Electronic Supporting information (ESI) for

Experimental assessment of physical upper limit for hydrogen storage capacity at 20 K in densified MIL-101 monoliths

Hyunchul Oh [a], Dan Lupu[b], Gabriela Blanita[b] and Michael Hirscher*[a]

[a] Max Planck Institute for Intelligent Systems, Heisenbergstrasse 3, D-70569 Stuttgart, Germany

[b] National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Str., 400293 Cluj-Napoca, Romania

*corresponding author: Dr. M. Hirscher (hirscher@is.mpg.de)

Experimental

1.1 *Materials*

MIL-101 was prepared and purified as described in detail in [1].

1.2 *Preparation of monoliths*

Monoliths of 3.67 mm diameter were prepared from a known mass of MIL-101 powder in a cylindrical die of 3.67 mm, compressed with a manual hydraulic press by fine adjustment of the anvil height to control the penetrating depth of the stainless steel punch. The envelope densities of the pellets were calculated from their degassed mass measured after the p-c-T experiments, when all the water content is lost during the activation 20 h at 220 °C in vacuum down to a residual pressure of $2\text{x}10^{-5}$ mbar.

1.3 *Characterization*

X-ray diffraction patterns*:* The powder XRD analyses were performed with a Bruker D8 advanced diffractometer with Cu Kα radiation (40 kV, 40 mA).

Low-pressure N_2 BET measurements: Specific surface area measurements at 77 K were carried out using Quantachrome Autosorp-1 MP instrument with N_2 gas using optimized protocols, the MIL-101 compressed pellet and powder samples were priorly degassed at 490 K for overnight. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. Pressure range for BET calculation were chosen according to Rouquerol's suggestions[2]. (see details in supporting information)

Cryogenic low-pressure high-resolution H_2 BET measurements*:* The hydrogen adsorption isotherms of the MIL-101 compressed pellet and powder samples at 19.5 K were measured with laboratory-designed volumetric adsorption equipment with temperature controlled cryostat and is described in details elsewhere [3]. Around 23 mg of pellet and powder were activated under ultra-high vacuum at 420 K for overnight prior to each measurement. For the laboratory-designed cryostat, the temperature control was calibrated by measuring the liquefaction pressure for hydrogen and nitrogen in the empty sample chamber at various temperatures. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method, selecting the p/p_0 range according to Rouquerol's suggestions[2] (see details in supporting information). The specific pore volume (SPV) was calculated according to Gurvich's rule [4]

$$\text{SPV} = n_{max} / \rho_{lq}$$

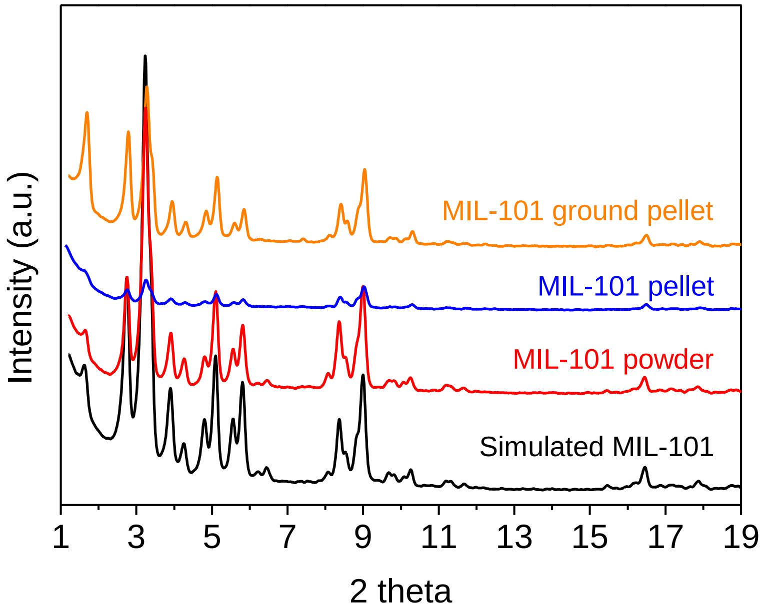
where n_{max} is the maximum uptake per material mass before liquefaction and ρ_{lq} is the density of the liquid.

