Volumetric hydrogen sorption capacity of monoliths prepared by mechanical densification of MOF-177

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Gravimetric and volumetric measurements of MOF-177 skeleton density

The skeleton densities of the MOF-177 powder and monoliths were determined using both gravimetric and volumetric techniques. For the gravimetric determination, the skeleton density, ρ_{sk} of the sample can be related to the measured mass according to the equation:

$$m_s = -\frac{m_v}{\rho_{sk}} \rho_{He} + m_v \tag{1}$$

A representative plot of m_s vs. ρ_{He} is presented in the Fig.S1. The skeleton density is determined from the slope and intercept of the m_s vs. ρ_{He}. For measuring the skeleton density using volumetric method, the sample was loaded into a Sieverts equipment and was out-gassed under conditions mentioned previously. After attaining the desirable level of out-gassing, a pre-determined amount of ultra-pure helium gas was admitted into the gas reservoir of the system. Once the equilibrium is attained, the gas then vented into the sample cell. The skeleton density of the sample can be determined using:

$$\rho_{sk} = \frac{m_s}{V_s - V_e} \tag{2}$$

where, V_s and V_e, respectively are the volume of the cell occupied by the helium gas with and without sample. The latter was obtained from the pressure and temperature of helium before and after expansion into the empty cell. Several measurements were performed and the average value of the skeleton density was finally obtained.

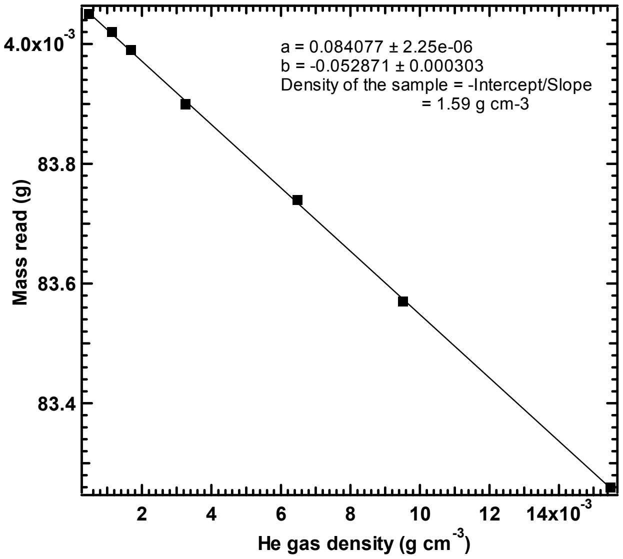

Fig. S1. Plot of mass read as function of helium gas density for the determination of MOF-177 skeleton density.

Void volume determination of MOF-177

The sample void volume here is defined as the whole space that is accessible to a gas, such as He. This includes all inter-crystalline spaces, interiors of all MOF cages and any other open empty regions. Since, the volume of the sample skeleton is not accessible to a gas, the void volume can be obtained as the difference between the bulk volume of the sample and its skeleton volume. For a given mass of the sample, therefore, we have:

$$V_v = \left(\frac{1}{\rho_b} - \frac{1}{\rho_{sk}} \right) \tag{3}$$

The sample void volumes of MOF-177 with different bulk densities were estimated from the skeleton density and the respective bulk densities. They are presented in Table S1 below:

Table S1. Bulk densities and Total void volumes of MOF-177

ρ_b (gcm^{-3})	V_v(cm^{3}g^{-1})
0.207	4.19
0.385	1.96
0.420	1.74
0.510	1.32
0.580	1.08
0.620	0.97
0.725	0.74
0.820	0.58
0.890	0.48
1.090	0.28

Low-pressure nitrogen adsorption data

Low-pressure nitrogen adsorption data of MOF-177s measured at 77K using micromeritics ASAP 2020. The data is used to obtain the specific surface area and micropore volume, using the BET and DR models.

Table S2. Data of the volume of nitrogen adsorbed by MOF-177 as function of relative pressure.

