

Experiment Report Form



Experiment title: Gas storage properties of a supramolecular organic zeolite	Experiment number: CH-2388	
Beamline: ID31	Date of experiment: from: 24/01/2008 to: 28/01/2008	Date of report: 28/02/2008
Shifts: 12	Local contact(s): Michela Brunelli	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Consiglia Tedesco*, Department of Chemistry, University of Salerno, Italy

Loredana Erra*, Department of Chemistry, University of Salerno, Italy

Valeria Cipolletti*, Department of Chemistry, University of Salerno, Italy

Carmine Gaeta, Department of Chemistry, University of Salerno, Italy

Placido Neri, Department of Chemistry, University of Salerno, Italy

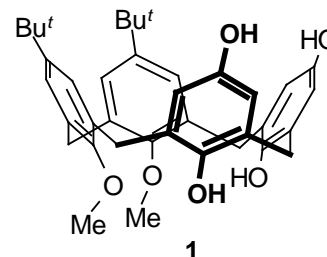
Report:

At the Dept. of Chemistry of the University of Salerno we prepared and characterized a new crystalline solid based on *p*-Bu^t-calix[4]dihydroquinone **1** revealing the simultaneous existence of water channels and very large hydrophobic cavities (988 Å³). The compound has a cubic structure ($a=36.412(4)$ Å) with 48 calixarene molecules and 155 water molecules in the unit cell.

Interestingly the supramolecular framework is preserved also after the removal of channel water molecules, as shown by thermogravimetric and X-ray powder diffraction (XRPD) measurements.^[1]

The simultaneous presence of networked channels, filled with easily removable water, and isolated hydrophobic cavities may prelude to potential applications of nanotechnological interest.^[2]

High resolution XRPD measurements have been devised to characterize the guest uptake and release properties of this new material using several gases under different temperature and pressure conditions. To probe the size and molecular affinity of the host channels, gases with different size and polarity have been used.



Experimental details

High resolution XRPD measurements have been performed at ID31 beamline (wavelength 0.80314(4) Å) using a rotating glass capillary cell with gas handling system to allow in situ studies by powder X-ray diffraction. The cell can be used to follow solid-state chemical reactions under vacuum or at gas pressures up to around $7 \cdot 10^5$ Pa.^[3]

1.0 mm Lindemann capillaries were filled under inert atmosphere with anhydrous powder samples and then mounted on the gas cell. Outside the experimental hutch samples were preliminary evacuated using a turbomolecular pump (10^{-5} mbar) and then loaded with the appropriate gas for 15-30 minutes.

The cell was disconnected from the gas supply and mounted on a goniometer head to perform the X-ray diffraction measurements. A liquid nitrogen cryostat (Oxford Cryostream) has been used to perform the measurements under controlled temperature.

A list of the used gases and conditions is reported in the following table:

Gas	Pressure (atm)	Temperature range(K)
CO ₂	2	298-223
C ₂ H ₂	0.5	298-173
CH ₄	2	298-100
Xe	2	298-123

For comparison measurements in the same temperature range have been performed also on a non-anhydrous sample and on an evacuated sample.

9 shifts were allocated in the period 29/06/2007-02/07/2007, unfortunately technical problems did not allow to perform any measurement on gas loaded samples and 12 shifts were re-allocated in the period 24/01/2008-28/01/2008.

Results

Most promising results have been obtained for samples loaded with CH₄, the corresponding X-ray diffraction patterns are reported in Fig. 1. As it is evident from the inset of Fig. 1, in spite of the fact that temperature is decreased peak positions do not correspondingly shift.

