Gas Storage

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Acetylene Absorption and Binding in a Nonporous Crystal Lattice**

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Finding an economical and technologically viable way to capture highly flammable gases such as acetylene, hydrogen, and methane is very important for their production, transportation, and delivery.[1] Several methods have been proposed based on physical adsorption by activated carbon,[2] zeolites,[3] carbon nanotubes,[4] metal–organic frameworks,[5] and other porous and nonporous materials.[6] However, each method has its technical challenges and no ideal method has emerged thus far. Although storage in compressed cylinders provides an alternate technology,[7] acetylene gas, a key component for the synthesis of diverse organic compounds, petrochemicals, electric and electronic materials, cannot be compressed above 30 psia or 15 psig at room temperature or it explodes, even in the absence of oxygen.[8] Acetylene dissolves readily in acetone and is delivered in a steel cylinder containing acetone along with other porous materials to prevent polymerization when the gas is stored under pressure (solubility of acetylene in acetone at 1 atm and 15 °C equals 20 liters per liter of acetone). Therefore the search has begun to find a method of storing acetylene gas at room temperature while compressed well above its critical limits.[9]

In this context, metal–organic frameworks are well-investigated for storage and separation of gases[10] whereas organic crystals assembled by means of noncovalent forces and van der Waals interactions have largely been neglected as gas sorption substrates owing to close packing phenomena which generally do not lead to conventionally porous structures. Many inclusion compounds often possess zero-,

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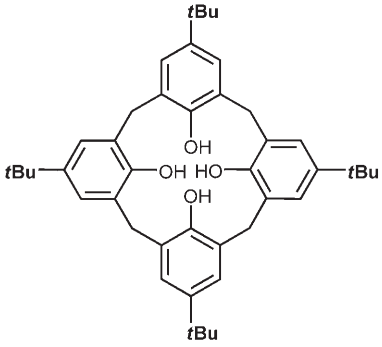
one-, two-, or three-dimensional solvent-accessible space with guest molecules located in cavities or channels. It is therefore attractive to envision facile removal of the solvent molecules from these materials to yield highly porous host lattices analogous to those of zeolites. In reality, the process of desolvation is almost always accompanied by reassembly of the host molecules in the solid state to form one or more so-called apohost phases, where the pure compound is once again efficiently packed. However, a few organic compounds are exceptions to this phenomenon[6,11] (e.g. tris-*o*-phenylenedioxycyclotriphosphazine, which forms a porous hexagonal host framework stabilized by weak intermolecular interactions with a minimum pore diameter of 4.6 Å). These nanoporous crystals show high sorption capacity values for methane and carbon dioxide at 195 K.[11b] Calix[4]arene has the ability to entrap highly volatile guests such as CF_3Br, CF_4, and CH_4 well beyond their normal boiling points such that the host lattice must disassemble itself to release the guest molecules.[12] In a continuation of this work, we have extended our sorption studies on the low-density polymorph of *p-tert*-butylcalix[4]arene (**1**) to entrap the highly flammable gas acetylene, and to compare these results to those for carbon dioxide.



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Acetylene and carbon dioxide sorption experiments were conducted volumetrically using a specially constructed device.[13] A sample of 1.5 g of **1** was placed in the sample chamber ($V_s = 10.93\ cm^3$) and evacuated for several hours to remove any trace amount of gas. In separate experiments, acetylene and CO_2 were introduced at an initial pressure of 800 torr. Gas was absorbed over 3 h until equilibrium was reached (Figure 1). An occupancy study (Figure 2, that is, percentage occupancy versus equilibrium pressure) shows that the uptake of acetylene at standard temperature and pressure (STP) is approximately 2% by weight. This value corresponds to 39 $cm^3\,g^{-1}$ and is comparable to, or exceeds the values obtained for carbon nanotubes and inorganic zeolites such as Zeolite 4 A.[14] The seemingly nonporous crystals absorb 0.515 mol of acetylene per mol of host at 298 K and 1 atm pressure indicating complete filling of the available volume in the crystal structure (i.e. because two calixarenes are required to form one lattice void). The absorption and desorption isotherms for acetylene and CO_2 indicate a type I relationship between the equilibrium pressure and percentage of calixarene lattice voids occupied by the two gases. It appears that the occupancy of acetylene is 100% (Figure 2a) at 1 atm pressure whereas 80% of the cavities are filled by CO_2 at this pressure (3 atm of CO_2 pressure is required to fill the cavities completely, see Figure 2b). Interestingly, the absorption–desorption process for CO_2 is fast and no hysteresis was observed. However, acetylene shows a significant hysteresis effect (acetylene desorption is slower than absorption), implying considerable stabilization of the gas in the nonporous material.

