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

Ronny Pini1 · Humera Ansari1 · Junyoung Hwang1

Received: 9 November 2020 / Revised: 15 February 2021 / Accepted: 6 March 2021 / Published online: 25 March 2021
© The Author(s) 2021

Abstract
Gas adsorption at high pressures in porous solids is commonly quantified in terms of the excess amount adsorbed. Despite the wide spectrum of adsorbent morphologies available, the analysis of excess adsorption isotherms has mostly focused on microporous materials and the role of mesoporosity remains largely unexplored. Here, we present supercritical CO2 adsorption isotherms measured at $T = 308 \text{ K}$ in the pressure range $p = 0.02 - 21 \text{ MPa}$ on three adsorbents with distinct fractions of microporosity, $\phi_2$, namely a microporous metal-organic framework ($\phi_2 = 70\%$), a micro-mesoporous zeolite ($\phi_2 = 38\%$) and a mesoporous carbon ($\phi_2 < 0.1\%$). The results are compared systematically in terms of excess and net adsorption relative to two distinct reference states—the space filled with gas in the presence/absence of adsorbent—that are defined from two separate experiments using helium as the probing gas. We discuss the inherent difficulties in extracting from the supercritical adsorption isotherms quantitative information on the properties of the adsorbed phase (its density or volume), because of the nonuniform distribution of the latter within and across the different classes of pore sizes. Yet, the data clearly reveal pore-size dependent adsorption behaviour, which can be used to identify characteristic types of isotherm and to complement the information obtained using the more traditional textural analysis by physisorption.

Keywords
High-pressure gas storage · Textural characterisation · Physisorption · Excess and net adsorption

List of symbols

$N_a$ Total number of moles [mol]
$p$ Pressure [MPa]
$p_c$ Adsorbate critical pressure [MPa]
$T$ Temperature [K]
$T_c$ Adsorbate critical temperature [K]
$T_{reg}$ Adsorbent regeneration temperature [K]
$\omega(x)$ Absolute uncertainty of $x$
$V$ Volume [cm$^3$]
$V_a$ Volume of the adsorbed phase per unit mass of adsorbent [cm$^3$/g]
$V_a$ Volume of the adsorbed phase [cm$^3$]
$V_{met}$ Volume of lifited metal parts (MSB) [cm$^3$]
$V_{sk}$ Calibrated sinker volume (MSB) [cm$^3$]
$V_s$ Adsorbent skeletal volume [cm$^3$]
$V_0$ Buoyant volume (MSB) [cm$^3$]

Greek symbols

$\phi$ Total voidage [-]
$\phi_i$ Volume fraction of pores with width $< i$ nm [-]
$\rho_a$ Average adsorbed phase density [mol/L]
$\rho$ Molar bulk fluid density [mol/L]
$\rho_b$ Bulk fluid density [g/cm$^3$]
$\rho_B$ Adsorber bed density [kg/m$^3$]
$\rho_c$ Adsorbate critical density [mol/L]
\( \rho_L \)  
Bulk density of the saturated liquid [mol/L]

\( v_{\text{tot}} \)  
Specific total pore volume [cm\(^3\)/g]

1 Introduction

The adsorption of supercritical gases in nanoporous solids continues to find application in many areas of engineering, including processes operating from just above atmospheric pressure up to hundreds of atmospheres. Some examples include: the separation of industrial gas mixtures by pressure swing adsorption (operating pressure, \( p \approx 0.1 - 1 \text{ MPa} \)) [5, 22, 39]; gas storage at near-ambient temperature (\( p \approx 1 - 10 \text{ MPa} \)) [2, 7, 32]; and gas recovery and storage in deep porous rock formations (\( p > 10 \text{ MPa} \)) [4, 6, 19]. Experimental measurements of adsorption in porous solids at elevated pressures are inherently difficult, because of the presence of the dense (supercritical) bulk phase in a poorly defined dead space within the apparatus [20]. Under these conditions, the extent of adsorption is commonly quantified using the Gibbs excess formulation [35] (referred to as excess adsorption in this paper). This definition conveniently simplifies measurement interpretation by providing a measure for the amount of gas in the system in excess of the amount that would be present if the accessible volume (including the pores of the adsorbent) were occupied by the adsorbate gas in its bulk state at the same temperature and pressure. However, the accurate determination of the impenetrable volume of the adsorbent is not trivial, both experimentally [13, 17, 18] and numerically [10, 24, 38]. This argument has been used to favour a formulation that uses net instead of excess adsorption to report adsorbed amounts [3, 14]. Others have shown that these relative measures of adsorption (net and excess) are problematic in the approach to the thermodynamics of adsorption, which should instead use the absolute amount adsorbed [23]. The latter is also the quantity that is commonly used in the design and modelling of adsorption units, such as fixed-bed adsorbers.