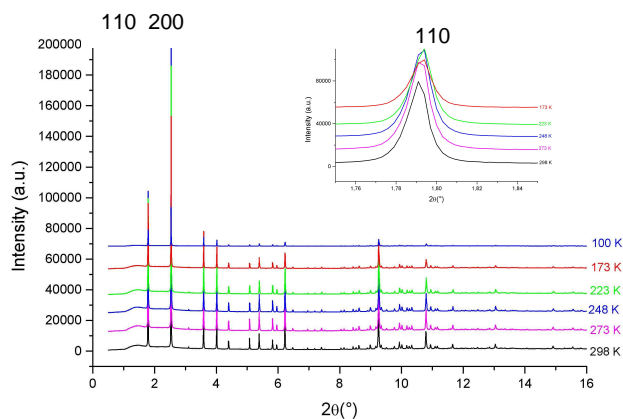
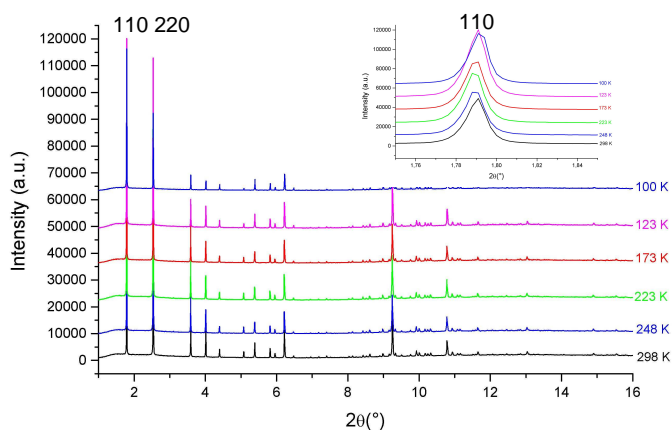


Fig. 1 X-ray diffraction patterns for CH₄ loaded sample. **Fig. 2** X-ray diffraction patterns for an evacuated sample.

For comparison measurements have been performed on an evacuated sample and the corresponding diffraction patterns are reported in Fig. 2.

Both for the methane loaded and evacuated samples the cell parameters have been evaluated by Le Bail refinement and the results are listed in Table 1. Fig. 4 shows that in the case of methane loaded samples the cell parameter is always greater than the corresponding evacuated sample at a given temperature.

While the evacuated sample shows a progressive decreasing of the lattice parameter with decreasing the temperature, the methane loaded sample shows an increase down to 248K and then a decrease. This probably indicates that methane is able to enter into the channels and this process is favoured by decreasing the temperature down to 248 K.

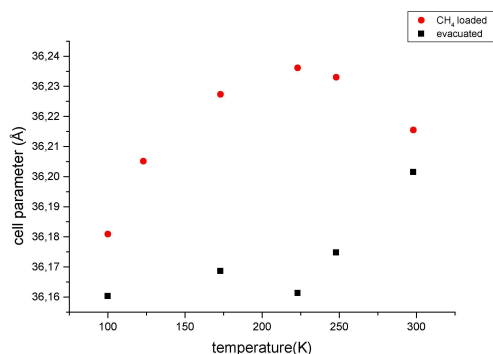


Table 1. Le Bail refinement results.

Temp. (K)	CH ₄ loaded			evacuated		
	%Rp fitted	%wRp fitted	<i>a</i> (Å)	%Rp fitted	%wRp fitted	<i>a</i> (Å)
298	3.77	5.10	36.2155(2)	8.22	11.68	36.2015
248	3.24	4.44	36.2330(3)	9.65	14.34	36.1748(4)
223	3.58	4.86	36.2361(2)	4.34	6.30	36.1613(4)
173	3.39	4.55	36.2273(2)	4.89	6.92	36.1686(3)
123	3.01	3.93	36.2051	-	-	-
100	4.31	4.50	36.1809(2)	7.28	8.95	36.1603(3)

Fig. 3 Cell parameter vs. temperature for an evacuated sample (■) and a CH₄ loaded sample (●).

As for CO₂, C₂H₂ and Xe the results are less significative, because after loading the gas the powder resulted not to be compact anymore. This is probably due to a surface tension effect, probably indicating that the gas is not entering into the pores of the calixarene framework. Probably pressure or time required for loading the gas should be increased.

References

- [1] C. Tedesco, I. Immediata, L. Gregoli, L. Vitagliano, A. Immirzi, P. Neri, *CrystEngComm* 2005, 7, 449-453.
- [2] P. K. Thallapally, B.P. McGrail, J.L. Atwood, C. Gaeta, C. Tedesco, P. Neri, *Chem. Mater.* **2007**, 19, 3355-57.
- [3] M. Brunelli, A. Fitch *J. Synchrotron Rad.* **2003**, 10, 337-339.