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Comparison of porous and nonporous materials for methane storage†‡§

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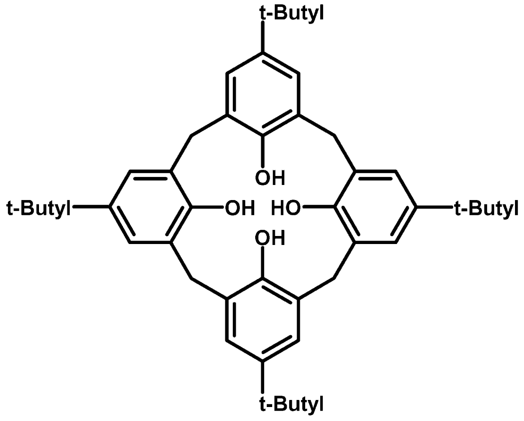
Sublimed, low-density *p-tert*-butylcalix[4]arene absorbs methane more readily at room temperature and 1 atm pressure than do either single wall carbon nanotubes (SWNT) or a comparative porous metal–organic framework (MOF-1).

Materials which store a high gravimetric density of hydrogen or methane are crucial for the development of alternatives to oil-based fuels. Target goals of 7 wt% hydrogen and 35 wt% methane have been set.[1] Several methods have been proposed for on-board hydrogen storage[2] based on compressed gas cylinders, chemisorption, and physical adsorption on porous and nonporous materials, but no ideal method has emerged. Parallel work on methane is being pursued.[3] In this regard physical adsorption of methane on porous materials with large surface area such as metal-organic frameworks and carbon nanotubes has attracted much interest, although limited success has been achieved in storing methane under ambient conditions. In our laboratory, we have focused on 'nonporous' materials for gas storage and separation.[4] In this communication we compare the methane uptake of nonporous, low-density *p-tert*-butylcalix[4]arene, **1**, with a porous metal–organic framework (MOF-1), **2**, and with single walled carbon nanotubes (SWNT), **3**, at room temperature and 1 atm pressure (Scheme 1).

The low density polymorph of **1** obtained at 280 °C under reduced pressure shows that the calixarene molecules are arranged in an up–down fashion to form skewed capsules, each with an estimated free volume of 235 Å^3 (Fig. 1). We have previously shown that the low-density polymorph of **1** absorbs N_2, O_2, CO and CO_2 under ambient conditions.[5] This polymorph has also been used to separate the hydrogen from a mixture of hydrogen and carbon dioxide.[5] Further, immersion of crystals of the low-density polymorph in liquid vinyl bromide results in a single-crystal to single-crystal phase transformation in which vinyl bromide diffuses completely through the crystal, filling each calixarene cavity and effecting the transformation from the monoclinic crystal system to the tetragonal one.[6]

In order to compare the gas sorption properties of **1–3** we prepared **2** using the literature procedure.[7] Heating a diethylformamide solution containing 1,4-benzenedicarboxylate and zinc nitrate hexahydrate for 24 h afforded the crystalline metal–organic framework **2**.[8] The crystal structure of **2** shows that the oxide-centered Zn_4O tetrahedron is edge-bridged by six carboxylates to give an octahedral arrangement, which reticulates into a three dimensional cubic network after removal of the solvent guests (Fig. 1). SWNT's were obtained from Carbon Nanotechnologies Inc. This material was converted into a gel in benzene and then freeze-dried to remove the benzene to give guest-free **3**. The first reports on gas sorption by MOF's claimed 4.5 wt% of H_2 (77 K and pressure of 1 atm) and 135 cm^3 (STP)/cm^3 of CH_4 (room temperature and 34 atm pressure). These sorption values have since been revised to 1.5 wt% of H_2 at same conditions. There have also been reports that SWNT's store 8.0 wt% of H_2 (77 K and pressure of 1 atm) but recent studies have revised the value down to 1 wt%.[9]

Sorption isotherms were recorded volumetrically on **1–3** using 80 mg of sample in each case. The sample of **1** (or **2** or **3**) was placed in the pressure chamber (V = 10.9 cm^3), and the chamber was evacuated for two hours to remove any trace of gas trapped in the host lattice. Fig. 2 presents the absorption isotherms of **1–3** in which methane was introduced with an initial pressure of 1 atm. The pressure in the sample chamber decreased with time and equilibrium was established after 4 h for the sample of **1**. At this pressure the molar ratio of the calixarene to methane was calculated to be 0.14 : 1. This result



Scheme 1

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† Dedicated to Professor George Gokel on the occasion of his 60th birthday.

‡ The HTML version of this article has been enhanced with colour images.