An attempt to resolve this debate is not within the scope of this contribution. Rather, by acknowledging that the most common experimental adsorption techniques cannot measure absolute adsorbed amounts directly, our aim is to provide a comparison of the concepts of net and excess adsorption by means of experiments. In fact, while the discussion in the literature considers almost exclusively adsorbents dominated by micropores [3, 14, 23], we present and analyse here measurements on materials that include mesopores (for the purpose of this discussion, the IUPAC classification of pores is adopted). The analysis has three main objectives. First, to present a systematic approach to data reporting that includes both net and excess adsorption isotherms, in addition to the relevant quantities needed to convert between the two (e.g. the skeletal volume of the adsorbent) and their uncertainty. Second, to demonstrate that the application of the absolute adsorption formalism to supercritical adsorption measurements on adsorbents with mesopores is difficult, because the latter remain filled only partially with the adsorbed phase, even at high pressures. Third, to discuss characteristic features of net and excess adsorption isotherms in relation to the textural properties of the adsorbent. In fact, the sample morphologies encountered in adsorption applications are many and varied, including ordered micro- (e.g. zeolites, carbon molecular sieves) or meso-porous adsorbents (e.g. mesoporous carbons and silicas); hierarchical adsorbents (e.g. micro-mesoporous zeolites); and disordered adsorbents (e.g. activated carbons and natural sorbents, such as clays and shale). In this endeavour, we build on previous indications that supercritical adsorption does reveal characteristic pore-size dependent behaviour [15, 33, 36] and provide an attempt to rationalise the results in a manner analogous to the classification of physisorption isotherms.

2 Supercritical adsorption in porous solids

High-pressure adsorption is also referred to as supercritical adsorption [44], because at elevated pressures many gases achieve the supercritical state. The latter is characterised by the absence of a bulk vapour-liquid (VL) transition, a condition that is attained for gases at a temperature or pressure above the critical point. Figure 1 shows isotherms of the bulk density as a function of pressure for three adsorptives that are commonly used for textural characterisation [42], namely \( N_2 \) at 77 K \( (T_c = 126 \text{ K}) \), Ar at 87 K \( (T_c = 151 \text{ K}) \), and \( CO_2 \) at 273 K and 313 K \( (T_c = 304 \text{ K}) \). The dashed vertical lines represent the VL transition, which for \( N_2 \) and Ar is conveniently attained at the standard atmospheric pressure. A similar behaviour is observed for \( CO_2 \) at 273 K, although a higher pressure (approx. 3.5 MPa) is required to reach condensation. On the contrary, the isotherm obtained for \( CO_2 \) at 313 K \( (T/T_c \approx 1.03) \) doesn't show any discontinuity and the density increases monotonically with pressure. This behaviour has two important implications for gas adsorption in porous solids. First, the density of the adsorbed phase is not well defined at supercritical conditions. For measurements carried out at \( T/T_c \ll 1 \) (e.g. \( N_2 \) and Ar), the VL transition controls by and large the adsorption process and it is safe to assume that the adsorbed fluid takes the density of the saturated liquid, \( \rho_L \). As example, the value \( \rho_L = 28.8 \text{ mol/L} \) is used for the textural characterisation of microporous solids with \( N_2 \) at 77 K \( (T/T_c = 0.6) \) [21, 30]. As shown in Fig. 1 for the two \( CO_2 \) isotherms, this choice becomes rather arbitrary for measurements carried out both slightly below and above the critical point, because the density shows a strong dependency on pressure. This uncertainty can lead to significant variations in the obtained textural parameters [29] and
challenges the interpretation of adsorption isotherms measured at supercritical conditions [1]. The second important implication is that the bulk adsorptive can reach liquid-like densities, comparable to the adsorbed phase, thereby affecting material balance calculations for adsorption systems, as discussed in the next section.

### 2.1 Excess and net adsorption

Consider a batch adsorber filled with solid adsorbent, which is exposed to an adsorptive gas at elevated pressures ($T/T_c > 1$). The total number of moles of the adsorbate, $N_t$, is given by the sum of the number of moles in the bulk fluid phase, $N_b$, and in the adsorbed phase, $N_a$:

$$N_t = N_b + N_a$$

where,

$$N_b = \rho_b (V\phi - V_a)$$

In Eq. 2, $\rho_b$ is the density of the bulk fluid phase, $V$ and $\phi$ refer to the adsorber volume and its total voidage, respectively; $V_a = N_a/\rho_a$ is the volume occupied by the adsorbed phase with average density, $\rho_a$. By reducing the free space available to the bulk phase, $V_a$ also reduces its mass by an amount proportional to $\rho_b$. However, the effect of this “correction” is difficult to estimate a priori, because for a supercritical gas $\rho_a$ is not well defined (see Fig. 1) and $V_a$ doesn’t necessarily correspond to the specific pore volume of the solid. Accordingly, adsorption calculations for supercritical gases are carried out by using the Gibbs adsorption excess [35], which can be obtained by recasting Eqs. 1 and 2:

$$N_{ex} = N_a (1 - \rho_b/\rho_a) = N_t - \rho_b V\phi$$

(3)

As shown by the left-hand side of Eq. 3, when $\rho_b \ll \rho_a \approx \rho_L$, $N_a \approx N_{ex}$, as it is the case for adsorption at sub-critical conditions. However, for $\rho_b \leq \rho_a$, the two adsorption quantities may differ significantly and an arbitrary choice of $\rho_a$ may no longer have a negligible impact on the material balance calculation. The right-hand side of Eq. 3 shows that $N_{ex}$ depends solely on quantities that can (in principle) be accessed either experimentally or numerically, providing a means to describe the extent of adsorption of the given adsorbate without knowledge of $\rho_a$. As anticipated in Section 1, a major point of contention is how to determine the adsorbent pore volume (and hence $\phi$) accurately.