ρ_b = 0.58 g cm^{-3}		ρ_b = 0.82 g cm^{-3}		ρ_b = 0.89 g cm^{-3}		ρ_b = 01.09 g cm^{-3}	
P/P$_0$	ml/g(STP)	P/P$_0$	ml/g(STP)	P/P$_0$	ml/g(STP)	P/P$_0$	ml/g(STP)
0.010	367.33	0.010	219.35	0.010	192.79	0.010	115.11
0.012	423.53	0.012	254.16	0.012	221.47	0.012	128.74
0.014	474.52	0.014	283.07	0.014	244.74	0.014	142.50
0.017	509.71	0.017	300.78	0.017	262.81	0.017	152.45
0.020	534.53	0.021	317.56	0.020	275.74	0.020	158.30
0.024	552.71	0.025	324.57	0.026	285.35	0.024	162.36
0.030	566.82	0.031	333.14	0.030	291.06	0.029	165.91
0.037	577.64	0.037	338.01	0.034	294.22	0.035	168.88
0.041	581.70	0.041	340.80	0.042	298.92	0.042	171.18
0.050	589.87	0.050	345.28	0.050	302.52	0.051	173.29
0.061	596.59	0.060	349.13	0.060	305.94	0.060	175.28
0.072	602.77	0.072	352.75	0.072	309.15	0.072	177.10
0.087	608.27	0.087	356.20	0.087	312.10	0.086	178.65
0.104	613.44	0.104	359.27	0.104	314.87	0.103	180.08
0.124	618.06	0.124	362.28	0.124	317.48	0.123	181.47

0.148	622.44	0.148	365.14	0.148	319.87	0.147	182.78
0.177	626.55	0.176	367.80	0.176	322.18	0.176	184.03
0.211	630.36	0.211	370.37	0.211	324.35	0.210	185.17
0.252	633.86	0.252	372.80	0.252	326.40	0.251	186.25
0.301	637.19	0.301	375.21	0.301	328.33	0.301	187.15

Powder X-ray Diffraction data of MOF-177. PXRD measurements were performed on pellets using a Bruker D8 Advance X-ray diffractometer enabled with Cu-Kα radiation.

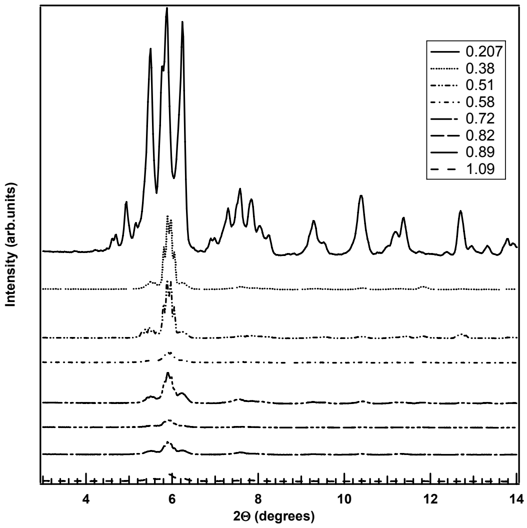

Fig. S2. Powder X-ray diffraction pattern of MOF-177 samples with bulk density of 0.207, 0.38, 0.51, 0.58, 0.72, 0.82, 0.89 and 1.09 g cm^{-3}.

Measurement of excess gravimetric hydrogen uptake

Hydrogen storage measurement was performed gravimetrically using the microbalance and volumetrically using a High Pressure Adsorption Characterization (HPAC) system based on Sieverts volumetric technique. The amount of hydrogen adsorbed in the sample in the gravimetric setup is determined from the data using:

$$m_{ads} = m_r + \rho_{H_2} \frac{m_v}{\rho_{sk}} - m_v \tag{4}$$

where, m_r, m_v and ρ_{H2} are the mass of the sample measured at hydrogen pressure P, mass measured in vacuum and gas density of hydrogen at given pressure and temperature. Once the adsorption was measured up to 13 MPa, the hydrogen was vented in steps to measure the desorption curve. The mass of hydrogen adsorbed was expressed in units of mol kg^{-1} employing the molar mass of hydrogen. The volumetric excess adsorption was obtained by multiplying the gravimetric excess uptake data with the respective sample bulk density. The total volumetric and gravimetric hydrogen uptake of the sample are calculated by

$$n_{tot} = n_{ex} + \rho_g V_v \tag{5}$$

where, ρ_g is the gas phase density and V_v is the sample void volume.

