (here Peng–Robinson). Simulations are defined in cycles, where during 1 cycle there have been N MC moves with N being the number of molecules. MC moves used for these simulations are random translation of a molecule, rotation, random reinsertion, insertion of a new molecule, and deletion of a randomly chosen existing molecule. We used 10^5 cycles. Henry

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Results

As an example of TAP experiments, pulse responses for Xe on IRMOF-1 are illustrated in Figure 1. The plots show the normalized throughput of Xe after passing through the IRMOF-1 bed as a function of the time. As expected, transient signals become sharper when the temperature increases, corresponding to faster Xe diffusion in the bed. The calculation of the heat was carried out by modeling the transient signals.

The isosteric heats of adsorption measured experimentally for various gases on IRMOF-1 and -3 are presented in Figure 2. Unfortunately, experimental heats of adsorptions are usually not reported in the open literature for IRMOF samples, making a comparison difficult. Two studies using $^{129}$Xe NMR have reported different values for Xe adsorption. Ooms and co-workers have measured a $\Delta H$ of 12 ± 2 kJ mol$^{-1}$ on IRMOF-1 in good agreement with our measurements, whereas Pawsey and co-workers report values in the range 5–6 kJ mol$^{-1}$ for both IRMOF-1 and IRMOF-3. The latter are significantly lower than with other classical nonpolar adsorbents such as carbon-based materials (usually in the range 15–20 kJ mol$^{-1}$).

When comparing the two IRMOFs in Figure 2, we can clearly see that functionalization of the framework with amino groups leads to an increase of adsorption heats for most of the gases (Kr, Xe, CH$_4$, and CO$_2$). Millward and co-workers arrived at the same conclusion when comparing the CO$_2$ isotherms on IRMOF-1 and -3. For N$_2$, the change is not significant (in the error margin), whereas the strongest increase is observed for Xe. There is a rough correlation with the adsorbate polarizabilities. N$_2$, which has the weakest polarizability ($\alpha = 1.74$ Å$^3$), shows no change, and Xe with the highest polarizability ($\alpha = 4.04$ Å$^3$) exhibits the largest increase. These results suggest that the electric field created by the amino groups in IRMOF-3 increases the adsorption strength for more polarizable adsorbates.

Isosteric heats of adsorption for HKUST-1 are presented in Figure 3. Confidence intervals are larger for n- and i-butane because transient signals are quite broad, making the modeling less accurate. Here also in the literature, experimental heats of adsorption for HKUST-1 are scarce. For Krungleviciute et al.,$^{37}$ and Wang et al.,$^{38}$ isosteric sorption enthalpies decrease sharply with the loading. Values of 14.0 and 35 kJ mol$^{-1}$ were measured at the lowest coverage for Ar and CO$_2$, respectively. Our measurements for CO$_2$ differ significantly for HKUST-1. Finsey et al. report 50 kJ/mol for n-butane.$^{39}$

Parallel to TAP experiments, CO$_2$ heats of adsorption were obtained by gravimetric measurements. Gas uptake was recorded from 0.2 to 133 kPa at 313, 333, and 353 K for the three MOFs as shown in Table 2. Enthalpy values were calculated by fitting experimental data with the Langmuir model and are reported in Table 2. The gravimetric measurements confirm the consistency of the TAP results for the three MOFs. Values obtained by TAP are higher than the heats of adsorption measured by the gravimetric method. This is due to the measurement conditions: TAP data are obtained at very low coverage, whereas for gravimetric measurements, the calculation is performed over a larger range of loading.$^{14,38}$

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(34) Ooms, K. J.; Wasylishen, R. E. Microporous Mesoporous Mat. 2007, 103 (1–3), 341–351.
In Figure 5, adsorption enthalpies obtained from experiment and simulation for IRMOF-1 and IRMOF-3 are compared for a variety of small gas molecules. The agreement between experiment and simulation is excellent for IRMOF-1 for all six gases. For IRMOF-3, the simulation results follow the same trend as the experiments, but the agreement is not as good. In particular, Xe and CO\textsubscript{2} show lower heats from simulation than from experiment.

For HKUST-1 (open symbols in Figure 6), the simulation results do not match experiment as well as for the IRMOF samples. We hypothesized that a possible explanation for this would be if molecules could access the small favorable pockets in the simulations but not in the experiments. To test this, we performed additional experiments in which the small cavities were artificially blocked using a 5 Å radius around the center of each pocket. These results (filled symbols in Figure 6) agree much better with the experimental results, suggesting that the small pockets are inaccessible in the experimental samples.

