Due to its clean combustion and high heating value, hydrogen is under consideration as a replacement for fossil fuels in mobile applications. To achieve this goal, however, an effective means of on-board storage is required,¹ prompting the U.S. Department of Energy to set 2010 storage system performance targets of 6.0 wt \% H₂ and 45 g H₂/L.² Recent work has exposed the considerable potential for cryogenic hydrogen storage in microporous metalorganic frameworks exhibiting robust three-dimensional network structures and high surface areas.³ In particular, frameworks consisting of tetrahedral \([ZnO]^6\) units linked via rigid arylcarboxylate ligands were found to adsorb large amounts of hydrogen reversibly at low temperature and moderate pressures. For example, at 77 K and pressures of up to 50 bar, \(ZnO(BDC)^3\) (MOF-5, BDC²⁻ = 1,4-benzenedicarboxylate) was shown to adsorb 5.2 excess wt \% H₂,⁴ while \(ZnO(BTB)^3\) (MOF-177, BTB³⁻ = 1,3,5-benzenetrizoate) exhibited a record uptake of 75 mg/1075 mg = 7.0 excess wt \% H₂.⁵ Here, we report conditions for the synthesis and handling of \(ZnO(BDC)^3\) that significantly increase its gas adsorption capacity, resulting in the highest gravimetric and volumetric loadings yet reported for a cryogenic hydrogen storage material.

The compound \(ZnO(BDC)^3\) serves as a prototype for an extensive family of metal-organic frameworks in which oxo-centered \(Zn^n\) tetrahedra (of the type encountered in basic zinc acetate) are connected through linear organodicarboxylates to give a cubic network structure.⁶ As formed from a solution assembly reaction, the pores within the structure are filled with guest solvent molecules. Remarkably, these guest molecules can be evacuated to leave a rigid metal-organic scaffold that is typically stable up to 400 °C under vacuum.⁶⁷ Despite this apparent stability, there is considerable variation in the reported gas adsorption properties of \(ZnO(BDC)^3\) (see Table 1).⁸⁻¹⁰ Depending on the preparation, the \(N_2\) uptake at saturation varies from 11.8 to 34.4 mmol/g, while the maximum \(H_2\) uptake varies from 1.3 to 5.2 excess wt \%.

In order to resolve these discrepancies and determine the true hydrogen storage capacity of \(ZnO(BDC)^3\), a variety of synthetic methods were explored. Ultimately, the highest surface area material was obtained by employing a modification of a previously reported method¹¹ in which the exposure to water and air was minimized. In this procedure, a 3:1 mixture of \(Zn(NO_3)^2\·6H_2O\) and \(H·BDC\) is dissolved in diethylformamide (DEF) and heated at 80 °C without stirring. The reaction is monitored visually until crystal formation has ceased (usually after 10 h), whereupon the heating is immediately stopped and the mixture is transferred to a nitrogen atmosphere. The colorless cube-shaped crystals are washed with anhydrous DMF and anhydrous CH₂Cl₂, and the exchanged guest solvent is removed under reduced pressure to afford pure \(ZnO(BDC)^3\).

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Table 1. Gas Adsorption Properties of \(ZnO(BDC)^3\) Resulting from Various Preparations

<table>
<thead>
<tr>
<th>preparation</th>
<th>(N_2) uptake* (mmol/g)</th>
<th>(SA_{BET}*) (m²/g)</th>
<th>(SA_{Langmuir}*) (m²/g)</th>
<th>(H_2) uptake* (excess wt %)</th>
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<tbody>
<tr>
<td>ref 9</td>
<td>11.8</td>
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<tr>
<td>ref 8</td>
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<tr>
<td>1</td>
<td>44.5</td>
<td>3800</td>
<td>4400</td>
<td>7.1</td>
</tr>
</tbody>
</table>

* Maximum uptake observed at 77 K. ª Surface area determined by fitting the \(N_2\) adsorption isotherm at 77 K to the BET or Langmuir equation. (BDC)²⁻ (I) in 70—80% yield. Significantly, raising the temperature or extending the duration of the reaction was found to afford a yellow-tinted product with reduced surface area.¹² Although conditions were identified under which DMF could be employed as a less costly alternative to DEF (see Supporting Information), the surface area of the resulting material was generally somewhat lower.