One can also ask the following question: given that the space which can be filled with gas is reduced by the presence of the solid, wouldn’t it be more effective to store gas in the vessel devoid of adsorbent? The answer to this question is found by considering another measurable quantity—the so-called net amount adsorbed [14], i.e.

$$N_{net} = N_t - \rho_b V = N_a - \rho_b (V_a + V_s)$$

(4)

where $V_s = V (1 - \phi)$ is the skeletal (impenetrable) volume of the adsorbent. Accordingly, when $N_{net} = 0$, $N_t = \rho_b V$, meaning that beyond this point the presence of the adsorbent diminishes the gas storage capacity of the container. When $N_{net} > 0$, adsorption is beneficial to gas storage and the maximum in the net adsorption isotherm thus identifies the pressure of maximum adsorptive storage capacity compared to compression alone [23]. The left-hand side of Eq. 4 also indicates that net adsorption is defined without prior knowledge of the adsorbent pore volume (and hence $V_s$). Therefore, this formulation provides a direct means to evaluate adsorptive storage capacity at high pressures without introducing potential errors associated with pore volume estimates. By the same token, the right-hand side of Eq. 4 indicates that the conversion from net to absolute adsorption only requires knowledge of the combined volume $V_a + V_s$. For a microporous solid, the latter is the solid volume that includes the micropores [23] and can be estimated with excellent accuracy without probing the micropore space [3, 29]. It will be apparent from this study that for adsorbents containing mesopores, the conversion from net (or excess) to absolute adsorption is more problematic.

---

**Fig. 1** Fluid density as a function of the pressure for $N_2$ (77 K), Ar (87 K) and CO$_2$ (273 K and 313 K), as obtained from NIST Chemistry Webbook [28]. The dashed lines represent the vapor–liquid transition; the symbols represent the corresponding liquid densities at the boiling point.
### 3 Case study: CO$_2$ and CH$_4$ on activated carbon

It is highly instructive to first apply the concepts of excess and net adsorption in the context of a case study. To this end, we consider a literature data set of supercritical CO$_2$ and CH$_4$ adsorption on a commercial activated carbon that covers a sufficiently large pressure range ($p < 50$ MPa) [43]. The measured excess adsorption isotherms ($T = 328$ K) are shown in Fig. 2a as a function of pressure. Both CO$_2$ and CH$_4$ isotherms exhibit a maximum, because they represent excess quantities, and their decrease at large pressures is largely determined by the fluid-specific bulk phase behaviour. The CO$_2$ isotherm falls abruptly above $p \approx 8$ MPa, before levelling off at $p > 25$ MPa, thereby mirroring the dependency of the fluid bulk density on pressure (dashed line). The CH$_4$ isotherm shows a behaviour that is qualitatively similar, albeit with smoother gradients in the excess amount adsorbed (and, accordingly, bulk density). This difference can be attributed to the experimental temperature, which for CO$_2$ and CH$_4$ corresponds to $T/T_c = 1.1$ and $T/T_c = 1.7$, respectively. We note that the fluid-specific bulk behaviour is also responsible for the intersection of the CO$_2$ and CH$_4$ isotherms, which in fact disappears when the data are plotted as a function of the bulk density (Fig. 2b). In this last representation the adsorption isotherms maxima occur at similar density values ($\rho/\rho_c \approx 0.3$), further indicating that density is the most suitable variable to plot thermodynamic data at elevated pressures [36]. An analogous “crossover effect” has been observed for excess adsorption data measured with the same adsorbate at different temperatures, suggesting an apparent increase of the excess amount adsorbed with temperature [9].

Both CO$_2$ and CH$_4$ excess isotherms are positive over the pressure range investigated by the authors, with CO$_2$ showing larger adsorption than CH$_4$. Thus, in both cases adsorption is contributing to store more fluid in the pore space of the material, as compared to the amount of fluid that would exist there at the same temperature and pressure as bulk fluid. On the contrary, the isotherms represented in terms of the net amount adsorbed (Fig. 2c) become negative at large pressures (the crossing point with the abscissa is at $p \approx 12$ MPa for CO$_2$ and $p \approx 23$ MPa for CH$_4$). The definition of net adsorption indicates that beyond this pressure, gas storage in the absence of the solid adsorbent would therefore be more effective, because the bulk fluid has reached a sufficiently large density. To facilitate the comparison with the corresponding bulk fluid behaviour (dashed lines), the net adsorption data are represented here as amount per unit bulk volume by using a bulk density of the packing, $\rho_B = 507$ kg/m$^3$. At $T = 55^\circ$C, this threshold density takes a value of $\rho_B \approx 12$ mol/L (for CO$_2$) and $\rho_B \approx 10$ mol/L (for CH$_4$), respectively. While the location of the crossing point in Fig. 2c does not depend on $\rho_B$, the amount of fluid stored prior to that does, highlighting the importance of adsorbent formulation and packing. We also note that the position of the isotherm maxima of the excess and net adsorption isotherm are not equivalent, whereby only the latter provide the correct location of the maximum adsorptive storage relative to pure gas compression.

