DOI: 10.1002/chem.200903218

Methane Adsorption in a Supramolecular Organic Zeolite

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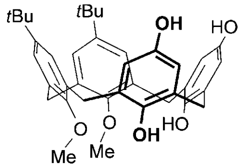
Dedicated to Professor A. Immirzi on the occasion of his 70th birthday

Gas storage in solids is an increasingly important research area with applications in the field of energy, environment, biology and medicine.[1] Because it concerns the adsorption of methane, the main component of natural gas fuels, the storage target for any solid to be effective in energy applications and compete with the compressed form is approximately 35 wt % or 180 v/v. Several different types of porous materials such as carbon materials,[2] zeolites,[3] silica gels,[4] MOFs[5] and polymers[6] have been recently examined in addition to organic crystalline microporous solids[7] and nonporous ones,[8] but no ideal candidates have emerged so far. In this paper we wish to report on the methane adsorption properties of a new microporous organic zeolite based on 1,2-dimethoxy-*p*-*tert*-butylcalix[4]dihydroquinone (Scheme 1), which has been recently characterised by our research group.[9]



Scheme 1. 1,2-Dimethoxy-*p*-*tert*-butylcalix[4]dihydroquinone.

The crystalline solid has a cubic structure (*a* = 36.412(4) Å) with networked channels and hydrophobic cages. The channels have minimum and maximum diameter of 3.9 and 8.5 Å, respectively, excluding van der Waals radii, and they are filled with easily removable water molecules. The hydrophobic cages show a gate diameter of 2.2 Å and can reach a maximum diameter of 11.2 Å (excluding van der Waals radii), and the estimated cage volume is about 1000 Å^3. Interestingly, the supramolecular framework is also preserved after the removal of channel water molecules.[10] Previous studies showed that the BET surface area corresponds to 230 m^2 g^{-1} (N_2 at 77 K) and that carbon dioxide can be absorbed at room temperature inside its nanochannels with high selectivity with respect to H_2 gas,[9] encouraging further studies towards methane adsorption.

Methane adsorption measurements were performed by using a home-made volumetric system.[11] Sorption isotherms have been carried out at 298, 278 and 203 K. Data have been collected at initial pressures between 0.5 and 3 atm. The adsorption isotherm at 203 K is reported in Figure 1, (see the Supporting Information for adsorption isotherms at 298 and 278 K). At 1 atm and 298 K our compound adsorbs 0.11 methane molecules for each calixarene molecule. For comparison, *p*-*tert*-butylcalix[4]arene[8b] adsorbs 0.14 methane molecules for each calixarene molecule under the same conditions. Under the mild conditions of ambient pressure and temperature our sample shows an efficiency for methane storage of 0.29 wt %, whereas in the case of CO_2 molecules the value was 0.5 wt %.[9]

The adsorption isotherm at 203 K is not of type I. The adsorption step at 2 atm could be interpreted by considering that at first the methane molecules enter the channels, interacting with the most favourite sites, and then upon increasing the pressure the channels are progressively filled.[5d]

Note that there are 90 methane molecules in the unit cell at 3 atm pressure, which approximately corresponds to a 1:2 ratio between calixarene molecules and methane molecules.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200903218.

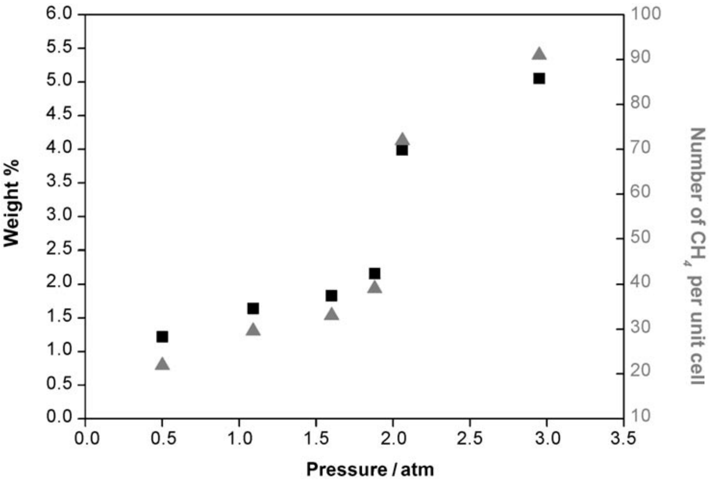

Figure 1. Adsorption isotherm for CH_4 at 203 K. The wt % is reported on the left vertical axis (■) and the number of CH_4 molecules per unit cell on the right vertical axis (▲).

Upon increasing the pressure and lowering the temperature a huge increase of methane uptake is determined: a value of 5 wt % of methane can be adsorbed at 203 K and 3 atm (Figure 1 and Figure S3 in the Supporting Information).

