Supporting Information File
Measurement and interpretation of unary supercritical gas adsorption isotherms in micro-mesoporous solids

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Abstract

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S1. Textural characterisation by subcritical adsorption

S2. Supercritical gas adsorption experiments

S3. Determination of adsorbed phase volume

S4. Mathematical fitting of the absolute adsorption isotherm

References

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3. Nguyen HGT, Espinal L, van Zee RD et al. (2018) *Adsorption* **24**: 531–539.
4. Nguyen HGT, Sims CM, Toman B, et al. (2020) *Adsorption* **26**: 1253–1266.

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S1. Textural characterisation by subcritical adsorption

Textural characterisation of the three adsorbents was carried out by physisorption analysis in a Quantachrome Autosorb iQ using Ar at $87\,\mathrm{K}$ in the pressure range $1\times10^{-7}-0.1$ MPa. Prior to the experiments, each sample was loaded in the equipment's external degassing station and regenerated at $473\,\mathrm{K}$ (ZIF), $573\,\mathrm{K}$ (MZ) and $393\,\mathrm{K}$ (MC) for 16 h. The sample was then transferred to the measuring station, where a measurement with helium was conducted to estimate the void volume of the measuring cell, followed by the measurement with Ar in both adsorption and desorption mode. For these experiments, $0.095\,\mathrm{g}$ (ZIF), $0.060\,\mathrm{g}$ (MZ) and $0.150\,\mathrm{g}$ (MC) of adsorbent were used. The experimental data were interpreted upon application of the non local DFT model (NLDFT) available within the instrument software to obtain surface area, pore volume and pore volume distribution (see Table 1 in main manuscript). To this end, the following models fitted to the desorption branch of the isotherm were used: silica/zeolite with cylindrical/spherical pores (ZIF), silica/zeolite with cylindrical pores (MZ) and carbon with cylindrical pores (MC).

S2. Supercritical gas adsorption experiments

A Rubotherm Magnetic Suspension Balance (MSB) was used to measure the high-pressure adsorption isotherms on the three adsorbents at $T = 308$ K in the pressure range $0.02 - 21$ MPa. The setup installed at Imperial College London is described in previous publications [1,2]; its reliability has been validated through the participation in a recent interlaboratory study, specifically by replicating both CO_2 and CH_4 high pressure adsorption isotherms on NIST Reference Materials RM 8852 (ZSM-5) [3] and RM 8850 (Zeolite Y) [4], respectively. The instrument provides high-resolution (10 μg) weight measurements at two measuring positions, namely MP_1 (the basket with the adsorbent) and MP_2 (the combined measured weight of MP_1 and a calibrated titanium sinker). These two readings are used to compute the amount of gas adsorbed and the gas bulk density at given pressure and temperature conditions. To this end, three sets of experiments are carried out, which are described next: (i) CO_2 gravimetry without adsorbent; (ii) Helium gravimetry with adsorbent; and (iii) CO_2 gravimetry with adsorbent.
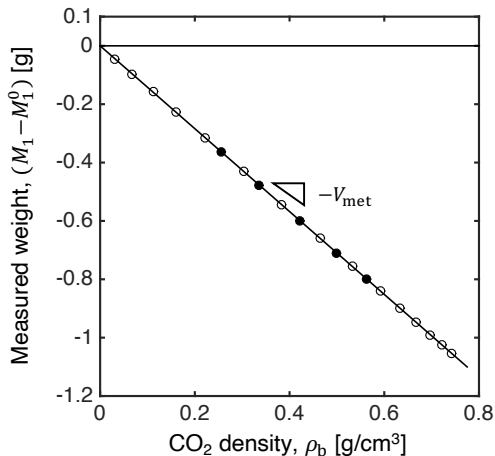

Figure S1: Measured weight ($= MP_1 - MP_{1,0}$) plotted as a function of the bulk density for the CO_2 gravimetry experiment without adsorbent. The temperature is $80\,^{\circ}\mathrm{C}$ and equilibrium pressure point were obtained in the range $2 - 30$ MPa. Empty symbols are measurements acquired upon charging gas in the measuring chamber incrementally up to the maximum pressure, while filled symbols are obtained upon depressurising the system. The slope of the regression line corresponds to $-V_{\mathrm{met}}$ in Eq. 5 of the main manuscript.

Figure S1 shows results from the calibration experiment carried out without adsorbent in the measuring cell and by using CO_2 as the probing gas; the latter is chosen, because it enables reaching bulk density values

that are equivalent to those measured during the gas adsorption experiment. From the slope of the regression line, the following estimate is obtained: $V_{\mathrm{met}} = 1.4195$ cm^3, with an uncertainty $u(V_{\mathrm{met}}) = 1 \times 10^{-4}$ cm^3.

