Interaction Of Hydrogen With MOF-5

Silvia Bordiga[1], Jenny G. Vitillo[1], Gabriele Ricchiardi[1], Laura Regli[1], Donato Cocina[1], Adriano Zecchina[1*], Bjørnar Arstad[2§], Morten Bjørgen[2], Jasmina Hafizovic[2] and Karl Petter Lillerud[2]

[1.]*Dipartimento di Chimica IFM and NIS Centre of Excellence, Via P. Giuria 7, I-10125 Torino, Italy.*
[2.] *Department of Chemistry, University of Oslo, P.O. Box 1033, N-0315 Oslo, Norway.*
[§]*Present address: SINTEF Materials and Chemistry, Dept. of Process Technology, N-7465 Trondheim, Norway.*

S1. Structural characterization of the metal-organic framework under study

The structure was determined by single crystal X-ray diffraction using a Siemens Bruker Smart CCD diffractometer. A total of 1310 frames were collected ($\Delta\omega$=0.3^{o}, 30 s per frame), covering one hemisphere of the reciprocal space. Data reduction and empirical absorption correction were carried out using the programs SAINT+[1] and SADABS,[2] respectively. The structure was solved by direct methods and refined using the SHELXTL[3] program package.

Single crystal data has been collected for the sample under study in three different conditions: 1) the crystal kept in the solvent by freezing it in a small droplet of solvent fixed within a nylon loop, 2) the sample dried at 80 °C in air over night, and finally 3) the sample after heating in nitrogen until a stable weight was obtained at 300 °C. The data sets were collected at 105 K and turned out to be very similar. The small observed differences are rationalized for by solvent effects.

When the sample is kept in the solvent the unit cell is cubic (a = 25.900). Upon drying, a small, but significant deviation from the cubic cell (a = 25.64; b=25.97 and c= 26.53) can be observed. This cell deformation reduces the quality of the data drastically; reflections are split, but often not sufficiently pronounced for the integration program (SAINT+) to handle the integration of the double and triple spots. The symmetry is clearly lower than cubic. Refinements in lower symmetry and a detailed structural description are in preparation. Only data from the dried crystals are given in Table S1, S2 and Figure S1 below.

The single-crystal data analysis reported below proves our prepared samples to be MOF-5 (IRMOF-1). Very similar results have been obtained for samples measured after heating to 300 °C in order to remove the solvent from the cavities. As we have performed the measures at low temperature (105 K), solvent molecules in the cavities will be more organized than at room temperature. We therefore observe a stronger contribution from the solvent molecules in the scattered X-ray intensities, compared to the earlier published structure data on MOF-5 which was collected at room temperature[4]. Most of the solvent guest molecules shown in the structure drawing displayed in Figure S1 have occupancies lower than one. The structure is accordingly less packed

than what the figure may give impression of. After heating to 300 °C, there is still some guest species left in the cavities, but the intensity is reduced to only 10% of the filling observed prior to the heat treatment of the sample.

Small changes in symmetry combined with ordering of species in the cavities might change the XRD-powder-pattern to a degree that makes it difficult to recognize the material. This is a phenomenon that is well known from zeolite materials. A series of samples where the crystal size is systematically increased from sub micrometer up to the 0.1 mm (sample used for the single crystal structure elucidation), has been synthesized. Figure S2 shows the XRD-powder-pattern of the sub micrometer material (used in the spectroscopic measurements). The top (a) curve is the measured diffraction pattern, the middle curve (b) is the calculated diffraction patterns without constrains on the intensities (a Pawley refinement), the bottom curve (c) is the powder-pattern calculated from the structure solution presented in Table S2 and Figure S1.

Allowing a small orthorhombic deformation of the cubic cell, we obtain a result which fits perfectly (with no extra peaks) with the experimental diffraction pattern. When the atomic positions from the structure solution (large crystals and 105 K) are added, we observe some deviation in the intensities, but the fit is still very good. The quality of the powder data does not allow a full Rietveld refinement of the structure.

Table S1. Crystal data and structure refinement for MOF-5.

