MOF stability and gas adsorption as a function of exposure to water, humid air, SO₂, and NO₂

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ABSTRACT

Gas adsorption and stability to liquid water, humid air, and acid gasses on metal organic frameworks have been studied using a high-throughput adsorption measurement system. Among the seven MOFs studied, Cu-HF, Zn-NDC, and Ni-NIC showed higher CO₂/N₂ sorption selectivities (8–12), mainly due to high CO₂ adsorption. Long term (5 days) NO₂ exposure, as well as exposure to liquid water, resulted in partial decomposition of the original structure of Zn-NDC with a corresponding 26–30% decrease in CO₂ adsorption capacity. No noticeable changes in X-ray diffraction (XRD) patterns were observed for the other MOFs with small variations in adsorption capacities, indicating structural robustness to acid gas and liquid water. Short-term exposure to humid air (3 d) and acid gasses (2 d) caused a decrease in CO₂ and N₂ adsorption capacity for Cu-HF and an increase in adsorption capacity for Ni-NIC. Measurements indicate that pore flexibility in Cu-HF, Zn-NDC, Ni-NIC and Cu-NH₂ is modulated by temperature: large SF₆ molecules are rejected from the pores at room temperature (as expected based on kinetic diameter), but N₂, which does adsorb internally at room temperature, is rejected from the pores at 77 K.

1. Introduction

The capture of CO₂ from fossil fuel combustion flue gas is the focus of significant research efforts in response to concern over the role of CO₂ in climate change. A significant fraction of CO₂ emissions comes from the burning of oil, coal, and natural gas [1]. Current technologies for capturing CO₂ from these sources are largely based on chemical absorption of CO₂ by amine solutions, but these suffer from a high energy penalty due to the high-temperature regeneration of the sorbent [2]. Furthermore, the regeneration process can cause sorbent loss and degradation [3]. Hence, there is a critical need to discover and develop more energy efficient and sustainable capture technologies [4].

Metal organic frameworks (MOFs) are one class of materials that has received considerable attention as possible components in CO₂ capture technologies [5]. MOFs are nanoporous materials with high surface area and well-defined pore structure that have potential applications in separation, catalysis, and gas storage [6,7]. There are an enormous number of MOFs that can be synthesized with various combinations of organic linkers and metal centers, providing an opportunity to tailor surface area, pore size, and surface functionality [8]. MOFs have been considered for use in CO₂ capture both as sorbents [9–13] and as components in membranes [14–16].

For practical CO₂ capture applications, the performance of MOFs that have been exposed to water vapor and acid gasses like SO₂ and NO₂ is critical, since these are ubiquitous components of post-combustion flue gas. However, to date there have been relatively few studies of MOF stability with respect to water [17–20] and, to our knowledge, there are a few studies of stability with respect to acid gasses [19,21,22]. In this study, we present adsorption properties of CO₂ and N₂ for seven MOFs by using a high-throughput (HT) sorption system described previously [19]. Additionally, the structural stability and dependence of adsorption and selectivity following exposure to humid air, liquid water, and acid gasses were investigated. The potential role of structural flexibility of the MOF frameworks on gas adsorption was examined by measuring SF₆ adsorption. Our results considerably extend the number of MOFs for which information on stability with respect to acid gasses is available, and demonstrates the value of the relatively inexpensive experimental methods we have developed to achieve this goal.

2. Experimental

2.1. Materials

Eight MOFs were synthesized for this study following the synthesis procedures from previous literature: \{CdZrSr(C₂O₄)₄·6H₂O\}ₙ
(denoted CdZrSr below) [23], \{[\text{Ni}_2(\text{NIC})_4(\text{µH}_2\text{O})]_{\text{C}_2\text{H}_5\text{OH}\text{H}_2\text{O}}\}_{\text{C}_4\text{H}_8\text{N}_2\text{Ni}}\}_{\text{ZnPO}_3}^{(\text{Cu-HF})} [29]. Details of the synthesis conditions for these materials are given in Supporting Information. The identity of each material was confirmed using powder X-ray Diffraction (PXRD) experiments. These MOFs were selected based on computational screening of a large number of previously reported MOFs using geometric characterization of the MOFs’ pore structures [16,30]. The MOFs were chosen to have pore limiting diameters (PLD) similar to or smaller than the nominal kinetic diameter of CO₂ and N₂ in order to consider materials that can potentially have both adsorption and diffusion selectivity favoring CO₂ over N₂. MOFs with pores that are large relative to the size of adsorbed molecules are typically not expected to have any diffusion selectivity for CO₂ relative to N₂ [31]. Table 1 lists the PLD and also the largest cavity diameter (LCD) for each material calculated using the methods of Haldoupis et al. [30] based on the assumption that the reported crystal structure for each material is rigid.