During the course of these investigations, \(ZnO(BDC)^3\) was observed to decompose in humid air. Exposure of a pulverized, desolvated sample of I to air for 10 min resulted in appearance of a new peak at 2θ = 8.9° in the powder X-ray diffraction pattern, indicating partial conversion to a second phase (see Figure 1). Further exposure to air produced an increase in the relative intensity of this peak, as well as the appearance of two additional peaks at 2θ = 15.8 and 17.8°, suggesting formation of a compound isostructural to \(Zn_2(OH)_2(BDC)_2\·2DEF\) (MOF-69C).¹³ After 24 h, the conversion of I into a solid of formula \(C_{24}H_{22}O_{18}Zn_4\) (2 = 1·5H₂O) was complete. In contrast, no reaction was observed upon exposure of I to dry O₂ or anhydrous organic solvents such as methanol, DMF, or DMSO. Thus, the decomposition of \(ZnO(BDC)^3\) can be attributed to atmospheric water. This is consistent with results concerning the immersion of nanoparticles of MOF-5 in water,⁸ as well as recent calculations predicting \(ZnO(BDC)^3\) to...
be unstable in the presence of more than 4% water by mass.\(^1\)

Importantly, gas adsorption measurements showed the decomposition product, \(\text{Zn}_4\text{O(BDC)}_3\), to be nonporous, with no significant uptake of \(\text{N}_2\) or \(\text{H}_2\) at 77 K. The differences in the gas adsorption capacities reported for \(\text{Zn}_4\text{O(BDC)}_3\) (see Table 1) could therefore potentially be explained as arising from variations in the degree of exposure to atmospheric or solvent water during sample preparation.\(^2\)

Comparisons of \(\text{N}_2\) adsorption data for samples of \(\text{Zn}_4\text{O(BDC)}_3\) prepared with (\(\text{I}\)) and without (\(\text{I}\)) exposure to air indeed reveal substantial differences. Compound \(\text{I}\) was produced via a procedure identical to that utilized for \(\text{I}\), but with isolation and desolvation performed in air without use of anhydrous solvents. Nitrogen adsorption measurements at 77 K revealed isotherms (see Figures S5 and S6) with maximum \(\text{N}_2\) uptakes of 35.8 and 44.5 mmol/g.

Figure 2. Hydrogen adsorption isotherms for samples of \(\text{Zn}_4\text{O(BDC)}_3\), prepared with (\(\text{I}\), filled symbols) and without (\(\text{I}\), open symbols) exposure to air, and as reported in ref 5 (green triangles). Data were measured at 77 (blue) and 298 (red) K and are shown as excess (squares) and total (circles) uptake.\(^4\) All isotherms showed full reversibility without hysteresis. Solid lines indicate the density (right-hand scale) of pure \(\text{H}_2\) gas.\(^5\)

4. Excess uptake is the amount of gas taken up in addition to what would be present in a container with a volume equal to the pore volume within the sample. Total uptake is the amount of gas contained within the volume of the crystals, which includes both surface-adsorbed molecules and pressurized gas within the pores.
12. The yellow color is likely due to decomposition of DEF to form guest oligomers that are not readily evacuated. Heating a solution of just Zn-BDC to 110 °C results in a clear yellow solution containing a range of higher molecular weight organic species.
16. Grand canonical Monte Carlo simulations suggest that these steps are associated with preferential initial adsorption of \(\text{N}_2\) molecules at the corners within the framework: Walton, K. S.; Snurr, R. Q. J. Am. Chem. Soc. 2007, 129, 8552.