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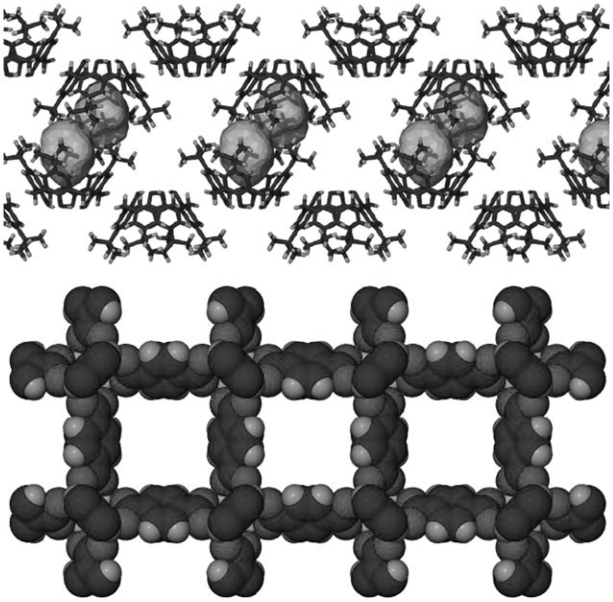

Fig. 1 X-Seed[13] representation of a bilayer packing of calixarene molecules in **1** (Top). The surface was generated using Connolly Molecular Surface.[14] Space fill representation of porous metal–organic frame work for clarity solvent molecules are removed (Bottom).

indicates 28% of the dimeric capsules are filled with methane at 1 atm pressure, a value which agrees well with that previously reported.[10] It has been shown that **1** is capable of accommodating two methane molecules within each dimeric capsule.[10]

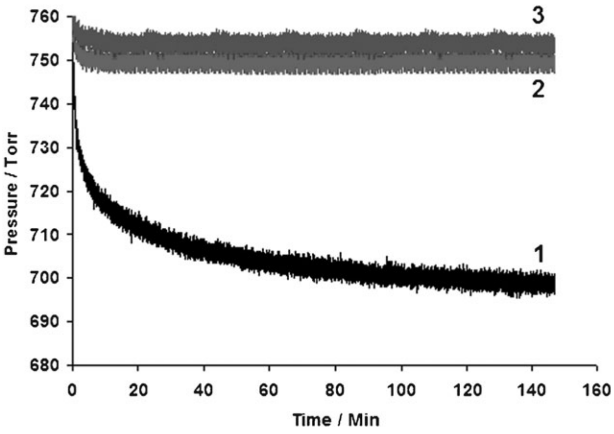

Fig. 2 Methane isotherms of samples **1–3** at room temperature.

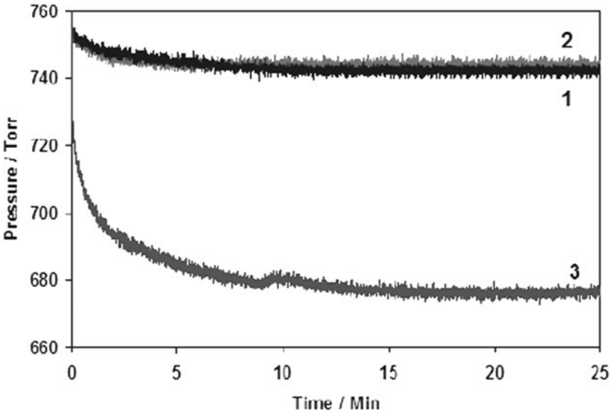

Fig. 3 Low temperature isotherms of methane in samples **1–3**.

Samples of **2** and **3** were activated by removing the guest molecules from the host lattice under reduced pressure with heating (sample **2** and **3** were evacuated at 150 °C and 60 °C for over 24 h under vacuum, respectively). The X-ray powder diffraction patterns of sample **2** before and after removing the solvent are identical, indicating that the MOF-1 framework is stable upon desolvation (see supplementary information, Fig. S1, S2 and S3). Methane was introduced into the chamber containing samples **2** and, subsequently, **3** with an initial pressure of 1 atm. For **2** and for **3**, no significant uptake of methane was observed (Fig. 2). In order to further investigate samples **1**, **2**, and **3** with regard to methane sorption, the sample chamber was cooled to -70 °C and methane was again introduced at a pressure of 1 atm. Under these conditions, methane uptake by samples **1** and **2** was marginal, but significant amount of methane uptake was observed in sample **3** (Fig. 3).

