Microporous Metal Organic Materials: Promising Candidates as Sorbents for Hydrogen Storage

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Materials that effectively store hydrogen are needed for use in fuel cell powered vehicles. Among the various candidate storage technologies including porous sorbents, reversible metal hydrides, chemical hydrides, compressed gas, and liquefaction, none is capable of meeting the DOE cost and performance targets.1 Porous metal coordination structures represent a promising new entry to the field of hydrogen storage materials.2 To fully exploit this new field, relationships between structure and storage properties must be developed to guide the further rational design and synthesis of tailored materials with significantly improved hydrogen adsorption capability. In this light, we have explored a new type of sorbent, microporous metal coordination materials (MMOMs) with pore dimensions comparable to the length scale of the molecular diameter of hydrogen.

The MMOMs share physical characteristics similar to those of single-walled carbon nanotubes (SWNTs) that have been under intense investigation as storage materials. Both are lightweight and composed of open channels based on aromatic carbon. In addition, MMOMs possess several advantageous features over SWNTs that are particularly promising for improving hydrogen adsorption. For example, the MMOMs incorporate metals that can bind hydrogen much more strongly than graphitic carbon, but not as strongly as when a true chemical bond forms as in the case of metal hydrides. Furthermore, the organic components can be modified to induce stronger interactions with H2. The open channels in MMOMs are perfectly ordered, allowing effective access of hydrogen to the interior space. The internal surfaces of MMOMs can easily be modified to change the channel curvature, thus enhancing the H2—sorbent interactions.3 The “one-pot” synthesis is simple, cost-effective, and highly reproducible. More importantly, the structures of these materials, including the metal building unit, pore dimension, shape, size, and volume, can be systematically tuned for the purpose of modifying and improving hydrogen uptake and adsorption/desorption properties.

In this Communication, we report the synthesis, structure, and room-temperature hydrogen adsorption of a novel MMOM, [Cu-(hfipbb)(H2hfipbb)0.5] [H2hfipbb = 4,4′-(hexafluoroisopropyl) idenebis(benzoic acid)] (I). Crystals of I were grown in reactions of hydrated copper nitrate salt and excess H2hfipbb in deionized water at 150 °C.4a The structure of I is a 3D interpenetrating framework containing unique and perfectly ordered microporous 1D open channels (microtubes) built upon a Cu2(hfipbb)4(H2hfipbb)2 paddle-wheel building unit.5

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Figure 1. Views of structure I. Top left: cross section of a single microtube. Blue balls, Cu; red balls, O; gray balls, C; light blue balls, F. Top right: side view of a single microtube. Bottom: Three-dimensional packing of microtubes.

The coordination geometry of each copper is square pyramidal with respect to the five ligands. Two copper atoms share four carboxylate groups of the hfipbb ligands located in the equatorial plane to form a paddlewheel-shaped motif with a Cu—Cu distance of 2.645 Å. Each paddlewheel unit connects to four adjacent paddlewheel units via the four remaining carboxylate groups of hfipbb ligands to form an undulated 2D neutral network with a 4p topology. The adjacent 2D layers are connected by monodentate carboxylate groups of H2hfipbb ligands binding to the apical position of the metals to generate a 3D network. The metal network based on Cu2 dimer has a highly distorted α-polonium topology.6 Two identical 3D networks interpenetrate to give rise to the final structure containing ordered arrays of 1D microtubes packing along the (101) direction. Two views of a single microtube are depicted at the top section of Figure 1. The bottom section of the same figure shows how these microtubes pack to give rise to a 3D structure. The salient features of these microtubes are that they contain curved internal surfaces featuring small windows (~3.5 × 3.5 Å, excluding the van de Waals radius of carbon) and larger cages (~5.1 × 5.1 Å). This is similar to the RPM1 system we reported earlier.7 Thermogravimetric (TG) analysis of I showed that the as-prepared sample was stable to 330 °C.8 The unusually high thermal stability is presumably a result of interpenetration.6,8

The hydrogen adsorption isotherm of I was obtained at 25 °C using a pulse mass analyzer according to a previously described procedure.9 The instrument measures mass changes by an inertial technique for a packed bed of adsorbent in a flowing stream of hydrogen (99.999%) as a program ramps the pressure from 1 to 48
The amount of hydrogen adsorbed was stable throughout the 20 atm. The isotherm is the average of eight complete pressure cycles.

As a further comparison, we also measured hydrogen uptake in MOF-5 ( pore dimensions approximately 7.7 × 7.7 Å) using the same conditions. The material was synthesized according to the published procedure.11 The hydrogen isotherm taken by our procedure essentially agrees with that reported, which covered a range of pressures up to 20 atm. We have extended the isotherm to higher pressures and find a storage capacity of 1.65 wt % at 48 atm. The accessible volume of MOF-5 (about 76.8% based on our calculations) is 6.6 times that of I (11.6%), but MOF-5 only takes up 1.8 times the amount of hydrogen. This suggests that pore volume is not the sole factor that determines the amount of gas adsorbed. The quality of the pores that contribute to the pore volume must be considered as well. One critical aspect of pore quality is the relative size of the pores with regard to the gas that is taken in. An optimal material would have pores that fit the size of the gas molecules well and have the largest possible pore volume. Note the differences in the pore dimensions and shapes of the two structures. Positive evidence for a restricted pore size in I was found by comparing isotherms we have obtained for methane with those for hydrogen. In the case of I, the molar ratio of methane to hydrogen sorbed at 48 atm was 0.75, while for the larger pore size material of similar structure it was 1.7.12 Based on the adsorption results on the pure gases, this represents a striking inversion of selectivity that is apparently related to the pore dimensions.

Note also that I gives a significantly higher volume density.1 0.0147 g H₂/cm³, as compared to 0.0099 g H₂/cm³ for MOF-5. This also points to a more effective use of available pore volume by the material with smaller pore size. Thus, tailoring pore size to fit the molecular diameter of the stored molecule seems to have virtue. This result points toward more optimal designs for MMOMs that retain a small pore size but have larger total pore volumes. In this way, it may be possible to approach the DOE target value (0.036 g H₂/cm³ for 2005) without resorting to pressures much higher than those used here.

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Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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