Electronic Supplementary Information

BET specific surface area and pore structure of MOFs determined by hydrogen adsorption at 20 K

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The MIL-101 sample was kindly provided by the group of professor Gérard Férey and synthesis is described elsewhere[1]. For removal of solvent molecules the material was evacuated at 495 K for 13 h.

19.45 mg of MIL-101 were evacuated in high vacuum at room temperature over night prior to each measurements. Nitrogen and hydrogen adsorption measurements were performed in an fully automated Sievert's apparatus, Autosorb 1b (Quantachrome). Nitrogen adsorption was measured by cooling with the commercially available nitrogen bath cryostat, while for hydrogen adsorption a self-build temperature-controlled cryostat was used.

The nitrogen adsorption and desorption isotherm is shown in figure 1. BET SSA is calculated in the pressure range of $P/P_0 = 0.05 - 0.1$ which fulfills the criteria of a rising $n(1-\frac{P}{P_0})$ as suggested by Rouquerol et al.[2]. The BET SSA is determined to 2761 $m^2\,g^{-1}$ and the specific pore volume according to Gurvich's rule[3] at $P/P_0 = 0.95$ to 1.51 $cm^3\,g^{-1}$.

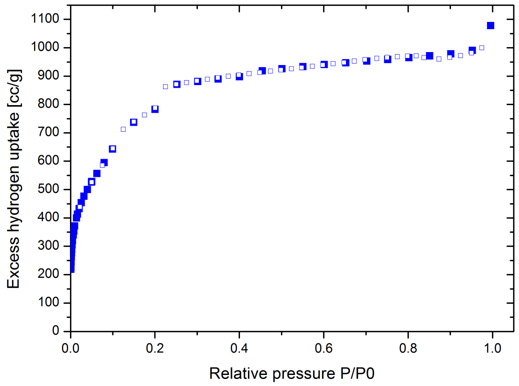

Fig. 1 Nitrogen adsorption (filled squares) and desorption (open squares) isotherms of MIL-101 at 77 K.

For the self build cryostat, the temperature control was calibrated by measuring the liquefaction pressure for hydrogen in the empty sample chamber for various temperatures. The hydrogen adsorption isotherms were measured at 19.5 ± 0.3 K corresponding to a liquefaction pressure of $P_0 = 78 \pm 4$ kPa. The cross-sectional area of hydrogen (A_{H_2}) is calculated for hexagonal closest packing of the bulk liquid with a molecular volume of 28.35 cc mol^{-1} (20 K) which yields $A_{H_2} = 14.2$ Å^2. Over the time of measurement the temperature was kept constant to ± 0.1 K. The adsorption isotherm was measured twice over the whole pressure range and additionally several times just at pressures of $P/P_0 = 0.05 - 0.8$. A control measurement with approximately double sample mass was performed and yielded the same saturation uptake per mass. Desorption was measured in a separate measurement owing to the long measurement time of approximately 10 h for the adsorption. For desorption few adsorption points in saturation at high P/P_0 were measured and than desorption was started.

The specific pore volume (SPV) is calculated according to Gurvich's rule[3]

$$SPV = \frac{n_{max}}{\rho_{lq}} \tag{1}$$

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

Liquefaction of the adsorbed hydrogen occurs $P = 76$ kPa. It is not shown in figure 2 and 3 because as soon as hydrogen is getting liquefied in the sample holder the set-up is becoming extremely sensitive to temperature fluctuations. When reaching $P = 76$ kPa the data points show an extreme fluctuation in pressure since the temperature stability of the cryostat of ± 0.1 K is not good enough. However, at pressures below $P = 76$ kPa the hydrogen uptake can be accurately measured with good reproducibility.

References

1 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
2 F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, 1999.
3 L. Gurvich, *J. Phys. Chem. Soc. Russ.*, 1915, **47**, 805.