At room temperature the uptake of methane by nonporous material **1** is high compared to that of porous metal-organic framework MOF-1 (surface area $\sim$4000 $m^2\ g^{-1}$) and SWNT's ($\sim$2000 $m^2\ g^{-1}$). It appears that large cavities with high surface area are not required to enhance the storage capacity and, In fact, the larger cavities lead to a decrease in the strength of the interaction between the adsorbent surface and the methane.[11]

Unlike conventional porous materials such as **2** and **3**, which uptake and release guest molecules, no channels or cavities are found in **1**. However, gas molecules diffuse through the seemingly nonporous lattice without disrupting the arrangement of the host molecules. As described earlier, at room temperature the aromatic and hydroxyl groups at the lower rim of the calixarene 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. We speculate that the cooperative rotation of the *tert*-butyl groups allows the gas molecules in **1** to diffuse through the crystals. The 'nonporous' nature of **1** was further supported by measuring the dinitrogen adsorption isotherms at 77 K and 1 atm pressure. The low BET surface area of 15 $m^2\ g^{-1}$ for **1** indicates that **1** is nonporous at 77 K (see supplementary information, Fig. S4). X-Ray crystallographic results on the structure of **1** at 295 K show that all *tert*-butyl groups are disordered, while at 195 K only one *tert*-butyl group is disordered. Thus, both the X-ray crystallographic work and BET measurements are consistent with **1** being nonporous at 77 K, and with the porosity of **1** at room temperature being linked to the motion of the *tert*-butyl groups which guard the cavities.

Several attempts to collect single crystal X-ray diffraction data on **1** with methane revealed only diffuse electron density.

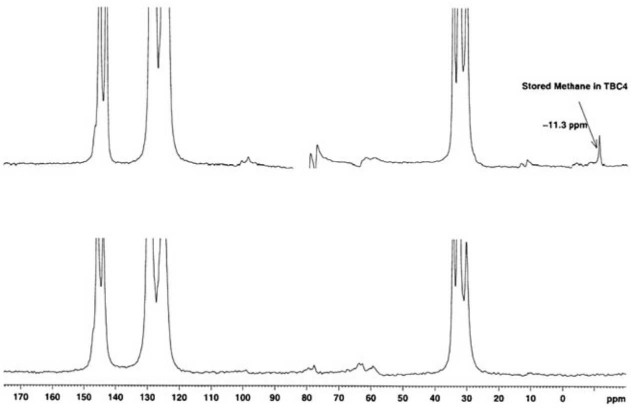

Fig. 4 ^{13}C MAS NMR of sample **1** (Bottom). The sharp signal at −11.3 ppm indicates the stored methane in **1** (Top).

However, solid-state NMR techniques¶ proved effective in the detection of the absorbed methane in calixarene cavity **1** under ambient conditions. Fig. 4 shows a comparison of the solid-state NMR spectra of pure host and host with absorbed methane. The ^{13}C resonance of the guest methane is found at −11.3 ppm. A few reports of methane stored in zeolites and porous cyclotriophosphazene derivatives have appeared in the literature, with ^{13}C chemical shifts ranging from −5 to −9 ppm. The exceptional upfield shift in nonporous **1** (−11.3 ppm) may be due to stronger binding of the methane in **1** compared to the previous reports for binding in porous materials.[12]

The results presented herein emphasize three important points. First, large pores do not necessarily lead to sorption of gases such as methane. The tight fit imposed by calixarene **1** provides van der Waals stabilization for methane, even at room temperature. Second, nonporous organic solid **1** exhibits a thermal window for methane sorption. At −70 °C, the thermal motion of the host molecules (most important for the *tert*-butyl groups guarding the entrance to the cavities) is reduced and the crystals are nonporous with regard to methane sorption. Third, while the details of the mechanism for the evolution of porosity in seemingly nonporous organic solids such as **1** is not yet known, it is clear that any such mechanism must involve communication among host molecules in the crystalline lattice, leading to transport of small molecules from one cavity to another and, ultimately, throughout the crystalline solid.[4,5,10,15]

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¶ Solid state NMR was done on a Bruker DRX300 wide bore spectrometer equipped with a 7 mm CP-MAS probe. The operating frequencies are 300.13213 (^{1}H) and 75.47359 (^{13}C). About 200 mg of finely ground powder was used to fully pack a 7 mm Zirconia rotor. For all the samples proton decoupled ^{13}C CP-MAS (Cross Polarization1 with Magic Angle Spinning) was performed at spinning rate of 5 KHz. TOSS (Total Suppression of Sidebands) was applied to remove the sidebands caused by spinning. The total time for data collection ranges from a few hours to overnight. The spectra were collected with 2K data points with a 34 ms acquisition time and 2 s of relaxation delay. Data was zero-filled to 8 K and a 5 Hz line-broadening was also applied. The external chemical shift reference was CO carbon of glycine at 176.03 PPM.

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