An important issue when using small-pore MOFs is whether molecules of interest can penetrate into the pores of the MOF. A standard characterization of this issue is to create surface area from the Brunauer–Emmett–Teller (BET) model applied to N₂ physisorption measurements at 77 K. The BET surface areas for each MOF, measured after activation at 180–200 °C for 20 h under 0.02 atm vacuum at room temperature. The measure-ments were repeated in triplicate. Two different samples of Cu-HF were used, which differed in their activation temperatures. The sample denoted Cu-HF1 (Cu-HF2) below was activated at 280 °C (190 °C).

### 2.3. Stability tests

To provide information on the stability of each MOF with respect to water and acid gasses, gas adsorption (with dry, single component gasses) was measured before and after exposure of MOF samples to humidity and, separately, acid gasses in humid air. In each case, the MOFs were evacuated at 130 °C under vacuum for 20 h after the exposure prior to the adsorption measurements. In real applications it is of course vital that materials for CO₂ capture perform effectively during exposure to humidity and acid gasses. Although our protocol does not probe this situation, any material that is not stable after the staged exposure in our experiments should certainly be rejected from consideration from further development. In this way, our approach defines an efficient means to make go/no-go decisions regarding the viability of individual MOFs for CO₂ capture applications.

Samples were exposed to air with relative humidity of 80% for 3 days at room temperature. To test MOFs with acid gasses, the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Reference code, largest cavity diameter (LCD), pore limiting diameter (PLD), and surface area predicted by theory and measured by N₂ physisorption at 77 K. The CuHF results are from sample CuHF1.</th>
</tr>
</thead>
<tbody>
<tr>
<td>REFCODE</td>
<td>LCD, Å</td>
</tr>
<tr>
<td>CdZrSr</td>
<td>BEVQID</td>
</tr>
<tr>
<td>Ni-NIC</td>
<td>VOCNOQ</td>
</tr>
<tr>
<td>La-Cu</td>
<td>XOHHJA</td>
</tr>
<tr>
<td>Eu-Cu</td>
<td>DONYIY</td>
</tr>
<tr>
<td>Zn-NDC</td>
<td>JANEX</td>
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<tr>
<td>ZnPO₃</td>
<td>OHWI</td>
</tr>
<tr>
<td>Cu-HF</td>
<td>ESIPUR</td>
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</tbody>
</table>

![Fig. 1. Adsorption kinetics of the MOFs with initial pressure of 14 psi at 30 °C. (a) CO₂, (b) N₂.](image)
MOFs were exposed to 15 ppm of SO₂ for 2 days (short-term) or 5 days (long-term) and then 15 ppm of NO₂ for 2 days or 5 days in humid air (80% relative humidity) at 27 °C. These gas mixtures were prepared using salt solutions according to the literature [34]. The 15 ppm of SO₂ gas was generated with a 500 μg/ml NaHSO₃ aqueous solution with pH 3.7 at 45 °C. 200 ml/min of air flow transferred the generated SO₂ gas from reaction tube into a desiccator which has 80% relative humidity prepared with a saturated NaCl solution. The 10 ppm of NO₂ gas was generated by using the same apparatus under different conditions (800 μg/ml of NaNO₂ aqueous solution with pH 3 at 45 °C with 100 ml/min of air flow). Gas concentrations were verified with Dräger-Tubes (Dräger, Germany).

We also investigated the stability of MOFs with respect to liquid water. Deionized water was dropped onto each MOF in the sample chamber of the HT sorption system and then MOFs were left for 2 days at room temperature. The MOF samples were evacuated at 130 °C under vacuum for 20 h after the exposure prior to the adsorption measurements.