This case study shows that the two frameworks of excess and net adsorption provide consistent, yet complementary

---

**Fig. 2** Supercritical CO$_2$ and CH$_4$ adsorption at $T = 328$ K on activated carbon rods (Norit R1) represented as a excess amount adsorbed as a function of pressure; b excess amount adsorbed as a function of the reduced density; and c net amount adsorbed as a function of pressure. The data have been reproduced from [43]. In c, a bulk density of the packing, $\rho_B = 507$ kg/m$^3$ has been assumed. The dashed lines represent bulk density data obtained from the NIST chemistry WebBook [28], from where also the critical properties of the pure adsorbates have been obtained: $T_c$(CO$_2$) = 304.1 K, $\rho_c$(CO$_2$) = 7.37 MPa, $\rho_c$(CO$_2$) = 10.62 mol/L; $T_c$(CH$_4$) = 190.6 K, $\rho_c$(CH$_4$) = 4.60 MPa, $\rho_c$(CH$_4$) = 10.14 mol/L.
insight into some important elements of supercritical adsorption in porous solids. While the focus here has been on comparing two gases on an adsorbent largely dominated by microporosity (approx. 75% of the pore volume [1]), we will expand the evaluation in this study by considering three classes of materials characterised by distinct fractions of mesoporosity.

4 Materials and methods

We consider three adsorbent materials, namely a zeolitic imidazolate framework (ZIF), a mesoporous zeolite (MZ) and graphitised mesoporous carbon (MC). ZIF (Basolite Z1200 or ZIF-8, CAS Number 59061-53-9) and MC (CAS Number 1333-86-4) were purchased from Sigma-Aldrich and used as provided. MZ is a non-commercial hierarchical ZSM-5 zeolite with interconnected micro- (∼0.54 nm) and meso-pores (∼15 nm) that was kindly supplied for this study (see Acknowledgments). The gases used in this study were procured from BOC, namely CO$_2$, Ar and He at purities of 99.999%; for the supercritical adsorption experiments, CO$_2$ was purchased at a purity of 99.995%.

4.1 Subcritical adsorption

Table 1 Textural properties of the three adsorbents obtained upon fitting a NLDFT model to subcritical Ar (87K) adsorption data. SSA: specific surface area; $v_{\text{tot}}$: specific total pore volume; $\phi_2$: volume fraction of pores with width <2 nm; $\phi_{20}$: volume fraction of pores with width <20 nm

| Material | SSA (m$^2$/g) | $v_{\text{tot}}$ (cm$^3$/g) | $\phi_2$ (%) | $\phi_{20}$ (%) |
|----------|---------------|----------------------------|--------------|---------------|
| ZIF      | 1485          | 0.72                       | 70           | 95            |
| MZ       | 1399          | 0.48                       | 38           | 75            |
| MC       | 218           | 0.46                       | <0.1         | 92            |

Fig. 3 Ar (87K) adsorption isotherms measured in both adsorption (filled symbols) and desorption (empty symbols) mode on a ZIF, b MZ and c MC. The inset in each panel shows the cumulative pore size distribution (normalised by the total pore volume, $v_{\text{tot}}$). STP conditions are defined as 273.15 K and 1 atm. $p_0$ is the saturation pressure at the measurement temperature (∼760 torr).

Textural characterisation of the three adsorbents was carried out by physisorption analysis in a Quantachrome Autosorb iQ using Ar at 87K in the pressure range $1 \times 10^{-7} - 0.1$ MPa to obtain estimates of surface area, pore volume and pore volume distribution (Table 1, details provided in Section S1). The measured Ar adsorption isotherms are plotted in Fig. 3. ZIF shows a larger total amount adsorbed (580 cm$^3$(STP)/g) as compared to MZ and MC (360–380 cm$^3$(STP)/g), indicating a larger total pore volume ($v_{\text{tot}} \approx 0.7$ cm$^3$/g for ZIF vs. $v_{\text{tot}} \approx 0.5$ cm$^3$/g for both MZ and MC). Based on the IUPAC classification of physisorption isotherms [42], ZIF shows Type I(a) behaviour–typical of microporous solids, albeit with a small hysteresis loop of Type H2(a), indicating the presence of pores wider than 4 nm. For MZ the isotherm is a composite of Type I(a) ($P/P_0 < 0.6$) and Type IV(a) with hysteresis of Type H1 ($P/P_0 > 0.6$), which is characteristic of dual-porosity adsorbents with both micro- and meso-pores. MC shows Type IV(a) behaviour with hysteresis of Type H1, which is characteristic of mesoporous adsorbents with a narrow range of uniform mesopores. This characteristic features are reflected in the obtained cumulative pore size distribution curves, which are shown as inset in each panel of Fig. 3. Micropores ($d < 2$ nm) contribute to about 70% and 38% of the total pore volume of ZIF and MZ, respectively, while they are absent in MC. For the latter, approximately 90% of the total pore volume is found in pores of widths 4 – 20 nm. Therefore, the relative amount of mesoporosity increases in the order ZIF < MZ < MC. As given in Table 1, ZIF and MZ possess similar specific surface area (1400 – 1500 m$^2$/g), which is much larger than the value obtained for MC (approx. 200 m$^2$/g).
4.2 Supercritical adsorption