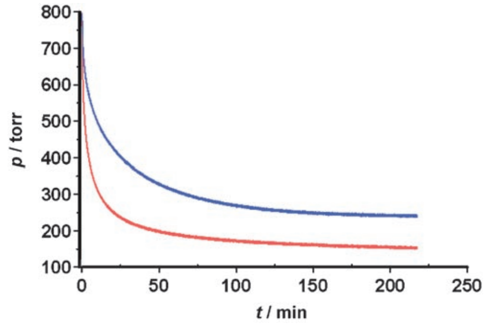

Figure 1. Sorption of acetylene (blue) and carbon dioxide (red) at room temperature and approximately 1 atm initial pressure.

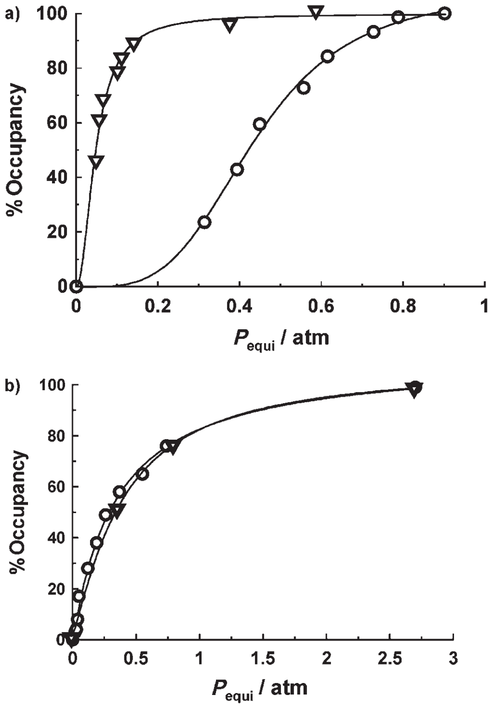

Figure 2. Absorption and desorption isotherms of acetylene and carbon dioxide at room temperature. a) Absorption values for acetylene are shown as circles while triangles represent desorption. Hysteresis in the sorption–desorption curves implies strong affinity towards acetylene. b) Sorption (circles) and desorption (triangles) isotherms for CO_2. Full occupancy of CO_2 was obtained at 3 atm pressure and no hysteresis is observed.

The calculated density of the absorbed acetylene at STP (using a void volume of 235 Å^3) is estimated to be 0.18 $g\,cm^{-3}$, which is equivalent to acetylene at 18 MPa and 90 times the compression limit for the safe storage of acetylene (0.2 MPa = 0.0021 g cm^{-3}; the density of the absorbed acetylene in the bulk material is 0.02 g cm^{-3} and is equivalent to 2 MPa at room temperature). To our knowledge this is the first report of an organic material which absorbs acetylene at room temperature and 1 atm pressure.

Although several attempts to collect single-crystal X-ray diffraction data for **1** with included acetylene failed, the remarkable stability of the acetylene in the host lattice facilitated identification of the gas in the crystal using solid-state NMR spectroscopy at ambient conditions (Supporting Information).[15] The resonance of the stored acetylene in the ^{13}C magic-angle spinning (MAS) NMR spectrum appears as a sharp signal at $\delta = 66.2$ ppm compared to free acetylene at $\delta = 71.8$ ppm. The exceptional upfield shift of -5.6 ppm is consistent with stronger binding of the acetylene in the host lattice and is shifted further upfield than any reported resonance of acetylene (Figure 3 a and b). Similarly, the ^{13}C MAS NMR spectrum of the sample containing CO$_2$ shows a signal for stored CO$_2$ at $\delta = 121.9$ ppm. An upfield shift of -3.5 ppm occurs for the stored gas compared to the gas phase CO$_2$, which appears at $\delta = 125.4$ ppm. However, the signal is close to that for one of the carbon atoms of the host molecule and this problem was overcome by performing a non-quaternary suppression (NQS) experiment in which suitable conditions were found to suppress the protonated carbon atoms of the host. A neat signal at $\delta = 121.9$ ppm was assigned to the non-protonated carbon of CO$_2$ stored in the crystal (Figure 4 b and c).