### Results and discussion

Fig. 1 shows the adsorption kinetics for each MOF for CO₂ (Fig. 1a) and N₂ (Fig. 1b) prior to the exposure of the MOFs to humid air or acid gasses. Adsorption was measured at 30 °C. The equilibrium loading was averaged over 0.4–0.8 h for CO₂ and 0.6–0.8 h for N₂, where trendline slopes for the adsorption curves remain below 0.008. The material-dependent equilibrium (final) pressures for these measurements ranged from 0.20 to 0.68 atm for CO₂ and 0.61 to 0.82 atm for N₂. As stated above, the final pressure in each experiment is dependent on the adsorption loading of the material being tested. The specific equilibrium pressures for each

<table>
<thead>
<tr>
<th>MOF</th>
<th>Before water vapor, atm</th>
<th>After water vapor, atm</th>
<th>After SO₂ for 2 d and NO₂ for 2 d, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>N₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>Cu-HF</td>
<td>0.197</td>
<td>0.660</td>
<td>0.245</td>
</tr>
<tr>
<td>Eu-Cu</td>
<td>0.592</td>
<td>0.776</td>
<td>0.578</td>
</tr>
<tr>
<td>ZnPO₃</td>
<td>0.653</td>
<td>0.803</td>
<td>0.653</td>
</tr>
<tr>
<td>Zn-NDC</td>
<td>0.354</td>
<td>0.796</td>
<td>0.333</td>
</tr>
<tr>
<td>La-Cu</td>
<td>0.680</td>
<td>0.844</td>
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<tr>
<td>Cd₂Zr</td>
<td>0.633</td>
<td>0.776</td>
<td>0.612</td>
</tr>
<tr>
<td>Ni-Nic</td>
<td>0.238</td>
<td>0.667</td>
<td>0.156</td>
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</table>

Fig. 2. (a) CO₂ and N₂, (b) adsorption capacities and sorption, (c) diffusion and (d) selectivities measured at 30 °C. White (before humid air), gray (after humid air for 3 d), and black (after SO₂-humid air exposure for 2 d and NO₂-humid air exposure for 2 d). Error bars represent standard deviation (n = 3).
MOF are reported in Table 2. Fig. 2a and b show adsorption capacities for CO2 and N2, respectively, obtained from the average adsorption values after reaching the final pressure in each experiment. To compare the adsorption measurements among different materials, the adsorbed amounts are normalized by dividing by the equilibrium pressure. Fig. 2c reports the adsorption selectivity as the ratio of the CO2 and N2 normalized adsorbed amounts. Cu-HF, Zn-NDC, and Ni-NIC showed relatively high CO2 and N2 adsorption compared to the other MOFs.

Fig. 2 also shows the adsorption loading of CO2 and N2 after each sample had been exposed to humid air (3 days) and, separately, to acid gasses in the presence of humidity for 2 days each. There were no significant changes in adsorption loading after exposure to humid air and to acid gasses except for Cu-HF and Ni-NIC. The adsorbed amounts for both gasses decreased for Cu-HF and increased for Ni-NIC after exposure to humid air and acid gasses. From Fig. 2c, adsorption selectivities were 8 for Cu-HF and Zn-NDC and ranged from 8 to 12 for Ni-NIC, similar to the range observed for ZIF-90, ZIF-8, ZIF-7, and Zn-TTC in our previous study [19]. Relatively low adsorption selectivities, ~4, were observed for Eu-Cu, ZnPO3, La-Cu, and CdZrSr. With the exception of Eu-Cu and Ni-NIC, the adsorption selectivity was insensitive to exposure to humidity and acid gasses. Eu-Cu and Ni-NIC showed increased selectivity following humid air and acid gas exposure. Small changes in PXRD patterns were observed for some of the MOFs: reduced intensity at 9°, 18°, and 21° for Zn-NDC; reduced intensity at 6° and 7° and increased intensity at 7° for ZnPO3; width changes at 13°, 23°, and 32° for CdZrSr; peak disappearance at 8° and increased intensity at 13° and 15° for Cu-HF; increased intensity at 12°, 30°, and 42° for Eu-Cu. However, no changes in PXRD patterns were observed for Ni-NIC and La-Cu after humid air and acid gas exposure (Fig. S1 in Supporting Information), indicating that the humid air and acid gasses had little or no effects on crystal structure.