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 detailed experimental procedure, including the analysis of experimental uncertainties, is described in Section S2, while key parameter values are reported in Table 2. Briefly, this instrument provides high-resolution (10 \( \mu \)g) 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 [11]. 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. For (i) and (ii), the probing gas is charged into the MSB initially evacuated to obtain weight measurements (\( MP_1 \) and \( MP_2 \)) at several pressure points. Under the assumption of negligible gas adsorption, the following two equations apply:

\[
MP_1(\rho_b, T) = MP_{1,0} - \rho_b V_0 \tag{5a}
\]

\[
\rho_b = \frac{(MP_{2,0} - MP_{1,0}) - (MP_{2}(\rho_b, T) - MP_{1}(\rho_b, T))}{V_{sk}} \tag{5b}
\]

where \( MP_{1,0} \) and \( MP_{2,0} \) are the weight measurements under vacuum; \( V_{sk} \) is the volume of the calibrated sinker and \( V_0 \) is the volume of the lifted parts in measuring position 1. For experiment (i) \( V_0 = V_{net} \) and for experiment (ii) \( V_0 = V_{net} + V_s \), where \( V_{net} \) and \( V_s \) are the volume of the lifted metal parts and the skeletal volume of the adsorbent, respectively. In both cases, the volume \( V_0 \) is estimated from the weighted linear regression of \( MP_1 \) plotted as a function of \( \rho_b \). Measurements obtained from experiment (i) are presented in Fig. S1 and the value of \( V_{net} \) is reported in Table 2 together with its uncertainty, \( u(V_{net}) \). Estimates of \( V_s \) and \( u(V_s) \) obtained in the experiments with adsorbent and Helium as probing gas are also presented in Table 2 and will be discussed in Section 5.

The adsorption isotherms were measured by charging the adsorbate (\( CO_2 \)) into the MSB initially evacuated to obtain weight measurements at several pressure points. The net mass adsorbed is computed as:

\[
m_{net} = m_a - \rho_b(V_s + V_a) \tag{6a}
\]

\[
m_{net} = MP_1(\rho_b, T) - MP_{1,0} + \rho_b V_{net} \tag{6b}
\]

while the following equation is used to compute the excess mass adsorbed:

\[
m_{ex} = m_a - \rho_b V_a \tag{7a}
\]

\[
m_{ex} = MP_1(\rho_b, T) - MP_{1,0} + \rho_b(V_{net} + V_s) \tag{7b}
\]

where the density of the bulk adsorptive \( \rho_b \) at each pressure point is obtained from Eq. 5a, while \( MP_{1,0} \), \( V_{net} \) and \( V_s \) are known from experiments (i) and (ii). The experimental results of the adsorption experiments are reported in terms of the molar net (or excess) amount adsorbed per unit mass of adsorbent:

\[
n_i = \frac{m_i}{M_m m_s} \tag{8}
\]

where the subscript \( i \) refers to net or ex, \( M_m \) is the molar mass of the adsorbate (for \( CO_2 \), \( M_m = 44.01 \) g/mol) and \( m_s \) is the mass of adsorbent.

## 5 Results

### 5.1 Net adsorption isotherms

The experimental \( CO_2 \) net adsorption data are plotted in Fig. 4 as a function of the molar bulk density, \( \rho \), for

| Parameter | ZIF | MZ | MC |
|-----------|-----|----|----|
| \( V_{sk} \pm u(V_{sk}) \) cm\(^3\) | 4.364 ± 0.002 | | |
| \( V_{net} \pm u(V_{net}) \) cm\(^3\) | 1.4195 ± 0.0001 | | |
| Adsorbent | | | |
| \( T_{reg}/K \) | 473 | 573 | 393 |
| \( m/g \) | 0.6840 | 1.144 | 1.007 |
| \( V_c/cm^3 \) | 0.451 | 0.451 | 0.599 |
| \( u(V_c)/cm^3 \) | 0.001 | 0.003 | 0.001 |
| Helium gravimetry | | | |
| \( T/\degree C \) | 120 | 80 | 80 |
| \( p/MPa \) | 1–20 | 0.5–12 | 0.5–20 |
| \( CO_2 \) adsorption experiment | | | |
| \( T/K \) | 308, 313 | 308 | 308 |
| \( p/MPa \) | 0.02–25 | 0.02–21 | 0.02–21 |
| \( u(n_{net})/(\mu mol/g) \) | 1–17 | 1–12 | 1–14 |
| \( u(n_{ex})/(\mu mol/g) \) | 1–32 | 1–47 | 1–31 |
measurements carried out at $T = 308$ K on (a) ZIF, (b) MZ and (c) MC. The three isotherms show a similar behaviour: after the initial increase in $n_{\text{net}}$, the experimental data outline a maximum and fall off with a further increase in the bulk density. Yet, the maximum net amount adsorbed, the density at which $n_{\text{net}} = 0$ and the shape of the descending part of the isotherm differ among the three adsorbents, reflecting the characteristic features of their pore volume distribution. In particular, the isotherms measured on both ZIF and MZ are characterised by a steep initial increase and a sharp maximum, which can be attributed to the presence of micropores. Their contribution to adsorption is also reflected in the location of the crossing point with the abscissa, $\rho(n_{\text{net}} = 0)$, which decreases in the order ZIF (9 mol/L) > MZ (8 mol/L) > MC (6 mol/L). This trend indicates that an adsorbent with a large amount of microporosity features a wider pressure range, where gas adsorption is beneficial to gas storage. A similar decreasing trend is observed for the measured isotherm’s maximum, namely ZIF (6.7 mmol/g) > MZ (2.5 mmol/g) > MC (0.8 mmol/g), which directly relates to the material’s storage capacity. As anticipated previously, the location where $n_{\text{net}} = 0$ is unaffected by the choice of the specific quantity used to report adsorption (moles per unit mass or per unit volume) and the observed trend has therefore general validity. However, the positive branch of the isotherm, including the maximum net amount adsorbed per unit volume, does depend on the bulk density of the material, which may differ among the three adsorbents considered here. Accordingly, any further calculation of the gas storage capacity, including the comparison of different adsorbents, should be carried out on a volume basis.