Figure 7 (open symbols) shows the temperature dependence of the heats of adsorption of \textit{n}-C\textsubscript{4}H\textsubscript{10} and CO\textsubscript{2} in HKUST-1 predicted by simulation. There is a surprisingly large temperature dependence for these guest molecules (about 20 kJ/mol for \textit{n}-C\textsubscript{4}H\textsubscript{10}). This is due to the large adsorption enthalpy in the small pockets and the fact that at higher temperature the molecules are driven out of the pockets. From simulation results, we have indeed observed that adsorbates prefer to move to the bigger pores where the adsorption enthalpy is not as favorable. This phenomenon was also reported very recently elsewhere.\textsuperscript{40}

This temperature dependence is much lower when these pockets are blocked (Figure 7, filled), and the values for the blocked case are in better agreement with experiment. A similar effect has been found as a function of loading by Chmelik et al.\textsuperscript{12} They report that heats of adsorption for neo-pentane, \textit{n}-butane, isobutene, and 2-methylbutane drop off 20 kJ mol\textsuperscript{-1} above 10 molecules per unit cell in HKUST-1. Our results also match well the study performed by Garcia-Perez et al.\textsuperscript{40} considering that our calculations were performed at slightly higher temperature for consistency matters with the experimental data. The close match in size between adsorbates and the small pockets leads to a high heat of adsorption and probably explains many of the discrepancies between simulation and experiment and among experimental data sets in the literature for HKUST-1.

To further investigate HKUST-1, we simulated N\textsubscript{2} isotherms with and without the small cavities artificially blocked. Our simulations are compared with recent experimental results from Chowdhury et al.\textsuperscript{41} In this work, the impact of preparation methods on adsorption isotherms are revealed. The preparation methods differ in the solvent used and the temperature conditions during synthesis, as well as in the drying procedure. Samples “A” are synthesized in water/ethanol at 413 K and then dried at 358 K, whereas samples “B” are prepared in DMF/ethanol at 373 K, which are then extracted by Soxhlet technique with MeOH and then dried at room temperature. Samples “B” are clearly of higher crystallinity and purity (no Cu\textsubscript{2}O phases), resulting in higher surface area of 1482 against 857 m\textsuperscript{2}/g for sample “B”. The same authors further show that these high/low values are representative of a number of published data from different groups. It shows that two distinct classes of compounds exist, which are characterized by BET surface areas (1) around 1500 m\textsuperscript{2}/g and (2) around 700–900 m\textsuperscript{2}/g, respectively. Simulated N\textsubscript{2} isotherms at 295 K are compared with experimental data obtained from samples “A” and “B” in Figure 8. The results show that the simulated unblocked isotherm agrees well with the experimental isotherm obtained from sample “B”, and the simulated blocked isotherm agrees well with the experimental results for sample “A”. It suggests that HKUST-1 samples in group 2 have inaccessible small pockets. The presence of impurities such as acids in the cavities or strongly bonded water molecules (due to the low-temperature desorption) may be responsible for the blockage of the side pockets. In Table 3, we further compare simulated Henry coefficients with literature values for “B” samples. Here again, we note very good agreement between experimental and theoretical studies.

\textsuperscript{40}Garcia-Perez, E.; Gascón, J.; Morales-Florez, V.; Castillo, J. M.; Kapteijn, F.; Calero, S. Langmuir 2009, 25 (3), 1725–1731.

Conclusions

Heats of adsorption have been measured for a systematic set of gases in three common MOFs (IRMOF-1, IRMOF-3, and HKUST-1). In addition, molecular simulations have been performed for the same systems. Agreement between simulation and experiment is excellent for IRMOF-1 and good for IRMOF-3. Simulations predict a large temperature dependence of the heat of adsorption in HKUST-1, which is reduced significantly when the small pockets are blocked. The combined experimental and simulation study sheds light on discrepancies found in the literature for adsorption in HKUST-1. We hope this study will stimulate experimentalists to examine the effect of temperature on the crystal structure (including the changes upon water adsorption on Cu site) and its effect on gas adsorption.

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Supporting Information Available: Tabulated adsorption enthalpies from experiment and simulation; XRD patterns; atomic charges for a large variety of related MOFs. This material is available free of charge via the Internet at http://pubs.acs.org.

Table 3. Henry Coefficients Obtained by Simulations for Various Adsorbates at 295 K in HKUST-1 (without Pore Blocking) Compared to Two Experimental Data Sets from the Literature.  

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>( H_k ) [mol/kg/Pa] exp</th>
<th>( H_k ) [mol/kg/Pa] exp</th>
<th>( H_k ) [mol/kg/Pa] simulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>( 6.24 \times 10^{-5} )</td>
<td>( 3.47 \times 10^{-5} )</td>
<td>( 6.0 \times 10^{-5} )</td>
</tr>
<tr>
<td>O(_2)</td>
<td>( 2.12 \times 10^{-6} )</td>
<td>( 2.8 \times 10^{-6} )</td>
<td>( 5.0 \times 10^{-6} )</td>
</tr>
<tr>
<td>Ar</td>
<td>( 3.09 \times 10^{-6} )</td>
<td>( 3.1 \times 10^{-6} )</td>
<td>( 4.85 \times 10^{-6} )</td>
</tr>
<tr>
<td>N(_2)</td>
<td>( 2.8 \times 10^{-6} )</td>
<td>( 3.1 \times 10^{-6} )</td>
<td>( 3.9 \times 10^{-6} )</td>
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