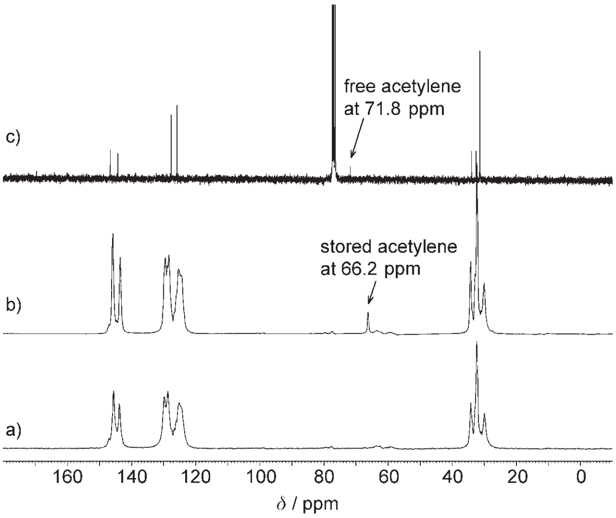

Figure 3. a) ^{13}C MAS NMR spectrum of sample **1**. b) Sharp signal at $\delta = 66.2$ ppm indicates the stored acetylene in **1**. c) ^{13}C NMR spectrum in chloroform, free acetylene at $\delta = 71.8$ ppm.

The solid-state structure of **1** features the calixarene molecules arranged in an up–down bilayer packing motif. The dimeric capsules are slightly offset relative to one another, and each dimeric capsule has an estimated free volume of approximately 235 Å^3 (Supporting Information). Our previous studies on a low-density polymorph of **1** and related calix[4]arene derivatives, obtained by vacuum sublimation at 280 °C, show absorption of various gases under ambient temperature and sub-ambient pressure.[6a,b,12] We also showed that immersion of this polymorph in liquid vinyl bromide for 15 minutes results in a single-crystal to single-crystal phase transition in which vinyl bromide diffuses through the crystal. The phase transition is characterized by an approximately 6 Å lateral shift of the bilayers relative to one another to allow guest diffusion and to achieve the thermodynamically most stable form.[6a] Unlike conventional porous materials that take up and release guest molecules, no channels are found in **1**. However, gas molecules diffuse through the seemingly nonporous lattice without disrupting the arrangement of the host molecules. To rationalize the occurrence of gas sorption, it is presumed that the upper-rim *tert*-butyl groups of the calixarenes play a critical role in gas uptake. In the solid state, the hydroxy groups at the lower rim of the calixarene have well-defined thermal ellipsoids and appear to be rigid, while the *tert*-butyl groups of the upper rim may rotate about the C(ar)−C(sp^3) bond, as evidenced by crystallographic disorder. The cooperative rotation of the *tert*-butyl groups would allow the gas molecules to diffuse through the crystals.[13,16]

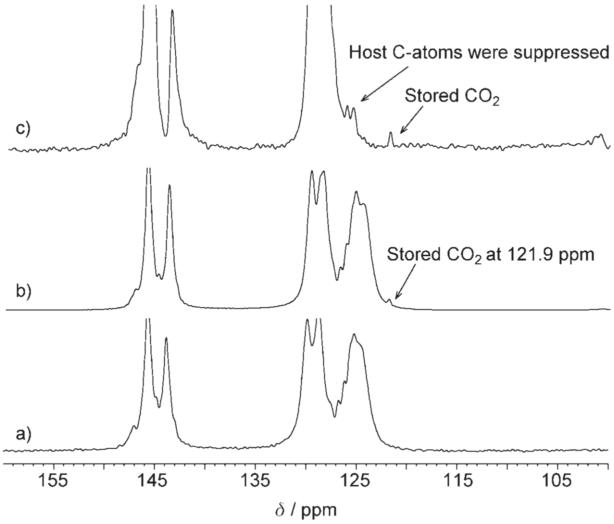

Figure 4. a) Solid-state NMR spectrum of sample **1**. For clarity, only part of the spectrum is shown. b) With stored CO$_2$ which give rise to the signal at $\delta = 121.9$ ppm. c) After host carbon atoms are suppressed using non-quaternary suppression.