A dashed line is plotted in each panel of Fig. 4 that has been obtained upon fitting the adsorption data measured at large bulk density values ($\rho > 15$ mol/L). As a means for comparison, solid lines are also shown in each plot with a slope $-\left(\frac{V_s}{m_s} + \frac{V_a}{m_a}\right)$, corresponding to the adsorbent’s specific skeletal volume. The larger value of the slope of the line fitted to the experimental data reflects the additional contribution of the adsorbed phase to buoyancy during the gravimetric adsorption experiment. In fact, from the definition of the net amount adsorbed, Eq. 6, the slope of the isotherm should approach the value $-\left(\frac{V_s}{m_s}\right)$ once adsorption saturation is reached. For the microporous ZIF, the descending part of the isotherm follows by and large the trend outlined by the dashed line, indicating that this condition may have indeed been attained. On the contrary, the isotherms measured on MZ and MC approach the trend-line only at large density values. The observed divergence of the experimental data from linearity is an indication of the distinct pore-filling behaviour of the adsorbed phase in micro- and meso-pores at supercritical conditions. The evident change in the slope observed for MZ at approximately $\rho = 7.5$ mol/L may be traced back to the characteristic dual-porosity structure of this material. These observations highlight the practical difficulty of applying this graphical approach to the interpretation of supercritical adsorption data measured on materials with a significant amount of mesoporosity. We will further expand on this point when discussing the excess adsorption data, which reveal these effects more strongly.

### 5.2 Helium gravimetry and adsorbent density

The results of the Helium gravimetry experiments on the three adsorbents are presented in Fig. 5, where the measured weight is plotted as a function of the gas bulk density. The three materials outline three distinct straight lines with...
slope $b = -(V_{\text{met}} + V_{s})/m_{s}$, thereby reflecting a difference in their specific skeletal volume. The constant $b$ was obtained by the method of weighted least squares, where the uncertainty in the measured weight, $w(MP_{1})$, was accounted for; the uncertainty in $b$ was then obtained by error propagation in terms of $w(MP_{1})$ values (see e.g. [16]). For each adsorbent, estimates of $V_{s}$ have been computed from the constant $b$ and are reported in Table 2, together with their uncertainty, $u(V_{s})$. It can be seen that $u(V_{s})/V_{s}$ is generally less than 0.5%, demonstrating that the material skeletal density, $\rho_{s}$, can be determined precisely. For the three adsorbents, the following values were obtained: $\rho_{s} = 1.517 \pm 0.003$ g/cm$^3$ (ZIF), $\rho_{s} = 2.532 \pm 0.006$ g/cm$^3$ (MZ) and $\rho_{s} = 1.681 \pm 0.008$ g/cm$^3$ (MC). These values compare favourably with those observed in the literature on either equivalent or similar adsorbent materials, e.g. $\rho_{s} = 1.482 \pm 0.002$ g/cm$^3$ for ZIF-8 [26], $\rho_{s} = 2.349 \pm 0.004$ g/cm$^3$ for ZSM-5 [26] and $\rho_{s} = 1.686$ g/cm$^3$ for the mesoporous carbon [34]. The observed differences are attributable among other aspects to the degree of sample activation. We note in fact that while the individual Helium gravimetry experiment yields a precise estimation of $\rho_{s}$, relative differences of approximately 2–3% were observed in this study between repeated experiments on the same sample, irrespective of the adsorbent used. These measurements are also shown in Fig. 5 (filled vs. empty symbols) and were carried out after the sample had been newly activated (e.g. after the completion of the adsorption experiment). While in Fig. 5 the differences between these repeated runs may appear to be negligibly small, they would yield small, yet noticeable differences in the computed excess amount adsorbed at large bulk densities. Without loss of generality, we can safely assume that the uncertainty in the computed excess amount adsorbed $u(n_{ex}) \approx \rho_{b} u(V_{s})/(M_{m} m_{s})$, where $u(V_{s})$ now refers to the difference in $V_{s}$ between repeated runs. It follows that $u(n_{ex}) = 0.1–0.2$ mmol/g at $\rho_{b} = 10$ mol/L and $u(n_{ex}) = 0.2–0.4$ mmol/g at $\rho_{b} = 20$ mol/L. These results also highlight the importance of regenerating the sample in situ and of carrying out the Helium measurement just before the adsorption experiment. Yet, the accurate estimation of the sample specific skeletal volume in microporous solids is still a matter of debate [3, 10, 14] and our observations extend this discussion to include adsorbents with mesopores.