High-resolution X-ray powder diffraction measurements (HR-XRPD) have been devised to characterise the structural modification upon guest adsorption. In situ studies have been performed at the ID31 beamline at the European Synchrotron Radiation Facility (Grenoble, France) by using a gas handling system.[12] In Figure 2 the corresponding HR-XRPD profiles are reported. As can be seen from the inset of Figure 2, despite the fact that the temperature is decreased, the peak positions do not correspondingly shift. Measurements have also been performed on an evacuated sample (the corresponding HR-XRPD profiles are reported in Figure S4 in the Supporting Information). For both the methane-loaded and the evacuated samples, the cell parameters have been evaluated by Le Bail refinement[13] and the results are reported in Figure 3 and Table S1 (see the Supporting Information). Although the evacuated sample shows a progressive decreasing of the lattice parameter with decreasing temperature, the methane-loaded sample shows an increase down to 223 K and then a decrease. This indicates that methane is able to enter into the channels, and this process is favoured by decreasing the temperature down to 223 K.

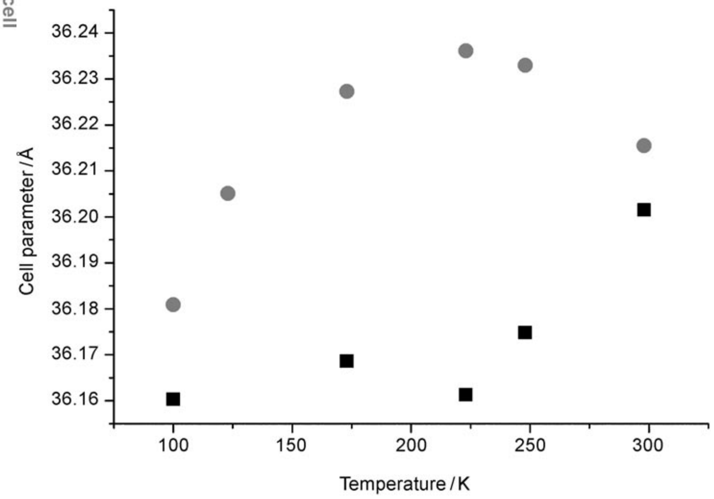

Figure 3. Cell parameter versus temperature for an evacuated sample (■) and a methane-loaded sample (●).

HR-XRPD data at 223 K and 2 atm have been used to locate the methane molecules inside the host structure. The guest adsorption does not involve any change in the crystal system and space group, and the refined lattice parameter is 36.2436(4) Å. To locate the methane molecules inside the host structure we used 1) the analysis of difference Fourier maps, 2) energy calculations[14] and 3) XRPD-based simulated annealing procedures.[15]

Difference Fourier maps, considering only the apo-host as a structural model, showed that the centre of the channels and cages are not occupied by any molecule, whereas higher electronic density can be detected near the wall of the channels. But the quality of the maps does not allow any conclusive results to be drawn (see Figure S6 in the Supporting Information).

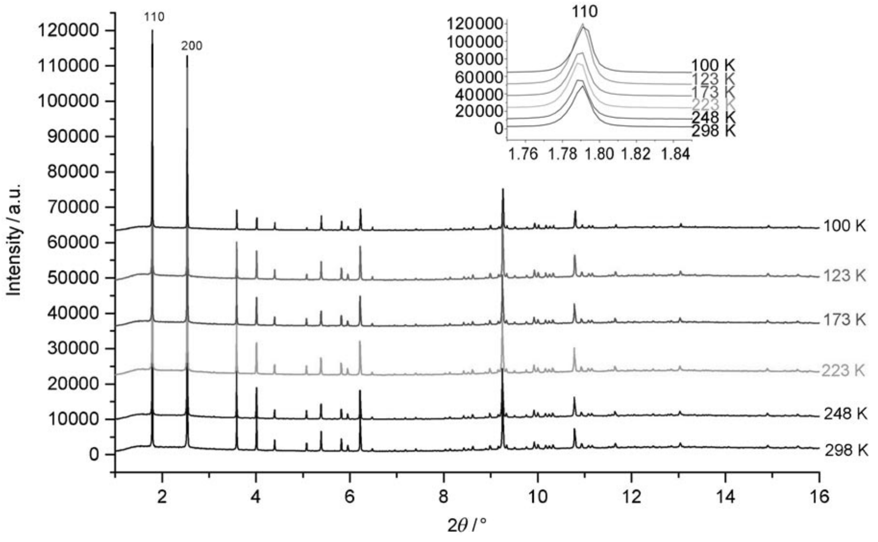

Figure 2. HR-XRPD profiles for a methane-loaded sample as collected in the temperature range 298–100 K. The inset shows the 110 reflection.