The adsorbed amount is reported in wt% which is defined as mass of hydrogen m_{ads} (absolute uptake) per mass of the system, which consists of the sample mass m_S and the adsorbed hydrogen.

$$\text{Hydrogen uptake (wt\%)} = m_{ads} / (m_s + m_{ads}) * 100$$

Sample characterization

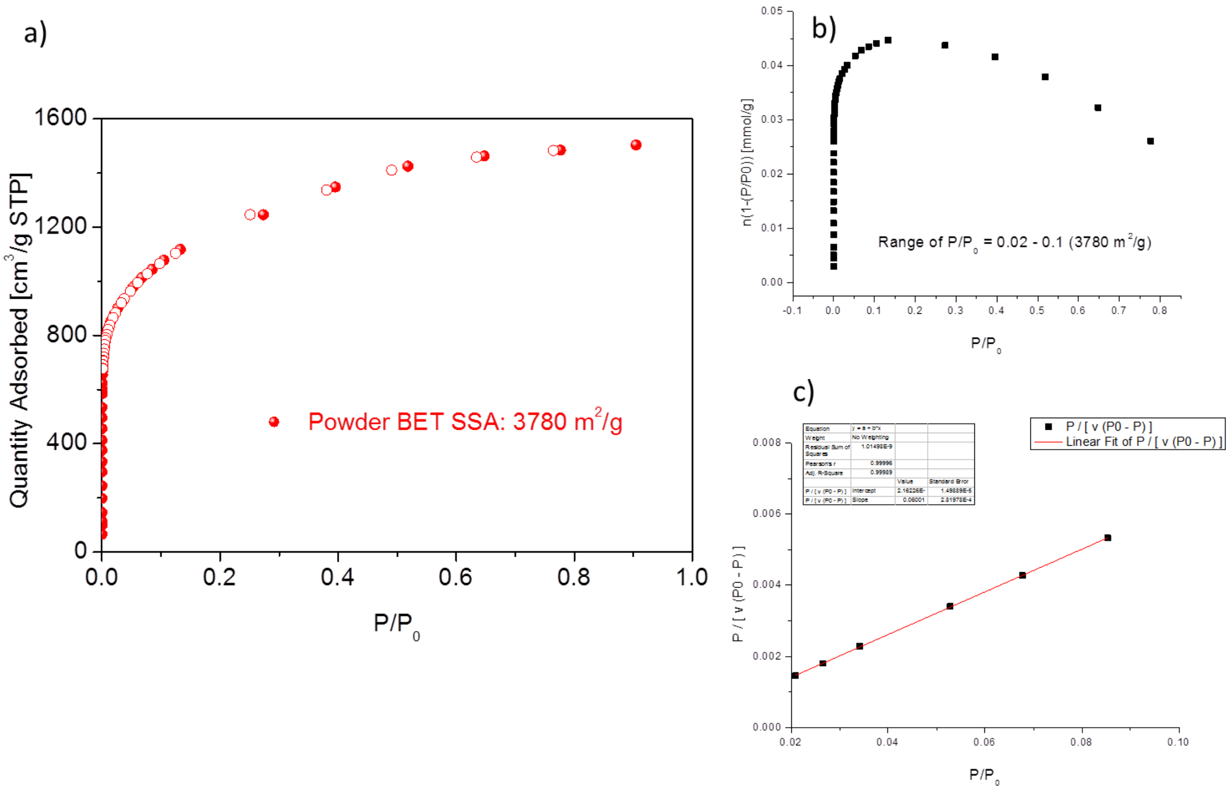
The PXRD patterns for MIL101 powder, compressed pellet and ground pellet are presented in Fig. S1 and compared to simulated one. The changes in the ratio of some peaks intensity for pellet can be explained by the preferential orientation of crystallites imposed by compression. As shown in detail in [1], this effect disappears in the patterns of the ground pellet and the ratios of intensities of Bragg reflexions return to the same characteristics of the starting uncompressed powder. Basically the structure is conserved up to densities close to the crystal density. However, irreversible effects are induced by mechanical pressure on the adsorption sites in the coordination environment of the metal, leading to decrease of SSA, pore volume and excess hydrogen adsorption [1].