FT-IR Assignment

ν		Tentative ν *2	Tentative ν *3
3340			
3228	Overtones or combination bands		
3131			
3054	Aromatic C-H Stretch		
2765			
2665			
2568	Overtones or combination bands		
2464			
2364	Overtones or combination bands		
2337	Overtones or combination bands		
2121	Overtones or combination bands		
2009	Overtones or combination bands		
1936	Overtones or combination bands		
1862	Overtones or combination bands		
1809	Overtones or combination bands		
1758	Overtones or combination bands		
1700	Overtones or combination bands		
1612	Strong assymetric stretching of carboxylate/C=C ring stretch	3224	
1558	C=C aromatic stretching/Overtones or combination bands	3116	
1515	C=C aromatic stretching/Overtones or combination bands	3030	
1407	Weak symmetric stretching of carboxylate	2814	
1307	In-plane C-H bending of aromatic/C-O stretching of carboxylic group	2614	
1284	In-plane C-H bending of aromatic	2568	
1184	In-plane C-H bending of aromatic/C-O stretch of -COO	2368	
1149	In-plane C-H bending of aromatic	2298	3447
1106	In-plane C-H bending of aromatic	2212	3318
1018	In plane C-H bending of aromatic	2036	3054
898	C-H out of plane bending of aromatics	1796	2694
860	C-H out of plane bending of aromatics	1720	2580
809	C-H out of plane bending of aromatics	1618	2427
779	C-H out of plane bending of aromatics	1558	2337
707	C-H out of plane bending of aromatics	1414	2121

2*ν and 3*ν are tentative positions of first and second overtones from different IR vibrations.