### 5.3 Excess adsorption isotherms

The excess adsorption isotherms measured on the three adsorbents at $T = 308$ K are plotted in Fig. 6 as a function of the molar bulk density, $\rho$. These have been obtained by conversion of the net adsorption data using the adsorbent’s skeletal volume obtained by Helium gravimetry. The three isotherms are positive over the pressure range investigated in this study, indicating that the (average) density of the adsorbed phase is larger than the density of the bulk fluid. The excess isotherms reveal more strongly the pore-size dependent adsorption behaviour already indicated by the analysis of the net adsorption isotherms. With increasing fraction of mesoporosity, the location of the isotherm’s maximum moves towards larger bulk density values, namely 2.6 mol/L (ZIF)< 4.6 mol/L (MZ) < 6.7 mol/L (MC). The ZIF and MC excess isotherms are characterised by a narrow maximum, thereby reflecting their rather uniform pore-size distribution, centred at approximately 1–2 nm and 10 nm, respectively. The broader maximum outlined by the isotherm measured on MZ is thus the direct manifestation of its dual-porosity structure that encompasses both micropores and (small) mesopores. ZIF features again the largest amount adsorbed ($n_{ex} \approx 8$ mmol/g), while lower, yet similar, values are observed for MZ and MC ($n_{ex} \approx 3.5$ mmol/g). In light of the textural parameter values reported in Table 1, this observation indicates that surface area is subordinate to pore volume in contributing to the extent of excess adsorption.

Another notable feature of the isotherms shown in Fig. 6 is the characteristic shape beyond their maximum. To facilitate the comparison between the three adsorbents, a dashed line is plotted in each panel of the figure that has been fitted to the data points at large bulk densities ($\rho > 15$ mol/L, corresponding to the last 4–5 points). These lines are thus equivalent to those shown in Fig. 4, but their slope differs...
by an amount equivalent to \(-V_s/m_s\) (Table 2). By analogy with the interpretation carried out on the net adsorption isotherms, the slope of the excess isotherm at adsorption saturation can thus be used to estimate the specific volume of the adsorbed phase [20]. The obtained values are \(V_a/m_s = 0.396 \text{ cm}^3/\text{g} \) (ZIF), \(V_a/m_s = 0.192 \text{ cm}^3/\text{g} \) (MZ) and \(V_a/m_s = 0.138 \text{ cm}^3/\text{g} \) (MC). We note that when the deviations in the measured value of \(\rho \) between repeated runs are taken into account (2–3%, see Section 5.2), these estimates of \(V_a/m_s\) may vary of up to 15–30%, with the largest uncertainty being observed with the mesoporous materials.

6 Discussion

Despite the advances in the accuracy of experimental techniques and the increased availability of experimental data, the actual mechanism of supercritical gas adsorption in porous materials remains elusive. On the one hand, interlaboratory studies continue to be conducted that aim at developing the standardisation required to obtain reliable high-pressure adsorption isotherms (see [25, 27] and references therein). On the other hand, there are still obvious challenges associated with the interpretation of the experimental isotherms themselves, which can be reported in terms of net and excess adsorption. While the meaning of these two formulations has been discussed at length [3, 14, 23, 29], their comparison by means of experimental data across a range of adsorbent morphologies has been lacking so far. The main objective of this paper was to fill this gap. To this end, we have adopted a systematic approach to the analysis of high-pressure adsorption isotherms measured on three morphologically distinct adsorbents by considering both net and excess formulations. Our intention has been to provide a detailed description of the entire analysis protocol, including the calibration experiments using Helium as the probing gas (with and without adsorbent in the balance) and the rigorous evaluation of experimental uncertainties of both the net and excess amount adsorbed. We hope that this paper will assist the experimental adsorption practitioner in developing their own understanding of the challenges associated with high pressure measurements. We also expect that these observations will provide new insight as to which theoretical adsorption model may be more suitable in correlating the experimental data. In the following, we evaluate the classical graphical approach for the analysis of excess adsorption isotherms and present a method to compute the absolute amount adsorbed that uses information from the independently measured pore volume distributions. Moreover, in the spirit of further improving standardisation protocols, we attempt to rationalise the results in a manner analogous to the classification of physisorption isotherms.

6.1 Absolute adsorption

The actual or absolute amount adsorbed in the pores of the material can be obtained by correcting the excess amount adsorbed with an independent estimation of the volume of the adsorbed phase, i.e. \(n_a = n_{ex} + \rho \nu_a\). In its simplest implementation, this correction uses an estimate of the pore volume, which can be obtained by textural analysis (see Section 4.1). If the solid is microporous, pore filling is attained at relatively low density values, thereby providing a means to compute the absolute amount adsorbed [23]:

\[
n_a = n_{ex} + \rho \nu \phi_2
\]  