SI figure S1. PXRD patterns of MIL-101powder and compressed pellet.

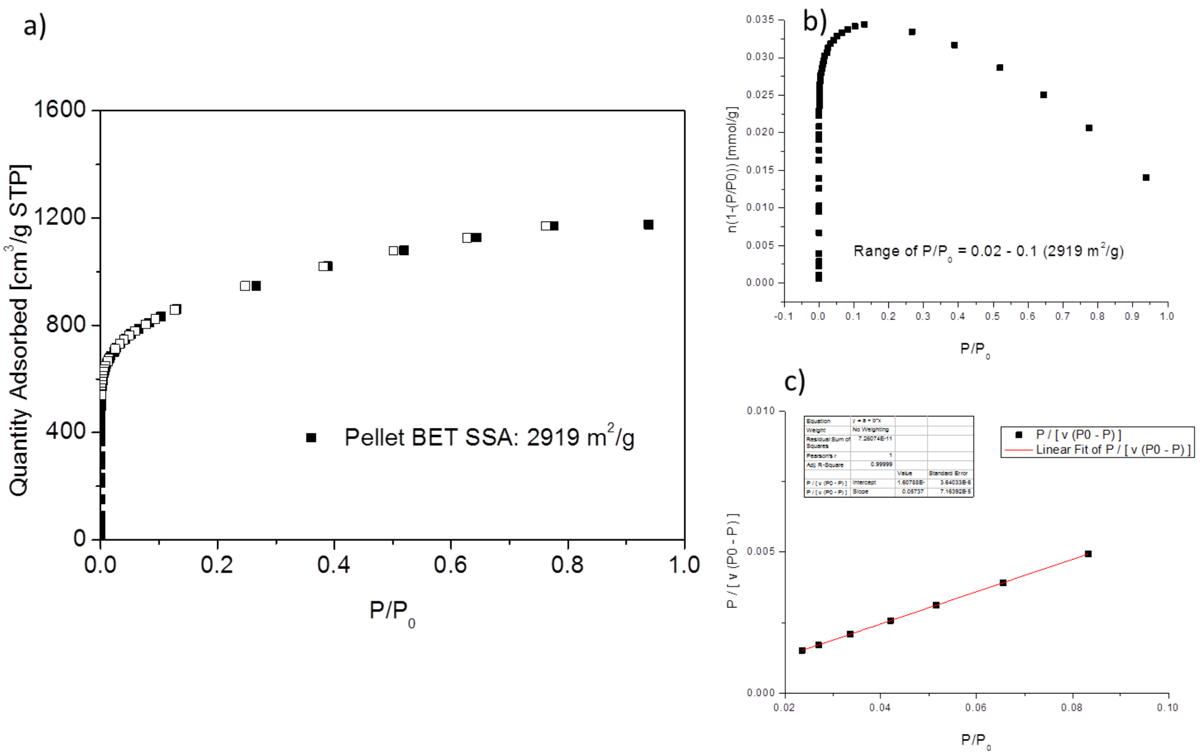
BET calculation

The specific surface area (SSA) is an important characteristic for microporous materials, which is typically determined from adsorption of nitrogen, argon or carbon dioxide. In order to determine the appropriate BET pressure range for microporous materials, $n_{ads}(1 - p/p_0)$ in the chosen pressure range always increases with p/p_0 as suggested by Rouquerol *et al*[5] (figure S2~S5, SI). Please note that P is absolute pressure and P_0 is hydrogen liquefaction pressure at 19.5 K, 1 bar.