Empirical formula	$Zn_4\ O_{13}\ C_{15}\ N_{3.57}$
Formula weight	699.67
Temperature	105(2) K
Wavelength	0.71073 A
Crystal system, space group	Cubic, Fm(-3)m
Unit cell dimensions	a = 25.652(5) A alpha = 90 deg.
	b = 25.652(5) A beta = 90 deg.
	c = 25.652(5) A gamma = 90 deg.
Volume	16879(6) A^3
Z, Calculated density	28, 1.927 Mg/m^3
Absorption coefficient	3.999 mm^-1
F(000)	9492
Crystal size	0.2 x 0.1 x 0.1 mm
Theta range for data collection	1.37 to 18.92 deg.
Limiting indices	-20<=h<=23, -22<=k<=23, -22<=l<=23
Reflections collected / unique	11979 / 394 [R(int) = 0.2273]
Completeness to theta = 18.92	99.2 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	394 / 0 / 49
Goodness-of-fit on F^2	1.989
Final R indices [I>2sigma(I)]	R1 = 0.1336, wR2 = 0.3861
R indices (all data)	R1 = 0.1394, wR2 = 0.3976
Extinction coefficient	0.0022(9)
Largest diff. peak and hole	1.773 and -0.761 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for MOF-5. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

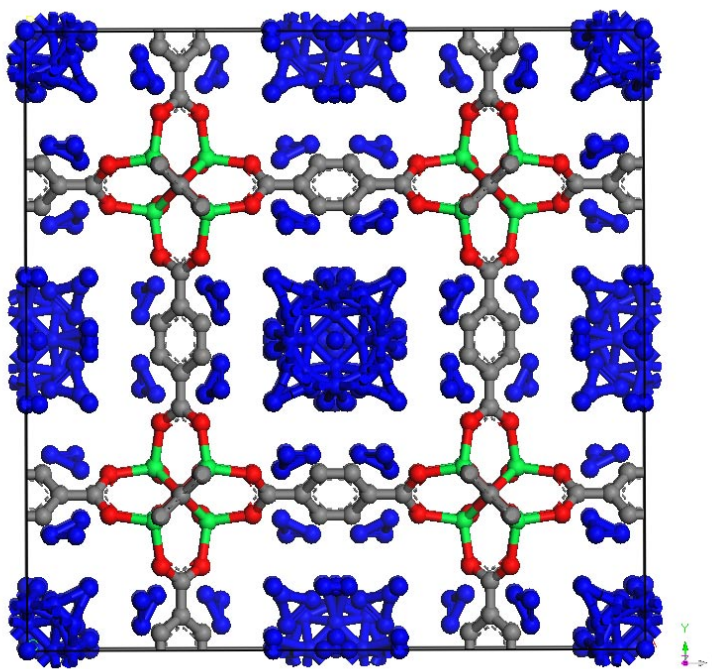|	x	y	z	U(eq)
Zn(1)	2068(1)	2068(1)	2068(1)	31(3)
O(0)	2500	2500	2500	33(9)
O(1)	2175(4)	2175(4)	1343(5)	64(5)
C(1)	2500	2500	1094(10)	71(8)
C(2)	2162(6)	2162(6)	259(8)	64(7)
C(3)	2500	2500	541(9)	48(7)
N(1)	0	0	0	81(17)
N(2)	3987(8)	1013(8)	1013(8)	60(20)
N(3)	1021(9)	4803(11)	0	100(16)
N(4)	510(15)	510(15)	510(15)	230(60)
N(5)	1000(7)	1000(7)	-160(8)	23(14)
N(6)	880(70)	2100(80)	880(70)	400(180)
N(7)	740(50)	430(50)	0	80(100)
N(8)	2170(30)	5800(30)	0	660(100)
N(9)	790(20)	1850(20)	390(30)	180(40)