The following experimental procedure was applied to carry out the adsorption experiments. After loading the sample in the measuring chamber, a degassing procedure was carried out by heating the system to T_{reg} and pulling vacuum for at least 12 hours. The system was subsequently cooled to the temperature used for the Helium gravimetry experiment to yield the measured weight under vacuum, $\mathrm{MP}_{1,0}$, (and, accordingly, the mass of adsorbent, m_{s}). The Helium gravimetry experiment with adsorbent was carried out at $T < T_{\mathrm{reg}}$ with an equilibration time of about 1 hour for each pressure point (see Figure 5 and Table 2 in the main manuscript). Prior to the adsorption experiment, the system was purged with CO_2 and the measuring chamber was evacuated. The adsorption isotherm was measured at $T = 308$ K, by exposing the adsorbent to the adsorbate at various pressures and allowing it to equilibrate for at least 60 min. Because of the absence of hysteresis in supercritical adsorption experiments, most isotherms points were taken in desorption mode for practical reasons. A settling time of 30 s, 1.5 min and 30 s was chosen to regulate the automatic cyclic operation of the MSB between the zero point and the two measuring points MP_1 and MP_2, respectively. All measurements were logged and, for each pressure and temperature combination, the average of the last five readings was taken as the equilibrium point used to compute the amount adsorbed. The uncertainty affecting the measured net, $u(n_{\mathrm{net}})$, and excess amount adsorbed, $u(n_{\mathrm{ex}})$, increases by and large linearly with the bulk density. The ranges observed for the measurements presented in this study are reported in Table 2 for each adsorbent and have been computed upon application of classic formula of error propagation on Eqs. $5 - 8$, as described in detail in previous publications [1,2]. These yield error bars that are negligibly small and that are therefore not shown in the plots presented in the main manuscript.

S3. Determination of the adsorbed phase volume

The following mathematical expression is used to describe the evolution of the adsorbed phase volume per unit mass of solid, $v_a = V_{\mathrm{a}}/m_{\mathrm{s}}$ (cm^3/g), as a function of the molar bulk density, $\rho = \rho_{\mathrm{b}}/M_{\mathrm{m}}$ (mol/L):

$$v_{\mathrm{a}} = \phi_2 \nu_{\mathrm{tot}} + (a_1 - \phi_2)\nu_{\mathrm{tot}} \frac{(a_2\rho)^{a_3}}{1 + (a_2\rho)^{a_3}} \tag{S1}$$

where ϕ_2 is the volume fraction of pores with width < 2 nm and ν_{tot} (cm^3/g) is the specific total pore volume (see Table 1 in the main manuscript); a_1, a_2 and a_3 are treated as adjustable parameters. Their values are reported in Table S1 and the the evolution of v_a is plotted in Figure S2 for the three adsorbents considered in this study.

Adsorbent	ν_{tot} [cm^3/g]	ϕ_2 [$-$]	a_1	a_2	a_3
ZIF	0.72	0.70	0.90	5	1
MZ	0.46	0.38	0.55	0.1	5
MC	0.48	0.007	0.66	0.1	5

Table S1: Values of the adjustable parameters to describe the evolution of the volume of the adsorbed phase with density.

The functional form of Eq. S1 was chosen so as to represent a pore-filling process whereby micropores (width < 2 nm) and very small mesopores (width < 3 nm) are readily filled at low bulk densities ($\rho < 2$ mol/L), while small mesopores (width $< 11 - 12$ nm) experience near-critical condensation starting at a bulk density of approximately ($\rho \approx 5$ mol/L). Using this conceptualisation, the value of parameter a_1 is set by the pore-size distribution measured by Ar at 87 K (see Figure 3 in the main manuscript), while the values of the parameters a_2 and a_3 were adjusted, so as to have a gradual increase in the adsorbed phase volume from $\rho \approx 5$ mol/L reaching saturation at $\rho \approx 15$ mol/L. Because of the absence of mesopores in ZIF, the values of the parameters a_2 and a_3 were chosen so as to reach adsorption saturation at $\rho < 2$ mol/L.
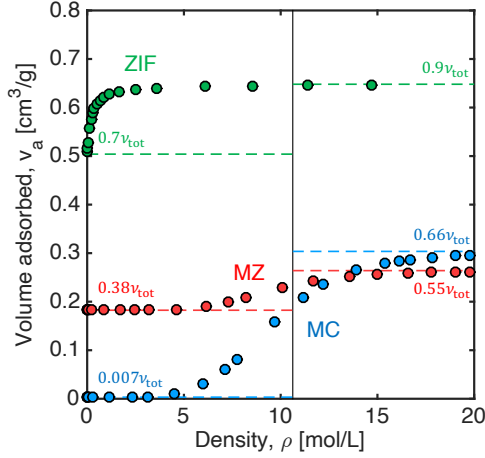
Figure S2: Volume of the adsorbed phase as a function of the bulk density for ZIF, MZ and MC. Parameter values are listed in Table S1.

S4. Mathematical fitting of the absolute adsorption isotherm

The absolute adsorption isotherms were fit to a three-parameter logistic function [4]:

$$n_{\mathrm{a}} = \frac{\gamma}{1 + \exp\left[(-\ln(\rho) + \alpha)/\beta\right]} \tag{S2}$$

where $n_{\mathrm{a}} = n_{\mathrm{ex}} + \rho v_{\mathrm{a}}$ is the absolute amount adsorbed (mmol/g), ρ is the bulk density (mol/L), and α, β and γ are the adjustable parameters. The latter are obtained upon minimising the following objective function:

$$\Omega = \sum_{i=1}^{N} (n_{\mathrm{a},i} - \widehat{n}_{\mathrm{a},i})^2 \tag{S3}$$

where n_{a} and $\widehat{n}_{\mathrm{a}}$ is the absolute amount adsorbed determined from the experiment and the model, respectively, and N is the number of experimental point in one isotherm. As indicated in a previous study [4], Eq. S2 (and its parameters) bears no physical significance and the function was chosen, because it can replicate the the form of the isotherm measured on the three adsorbents. The values of the fitted parameters are listed in Table S2.

Adsorbent	α	β	γ
ZIF	-0.359	1.08	13.0
MZ	0.349	2.42	6.93
MC	7.09	1.94	56.5

Table S2: Values of the fitted parameters used to describe the absolute adsorption isotherm for ZIF, MZ and MC.