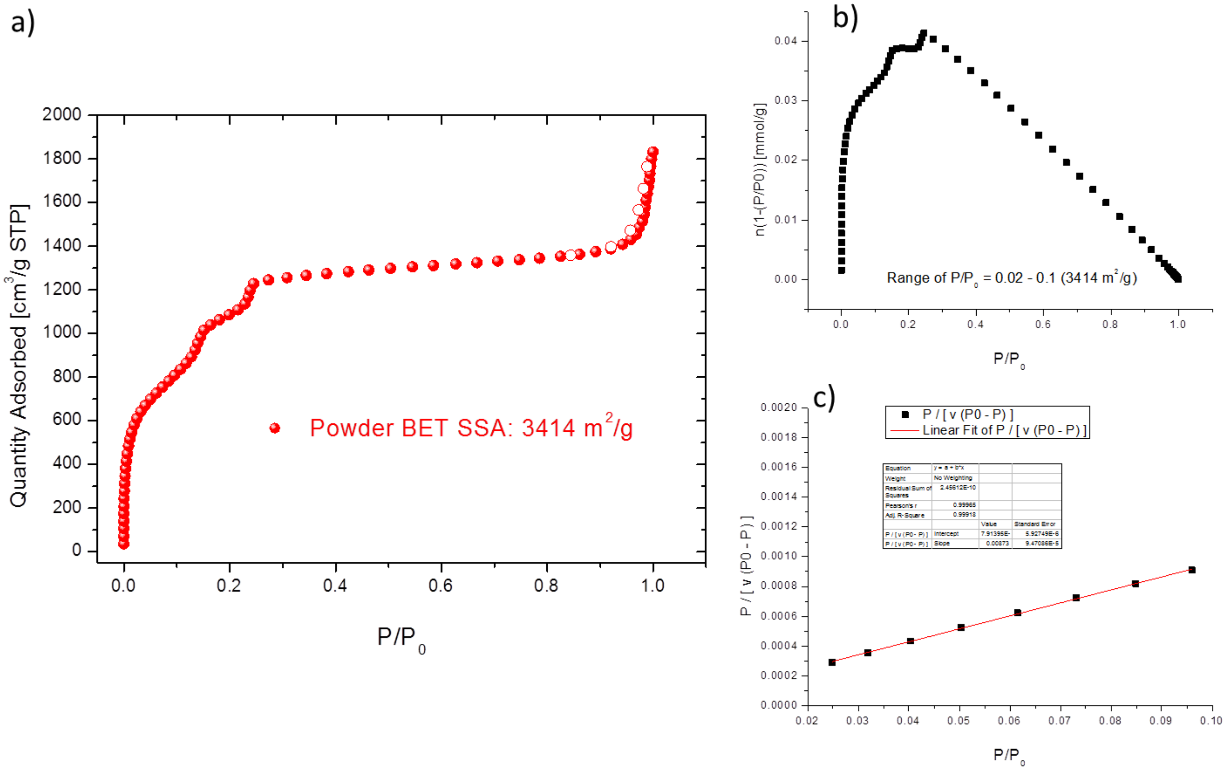


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.01498E-9		
Pearson's r	0.99996		
Adj. R-Square	0.99989		
		Value	Standard Error
P / [v (P0 - P)]	Intercept	2.16226E-	1.49889E-5
P / [v (P0 - P)]	Slope	0.06001	2.81978E-4