XPS Data

Fig. S3 gives survey scans of powder and monolith with density = 1.09 g/ml

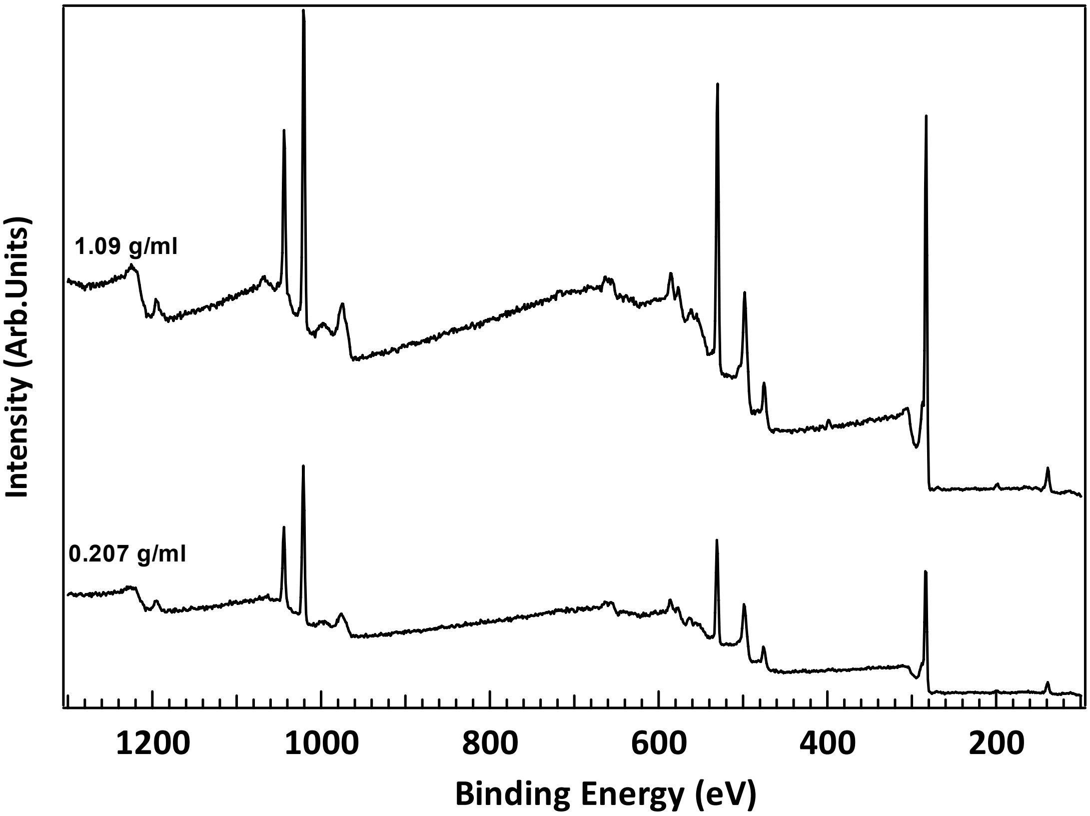

Fig. S3. XPS Survey Scans of powder and monoliths with bulk density1.09 g cm^{-3}.

Determination of the fraction of crystalline phase.

The sample gas-phase volume, V_g is defined as the volume of the region where the density of the adsorbent is same as the bulk-phase hydrogen. Since V_v gives the total sample void volume, the $V_g = V_v - V_a$ where V_a is the adsorption volume. V_g can be approximated as the volume of the sample not occupied by the solid phase. For samples with bulk density of 0.207 g cm^{-3}, the volume occupied by the solid phase is equivalent to the crystal volume. For higher density samples, the volume occupied by the solid phase has contributions from the crystalline and amorphous phases, V_C and V_A. Accordingly V_g is given as:

$$V_g = V_b - \left[aV_C + (1-a)V_A\right] \tag{6}$$

Here, V_b represents the specific volume of sample. The fraction of the crystalline phase a in the samples is determine by normalizing the micropore volume data with the data corresponding to the sample with bulk density 0.207 g cm^{-3}. This assumes that only crystalline phase contributes to the micropore volume. The Table S3 gives the fraction of crystals in the sample as a function of the bulk density.

Table S3. The fraction of crystalline phase in the MOF-177 samples and the gas-phase volumes.

ρ_g(g cm^{-3})	*a*	*1-a*
0.207	1	0
0.28	0.964	0.036
0.38	0.941	0.059
0.42	0.848	0.152
0.51	0.755	0.245
0.53	0.679	0.321
0.58	0.581	0.419
0.72	0.464	0.536
0.82	0.343	0.657
0.89	0.302	0.698
1.09	0.168	0.832

Fit using Modified Dubinin-Ashtakov Model

The modified Dubinin-Ashtakov fit was carried using the following global fit function which returns the n_{ex} as function of three independent variables: pressure, gas-phase density and bulk density.

$$n_{ex} = n_{\max} \exp\left(\left(\frac{RT}{\varepsilon}\right)^2 \ln^2\left(\frac{P_0}{P}\right)\right) - \rho_g V_a \tag{7}$$

Since the specific volume of the amorphous phase, V_A is unknown it is kept as a fit parameter. Also ρ_{max}, ε and P_0 are kept as fit parameters. In the original five parameter model the temperature dependence of ε was explicitly given as $\varepsilon = \alpha + \beta T$, where α and β are the enthalpic and entropic contributions to the characteristic free energy of adsorption. Here, since the isotherms were collected only at 77 K, α and β were not used explicitly. ε was assumed to be constant for all samples. The minimized standard error of estimate is 0.27. Table S5 gives the fit parameter. The data was fitted also with samples with density up to 0.53 g cm^{-3}, when the fraction of crystalline phase in the sample is high. This was done in order to check if the ε varies with the bulk density. The standard error of estimate was found to be 0.32. The fit parameters are appended in the Table S4. It can be seen that ε does not vary significantly with bulk density.

Table S4. The fit parameters for the modified Dubinin-Astakhov for densified MOF-177 samples

Parameters	All Data	Data up to 0.532 g cm^{-3}
ρ_{max} (g L^{-1})	78.6 ± 1.2	38.7 ± 0.6
ε (J mol^{-1})	2702 ± 45	2678 ± 48
P_0 (MPa)	55 ± 6	54 ± 6
V_A (cm^3 g^{-1})	0.68 ± 0.01	0.84 ± 0.03
χ^2	0.27	0.14