The configuration space of the host–guest system has been searched by applying a Monte Carlo method to find the guest preferential sites, assuming that the ratio between calixarene molecules and methane molecules is 1:2 as suggested by volumetric adsorption measurements, fixing the host framework, and considering $P1$ symmetry for the guest molecules. The list of preferential sites has been searched to find symmetry-related positions along the $Pn\bar{3}n$ space group, obtaining two possible sites (molecule A at 0.7553, 0.2957, 0.0768; molecule B at 0.7386, 0.2513, 0.3356).

Finally the host–guest structure has been solved by simulated annealing by using the program TOPAS[16] (R_{wp} = 6.4 %). The asymmetric unit contains two crystallographically independent methane molecules located inside the channels of the host structure approximately at the same positions indicated by the energy-driven simulation. The structure has been refined by the Rietveld method to R_{wp} = 5.3 %.[16]

The host structure does not show any significant alteration with respect to the previous model,[10] confirming that the material behaves as a supramolecular zeolite. The methane molecules are located inside the channels (Figure 4). One methane molecule (light grey) interacts directly through a CH–π bond[17] with one of the hydroquinone rings of the host framework (C_{Ar}–C_{CH4} 3.23 Å) and with another symmetry-equivalent methane molecule (C_{CH4}–C_{CH4} 3.68 Å) forming a ring of eight methane and eight calixarene molecules (Figure 4b). The other methane molecules (dark grey) are located in the middle of this ring and do not feature any specific interaction with the wall of the channels, which explains the presence of positional disorder at this site. Analogous CH–π interactions have been observed in microporous crystals of tris(*o*-phenylenedioxy)cyclotriphosphazene and methane by using solid-state NMR spectroscopy.[7a] With this structural model it is possible to calculate the remaining void volume[18] that corresponds to 1944 Å^3. Considering that approximately 1000 Å^3 must be attributed to cages, we can confirm that there is still space in the open channel network. In conclusion, we have shown that a calixarene-based solid behaves as a supramolecular zeolite by adsorbing a significant amount of methane inside its nanochannels, and CH–π bonds are responsible for the host–guest interactions.

Acknowledgements

We acknowledge Dr. Mark Johnson (ILL) and Dr. Irene Margiolaki (ESRF) for useful discussions, and Mr. Drew Fowler and Mr. Jian Tian (University of Missouri-Columbia) for their experimental support. We are grateful to ESRF for providing access to the ID31 beamline (Proposal No. CH-2388 and CH-2712) and to the beamline staff for experimental support. Italian MIUR is acknowledged for financial support.

Keywords: calixarenes · in situ powder XRD · methane adsorption · organic zeolites · pi interactions

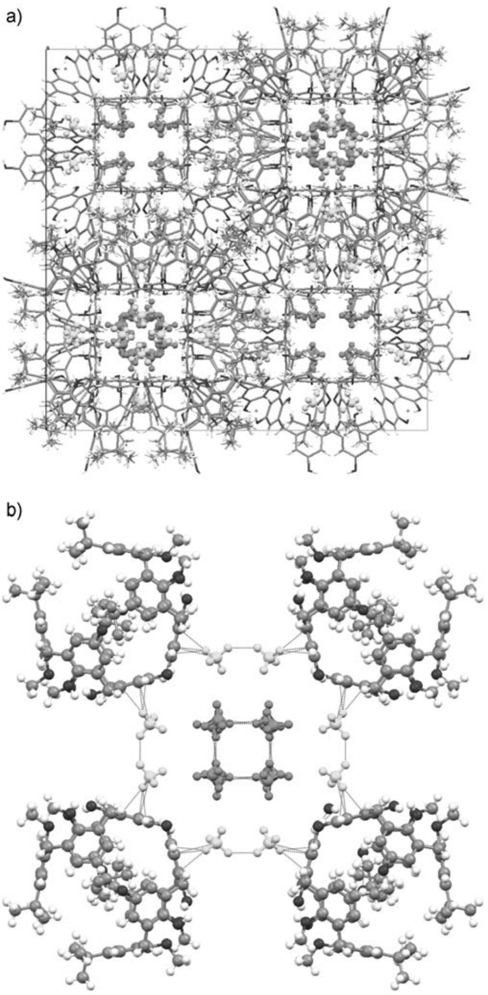

Figure 4. a) Space-filling model of the crystal packing along the *a* axis. Methane molecules are included in the host channels. b) Detailed view of the host–guest interactions in the upper-left corner of the cell. Methane molecules are located at the same height (around $^1/_4$ *a*), forming two rings perpendicular to the *a* axis.

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Received: November 24, 2009