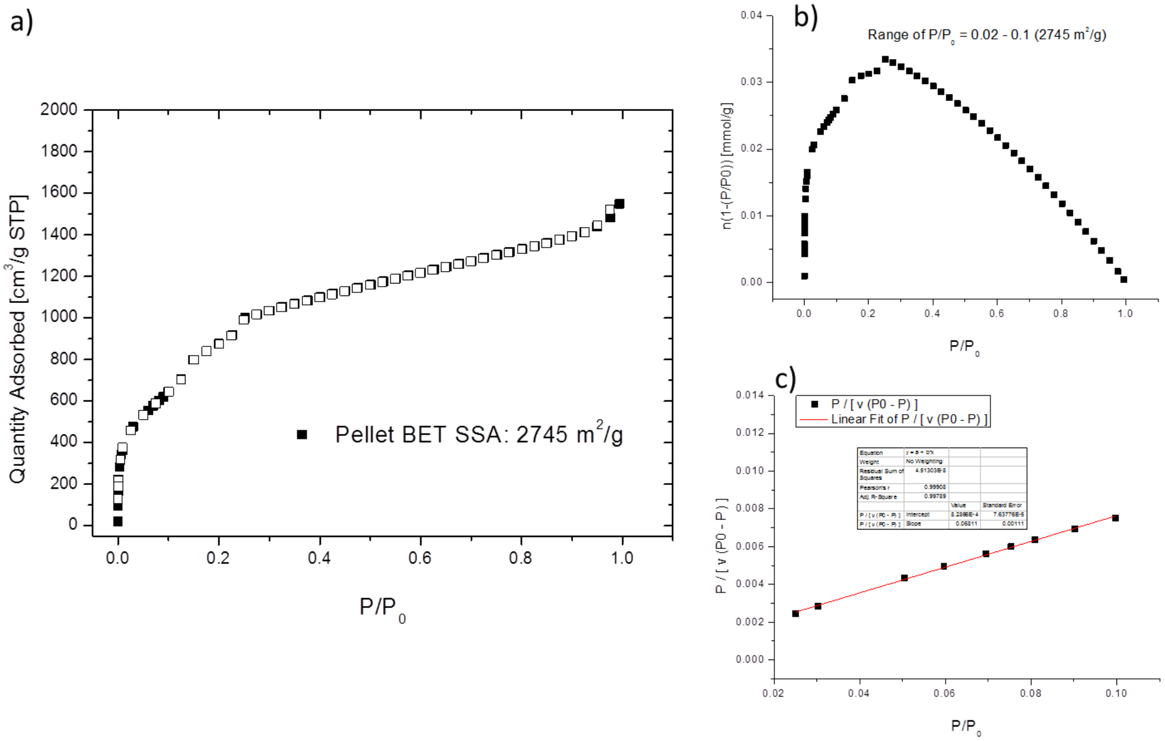
SI figure S2. a) hydrogen adsorption (closed symbol) / desorption (open symbol) isotherms at 19.5 K for powder MIL101. b) n(1-(P/P_0)) vs P/P_0, Only the range between P/P_0 = 0.02-0.1 satisfies the criterion for applying the BET theory. c) Linear fit of BET surface area plot



SI figure S3. a) hydrogen adsorption (closed symbol) / desorption (open symbol) isotherms at 19.5 K for compressed pellet MIL101. b) n(1-(P/P_0)) vs P/P_0, Only the range between P/P_0 = 0.02-0.1 satisfies the criterion for applying the BET theory. c) Linear fit of BET surface area plot

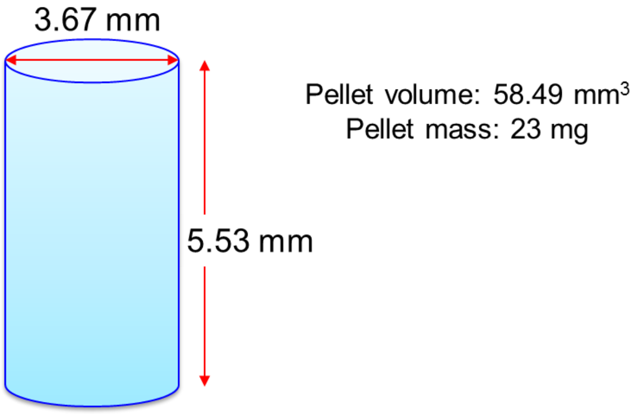


SI figure S4. a) nitrogen adsorption (closed symbol) / desorption (open symbol) isotherms at 77 K for powder MIL101. b) n(1-(P/P_0)) vs P/P_0, Only the range between P/P_0 = 0.02-0.1 satisfies the criterion for applying the BET theory. c) Linear fit of BET surface area plot