Figure S1. The MOF-5 lattice refined in cubic symmetry, solvent molecules refined as nitrogen atoms. The solvent molecules have a symmetry much lower than that of the MOF-5 lattice, the N-intensities will therefore not form patterns with chemical information when refined in this symmetry but they resemble a picture of the electron density in the MOF-5 channels.
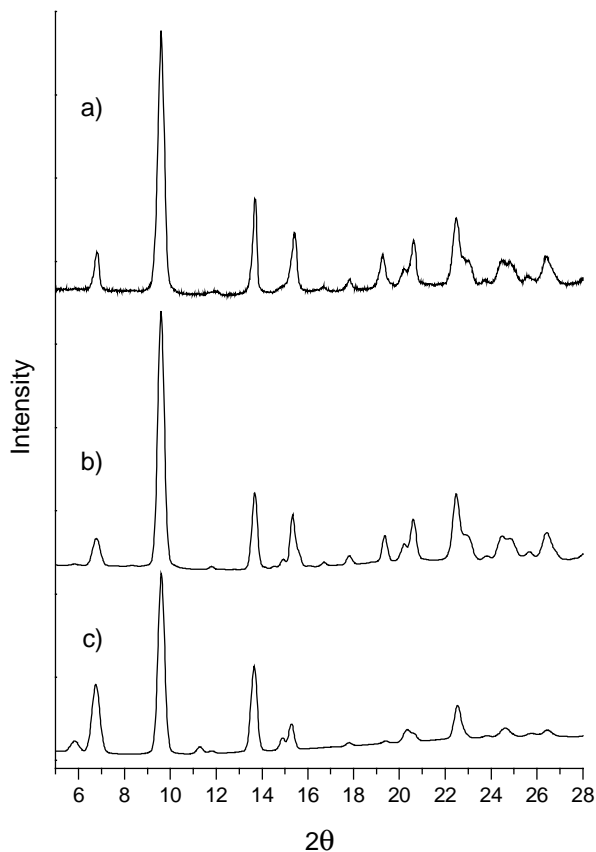
Figure S2. Observed and calculated X-Ray powder diffraction patterns of MOF-5. (a) The diffraction pattern of the sub-micrometer sample used for IR measurements; (b) calculated diffraction pattern without constrains on the intensities (a Pawley refinement); (c) Diffraction-pattern calculated from the structure solution presented in Table S2 and Figure S1.

As already mentioned, a thermal treatment at 300 °C maintains the structure of the original sample and leads to removal of 90% of the solvent present inside the cavities. We do not observe a significant weight change upon a further thermal treatment in the range of sample stability (room temperature to 400 °C).

S2. Volumetric characterization of MOF-5.

Adsorption measurements were performed with a commercial Micromeritics ASAP 2010 sorption analyzer on MOF-5 activated in vacuo at 250 °C. Surface area has been obtained by N_2 adsorption at 77 K; accessible microporous volume has been estimated by the t-plot (Harkins and

Jura thickness equation) of the N_2 adsorption data. The Langmuir surface area was 747 m^2/g and a microporous volume of 0.22 cm^3/g has been obtained. Both results do not agree with those reported in Ref 6, where, in our opinion, the surface area has been overestimated. In fact, for a material with a surface area of more than 3000 m^2/g, a much higher adsorption capacity should be expected.[5] Figure S3 reports the first and second isotherms (volumetric measurements) of hydrogen adsorption performed at 77 K in the 0-0.9 bar range for MOF-5 (black and red curves, respectively). For the sake of comparison, the experimental values obtained by Rowsell et al. (Ref. 6) under the same experimental conditions are also reported in Figure S3 (gray curve).

The final points of the red and black curves (hydrogen uptake at 0.9 bar) agree with what expected on the basis of the linear relationship between the microporous volume and the hydrogen uptake showed by Nijkamp et al. for carbonaceous materials.[5] Conversely, for a material with 1.04 cm^3/g as microporosity, as reported in Ref. 4, an hydrogen uptake of at least 3 mass% should be expected.
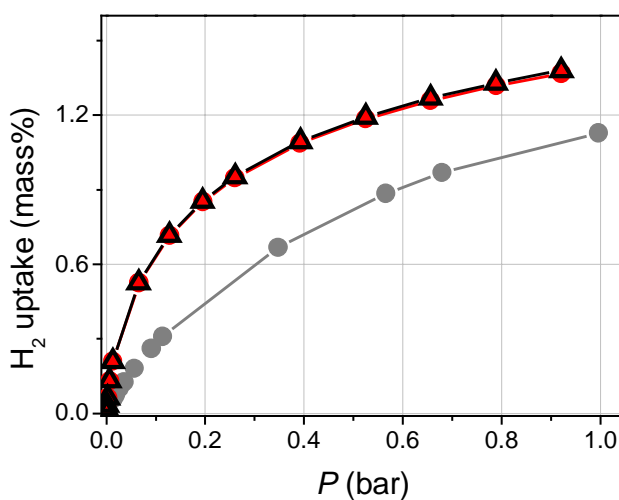
Figure S3. Hydrogen gas sorption isotherms on MOF-5 at 77 K in the 1·10^{-7}-0.92 bar range: first isotherm (**8**); second isotherm (,). Volumetric data reported in Ref. 6 are also shown for comparison (,).

References

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Complete Ref. 20 of the manuscript:

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