In conclusion, although metal–organic frameworks have been shown to facilitate the concentration of acetylene well beyond its normal safe limit, we have now shown that low-density organic materials can also be exploited as promising substrates for acetylene storage.

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[1] Special issue on Hydrogen Economy: *Science* **2004**, *305*, 957, and other articles in this issue.

[2] V. C. Menon, S. Komarneni, *J. Porous Mater.* **1998**, *5*, 43.

[3] a) D. W. Breck, *Zeolite Molecular Sieves: Structure, Chemistry, and Use*, Wiley, New York, **1974**; b) A. Corma, *Chem. Rev.* **1997**, *97*, 2373.

[4] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, M. J. Heben, *Nature* **1997**, *386*, 377.

[5] a) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705; b) S. Kitagawa, R. Kitaura, S.-I. Noro, *Angew. Chem.* **2004**, *116*, 2388; *Angew. Chem. Int. Ed.* **2004**, *43*, 2334.

[6] a) J. L. Atwood, L. J. Barbour, A. Jerga, B. L. Schottel, *Science* **2002**, *298*, 1000; b) J. L. Atwood, L. J. Barbour, A. Jerga, *Angew. Chem.* **2004**, *116*, 3008; *Angew. Chem. Int. Ed.* **2004**, *43*, 2948; c) P. K. Thallapally, G. O. Lloyd, J. L. Atwood, L. J. Barbour, *Angew. Chem.* **2005**, *117*, 3916; *Angew. Chem. Int. Ed.* **2005**, *44*, 3848; d) P. K. Thallapally, G. O. Lloyd, T. B. Wirsig, M. W. Bredenkamp, J. L. Atwood, L. J. Barbour, *Chem. Commun.* **2005**, 5272; e) J. A. Riddle, J. C. Bollinger, D. Lee, *Angew. Chem.* **2005**, *117*, 6847; *Angew. Chem. Int. Ed.* **2005**, *44*, 6689; f) L. Dobrzańska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour, *J. Am. Chem. Soc.* **2006**, *128*, 698.

[7] "National Hydrogen Energy Roadmap", United States Department of Energy, results from the National Hydrogen Energy Roadmap Workshop, Washington DC, April 2–3, **2003**.

[8] a) P. J. Stang, F. Diederich, *Modern Acetylene Chemistry*, VCH, New York, **1995**; b) J. C. W. Chien, *Polyacetylene: Chemistry, Physics, and Material Science*, Academic Press, New York, **1984**.

[9] We note that the current method of storing acetylene involves dissolution of the gas in acetone.

[10] R. Matsuda, R. Kitaura, S. Kitagawa, Y. Kubota, R. V. Belosludov, T. C. Kobayashi, H. Sakamoto, T. Chiba, M. Takata, Y. Kawazoe, Y. Mita, *Nature* **2005**, *436*, 238.

[11] a) J. L. Atwood, L. J. Barbour, A. Jerga, *Chem. Commun.* **2002**, 2952; b) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.* **2005**, *117*, 1850; *Angew. Chem. Int. Ed.* **2005**, *44*, 1816; c) C. Tedesco, I. Immediata, L. Gregoli, L. Viragilano, A. Immizi, P. Neri, *CrystEngComm* **2005**, *35*, 449; d) L. J. Barbour, *Chem. Commun.* **2006**, 1163.

[12] J. L. Atwood, L. J. Barbour, A. Jerga, *Science* **2002**, *296*, 2367.

[13] J. L. Atwood, L. J. Barbour, P. K. Thallapally, T. B. Wirsig, *Chem. Commun.* **2005**, 51.

[14] N. D. Lazo, J. L. White, E. J. Munson, M. Lambregts, J. F. Haw, *J. Am. Chem. Soc.* **1990**, *112*, 1990.

[15] ^{13}C MAS NMR spectra were recorded at 7.04 T static magnetic field on a Bruker Avance 300 spectrometer at 75.5 MHz at a spinning speed of 15 kHz obtained with 7 mm zirconia rotors (see Supporting Information).

[16] J. L. Atwood, L. J. Barbour, G. O. Lloyd, P. K. Thallapally, *Chem. Commun.* **2004**, 922.