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	4.51303E-8		
Pearson's r	0.99908		
Adj. R-Square	0.99789		
		Value	Standard Error
P / [v (P0 - P)]	Intercept	8.2866E-4	7.63776E-5
P / [v (P0 - P)]	Slope	0.06811	0.00111

SI figure S5. a) nitrogen adsorption (closed symbol) / desorption (open symbol) isotherms at 77 K for compressed pellet MIL101. b) n(1-(P/P_0)) vs P/P_0, Only the range between P/P_0 = 0.02-0.1 satisfies the criterion for applying the BET theory. c) Linear fit of BET surface area plot



SI figure S6. Schematic diagram of the compressed pellet MIL101

All measurements on pellets after adsorption isotherms showed a contraction of ~1% and the volume of the degassed pellet is 57.90 mm^3. This gives an envelope density 0.40 g/cm^3.

Excess volumetric adsorption

"The adsorption volume V_a (the space lying within the potential field of the solid) is interpreted as the microporous volume of the adsorbent and not the void volume (V_v) of the adsorbent" and V_v is experimentally measured by helium probing or calculated from the bulk and the skeletal density of the adsorbent[6], where it is pointed out that the part of the V_v *where negligible adsorption takes place* and where the density of the gas is the same then the bulk (V_g) is defined as:

$$V_g = V_v - V_a$$

We made additional measurements with helium, on larger amounts of MIL-101, to evaluate the skeleton volume of degassed pellets. Envelope density (degassed mass per pellet volume) for 0.155 g pellets is 0.40 g/cm^3, and the MIL-101 skeleton volume obtained was 0.0775 cm^3 which gives a skeleton volume 0.50 cm^3/g (skeleton density 2.0 g/cm^3). From the degassed pellet density, the specific volume 1/0.40 = 2.50 cm^3/g is obtained. Subtracting the skeleton and adsorption volumes gives

$$V_{total}(\text{envelope}) - V_{sk} - V_a = 2.50 - 0.50 - 1.50 = 0.50\ \text{cm}^3\ \text{g}^{-1}$$

as V_g available for compressed gas. This is not a negligible volume which might be taken into account to evaluate the total volumetric storage capacity.

The calculated crystal density reported for $Cr_3F(H_2O)_2O[(C6H4)\text{-}(CO2)2]3.nH2O$ is 0.62 g/cm^3 [7]. Eliminating all the H_2O molecules and changing F^- with Cl^- in our MIL-101, a degassed density 0.43 g/cm^3 can be calculated, corresponding to the formula $[Cr_3O(OOC\text{-}C_6H_4\text{-}COO)_3]Cl$ of fully degassed MIL-101.

This results in V_{sc}~2.33 cm^3/g specific volume for a "single crystal". The specific skeleton volume measured with helium was V_{sk}= 0.50 ± 0.02 cm^3/g for powder (skeleton density 1.9 ±0.1g/cm^3). The sum of skeleton specific volume (V_{sk}= 0.50 cm^3/g) and adsorption volume from hydrogen isotherm (1.9 cm^3/g for powder) is ~2.4 cm^3/g, practically the same with the specific volume of the crystal, taking into account the cumulative errors including the evaluation of crystal density, skeleton volume with helium and pore volume (with hydrogen) evaluation. This shows a negligible volume V_g available for compressed gas if the total volumetric adsorption is desired to be evaluated. The adsorption volume from hydrogen isotherm for powder V_a = 1.9 cm^3/g at 19.5 K is practically the same with

$$V_{sc} - V_{sk}=2.33-(0.50\pm0.02)=1.83\pm0.02\ cm^3/g$$

the volume "seen by helium". It was also concluded earlier[8] that in these conditions, at saturation (p/p_0 ~1), all the free volume within the crystal (metal centers, small to medium pores and larger pores) are filled with liquid-like hydrogen.

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Reference

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