Diffusion selectivities for the MOFs were estimated by using a micropore diffusion model (Eq. (1)) [35] assuming that mass transfer resistance in our experiments was dominated by intracrystalline diffusion:

$$1 - \frac{m}{m_c} = \frac{6}{\pi^2} \exp \left(-\frac{\pi^2 D_c t}{r_c^2}\right)$$  (1)

where $D_c$ is intracrystalline diffusity, $(m/m_c)$ is fractional uptake, $r_c$ is particle radius and $t$ is time. The adsorption kinetics where the
adsorbed amounts are between 70% and 90% of the equilibrium loading were used to estimate diffusivities in each sample. This late kinetic regime was chosen in order to mitigate the fact that Eq. (1) assumes a constant gas phase concentration (a condition that is not technically met by our experiment), since concentration changes more slowly towards the end of the transient regime. The diffusion selectivity is taken to be the ratio of the single component diffusion coefficients. The diffusion selectivities were 2 to 3.5 for Cu-HF, Zn-NDC, CdZrSr, and Ni-NIC. In large pore materials where diffusion can be approximated by Knudsen diffusion, N2 would diffuse faster than CO2, leading to a diffusion selectivity of ~0.8. Eu-Cu, ZnPO3, and La-Cu showed almost no diffusion selectivity for CO2 relative to N2 around 1 (Fig. 2d). The observed diffusion selectivity for ZnPO3 and CdZrSr was more sensitive to exposure to humidity and acid gasses than the adsorption selectivity was for the same materials.

An important caveat for interpreting these diffusion results is that our data does not allow us to verify the assumption that intracrystalline diffusion dominates mass transport in each sample chamber. A more thorough examination of this issue would require experiments with particles of multiple sizes for each material, a step that is beyond the scope of this work.

We further examined longer-term stability after 5 day exposures to SO2 and NO2 gas exposure for the Zn-NDC, Cu-HF, and Ni-Nic, which showed higher sorption selectivities than other MOFs. These MOFs were exposed to 10 ppm SO2 for 5 days, and then exposed to 10 ppm NO2 for 5 days under humid air with 80% relative humidity. The adsorption of CO2 and N2 was measured and XRD patterns were taken after exposure to each acid gas. In the 5 day stability test, an 18% lower CO2 adsorption capacity prior to exposure to humidity (0.082 mmol/g psi) was observed for sample Cu-HF2 than that measured in the short-term stability test (0.1 mmol/g psi), which used sample Cu-HF1. We attribute this deviation to the difference in activation temperatures of the separate Cu-HF samples. The XRD patterns for Cu-HF1 and Cu-HF2 showed clear differences after activation at these two different temperatures (Figs. S1 and S2 in Supporting Information). Ni-NIC showed increased CO2 and N2 adsorption capacities after the long-term SO2 exposure (Fig. 3 and Table 3), similar to the behavior observed after short-term SO2 and NO2 exposure (Fig. 2a and b). Adsorption and diffusion selectivities remained constant after the long-term acid gas exposure for all MOFs except Zn-NDC. The CO2 adsorption decrease of 30% for Zn-NDC resulted in a decrease of adsorption selectivity from 14.3 to 11.1 after the long-term NO2 exposure. Partial decomposition of the original structure in Zn-NDC was confirmed by PXRD patterns which showed peak disappearance and reduced peak intensity after the long-term NO2 exposure with humid air for 5 days (Fig. S2 in Supporting Information). There were no noticeable changes in PXRD patterns for Ni-NIC and Cu-HF after long-term exposure.

In practical applications involving flue gas, water adsorption could affect the performance of adsorbents. Thus, we investigated the stability and adsorption performance for Cu-HF, Ni-Nic, and Zn-NDC after exposure to liquid water. Adsorption capacities were measured and PXRD patterns were taken before and after exposure to liquid water for 2 days at room temperature. Ni-Nic and Cu-HF were stable with respect to liquid water exposure, giving similar adsorption capacities and PXRD patterns (Fig. S5 in Supporting Information) before and after the liquid water exposure. Zn-NDC, however, showed a decrease in CO2 adsorption by 27% (Table 3) and significantly reduced peaks in XRD patterns at 9.8°, 13.7°, 14.5°, 16.3°, 17.9° and 21° (Fig. 4). While the water vapor exposure of Zn-NDC resulted in no decrease in adsorption capacities (Fig. 2), PXRD peak intensities were reduced at 9.6°, 17.8° and 21° after the exposure to humid air (Fig. S1).

As we showed above, most of the materials we have examined showed negligible BET surface area when characterized with N2 adsorption at 77 K. The measurable loadings of N2 at room temperature in these materials, however, suggest that N2 is able to diffuse into the pores of these MOFs at non-cryogenic temperatures. To verify this observation, we used our adsorption apparatus to measure the adsorption of SF6 at room temperature with Cu-HF, Zn-NDC, and Ni-NIC. This measurement was also performed using Cu-NH2, another small pore MOF [36], SF6 is considerably larger and more polarizable than N2, so it adsors far more readily than N2 into pores that are accessible to both species [37]. The adsorption loading of SF6 was considerably lower than for N2 in all four MOFs (Fig. 5) Table 4. The small cavity diameters of the MOFs we have used and the small adsorbed amounts make it highly unlikely that any penetration of SF6 into the MOF pores occurred. These results support the observation that N2 can readily diffuse into these MOFs at room temperature, lending weight to the idea that internal pore flexibility must be accounted for in detailed molecular models of adsorbate diffusion in small pore materials [16,38]. They also indicate that the contri-

![Fig. 4](image-url)  
**Fig. 4.** XRD patterns of Zn-NDC before and after liquid water exposure for 2 d at 25 °C.

### Table 4

<table>
<thead>
<tr>
<th>MOF</th>
<th>LCD (Å)</th>
<th>PLD (Å)</th>
<th>Particle size (µm)</th>
<th>Experimental adsorption (mmol/g psi)</th>
<th>Estimated adsorption (mmol/g psi)</th>
<th>Estimated/Experimental, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-NIC</td>
<td>4.37</td>
<td>3.23</td>
<td>20</td>
<td>0.00183</td>
<td>0.00060</td>
<td>33</td>
</tr>
<tr>
<td>Cu-HF</td>
<td>4.85</td>
<td>2.73</td>
<td>83</td>
<td>0.00112</td>
<td>0.00016</td>
<td>14</td>
</tr>
<tr>
<td>Zn-NDC</td>
<td>3.18</td>
<td>2.61</td>
<td>102</td>
<td>0.00077</td>
<td>0.00012</td>
<td>16</td>
</tr>
<tr>
<td>Cu-NH2</td>
<td>4.13</td>
<td>2.62</td>
<td>30</td>
<td>0.00078</td>
<td>0.00043</td>
<td>55</td>
</tr>
</tbody>
</table>

*Particle size was estimated from SEM images (Fig. S4 in Supporting Information). Cu-NH2 was activated at 120 °C under vacuum for 5 h.*
butions to the adsorption loadings of N$_2$ and CO$_2$ in our samples are small.

4. Conclusions

Seven MOFs were characterized to identify sorption and diffusion selectivities of CO$_2$/N$_2$ before and after exposure to humid air, acid gasses and liquid water. Adsorption selectivities for Cu-HF, Zn-NDC, and Ni-NIC were similar to those for ZIFs and Zn-TTC, however lower than Co-NIC and Cu-PCN. Short term humid air (3 d) and acid gas (2 d) exposures caused CO$_2$ and N$_2$ adsorption capacity to decrease for Cu-HF and to increase for Ni-NIC. Adsorption selectivity, on the other hand, was unchanged except for an increase observed after exposure to humid air and acid gas for Eu-Cu$_2$ and Ni-NIC. In the long-term (5 d) acid gas exposure and the liquid water exposure, the original framework structures of Cu-HF and Ni-NIC remained stable with no decrease in adsorption capacity. However, according to the XRD patterns, Zn-NDC showed partial decomposition of the original framework concomitant with a decrease in CO$_2$ sorption capacity by 26–30%. The observation that N$_2$ can readily diffuse into these MOFs at room temperature lends credence to the idea that internal pore flexibility must be accounted for in detailed molecular models of adsorbate diffusion in small pore materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2013.02.002.

References