(9)
where \( v_{\text{tot}} \phi_2 \) is the specific micropore volume of the adsorbent. The primary limitation of Eq. 9 is its extension to systems with mesopores, which contribute to the adsorption process, but are unlikely to become fully saturated at supercritical conditions. Early findings by Specovius and Findenegg [36] have demonstrated that thick adsorbed layers can be formed in small mesopores (approx. 10 nm in width) over a temperature range of the order of 10 K above \( T_c \) and upon approaching the critical density of the fluid, \( \rho_c \). Yet, the same authors have estimated that these layers may only reach up to 5 molecular diameters of adsorbate molecules oriented parallel to the pore surface. Therefore, the estimation of the absolute amount adsorbed in systems with mesopores depends on knowing not only how the adsorbed phase may spread over a range of pore sizes, but also its dependency on the bulk density. Here, we conceptualise a pore-filling process whereby micropores (width < 2 nm) and very small mesopores (width < 3 nm) are readily filled at low bulk densities (\( \rho < 2 \text{ mol/L} \)), while small mesopores (width < 11–12 nm) experience near-critical condensation starting at \( \rho \approx 5 \text{ mol/L} \). The mathematical expression adopted to represent this process and its application to the three adsorbents considered in this study are described in Section S3. The absolute adsorption isotherms obtained upon application of this approach are shown in Fig. 7.

It is instructive to compare these results with those described in Sect. 5.3, where we adopted a graphical approach to interpret the descending part of the excess adsorption isotherm. In this model, if adsorption saturation were reached at high pressures, a plot of \( n_a \) vs. \( \rho \) should give a straight line with slope \(-V_a/m_c\). For ZIF, MZ and MC the obtained estimates of \( V_a/m_c \) correspond to approximately 55%, 40% and 30% of the total pore volume of the adsorbent, \( v_{\text{tot}} \), respectively (Table 1). The linearity of the ZIF excess isotherm beyond its maximum would suggest that the pores which drive the adsorption process in this material are filled entirely with the adsorbed phase at bulk density values \( \rho > 5 \text{ mol/L} \). The absolute isotherm shown in Fig. 7 was constructed by assuming that this pore volume includes all pores with width smaller than 3 nm (see also the inset plot in Fig. 3a). On the contrary, the estimate of \( V_a/m_c \) obtained for ZIF corresponds to the volume found in pores with width below 1.5 nm, yielding approximately 80% of the micropore volume (= \( v_{\text{tot}} \phi_2 \)) and only 55% of the total pore volume. Based on the considerations above, one would expect the adsorbed phase to occupy the entire pore volume available, as it has been previously observed for CO\(_2\) adsorption on 13X zeolite (> 95% micropore filling [29]). The micropore structure of zeolites is determined by the crystal lattice and it features micropores of width 1.2 nm with no distribution of pore sizes. On the contrary, ZIF possesses a distribution of pores over a broader range, including micropores and narrow mesopores (< 2.5 nm)–possibly limiting the degree of micropore filling. These observations highlight the difficulty in applying the graphical approach to estimate absolute adsorption with microporous materials characterised by a distribution of pore sizes.

The absence of micropores and/or the presence of an even larger amount of (larger) mesopores complicate the interpretation of the results obtained for MZ and MC and challenge the application of the graphical approach. While the estimate of \( V_a/m_c \) obtained for MZ matches the volume of micropores (= \( v_{\text{tot}} \phi_2 \)), the characteristic shape of the excess isotherm clearly shows that mesopores do also contribute to the adsorption process. MZ doesn’t have a distribution of micropores (see the inset plot in Fig. 3b). The absolute adsorption isotherm shown in Fig. 7 was obtained upon assuming that micropores are indeed readily filled at low bulk density values (\( \rho < 2 \text{ mol/L} \)), but that small mesopores (width less than 12 nm) experience condensation for \( \rho > 5 \text{ mol/L} \), reaching saturation at \( \rho \geq \rho_c \). The resulting absolute isotherm has the expected “Type I” shape, which would be impossible to obtain upon direct application of Eq. 9. A similar argument holds for MC, where in the absence of microporosity, the observed adsorption process at elevated pressures is interpreted as the result of near-critical condensation in mesopores with width less than 12 nm. The cumulative pore volume found in these mesopores corresponds to approximately 66% of the total pore volume and is substantially larger than the volume of the adsorbed phase.
estimated from the graphical method (\(\approx 0.3 v_{\text{tot}}\)). While the graphical approach is obviously inadequate for mesoporous materials, care should also be taken in adopting our proposed method to estimate the absolute adsorption isotherms. A conceptualisation where adsorbed molecules are considered to form as if they were a condensed phase of density \(\rho_a\) and volume \(V_a\) may be too simplistic [20], because it tacitly assumes that these properties are averaged over the entire mesopore size range and also neglects density profiles within pores themselves.

6.2 Towards a classification?

The classification of adsorption isotherms according to their characteristic shape is a tool of practical value, because it provides a link between the macroscopic behaviour observed experimentally and the textural properties of the adsorbent. However, the IUPAC classification has been traditionally based on the notion of absolute adsorption and does not explicitly consider excess (or net) adsorption. Supercritical adsorption experiments reported in the literature on both crystalline and ordered porous materials provide direct evidence of adsorption behaviour, which can be ascribed to a characteristic distribution of micro- and meso-pores. Some of the traditional adsorbent morphologies that have been investigated include: zeolite crystals, where adsorption is mainly within the micropores [29]; mesoporous silicas, such as Controlled Pore Glass (CPG) [33, 41], SBA-15 [9, 40] and MCM-41 [31]; and mesoporous carbons [1, 36]. These ordered porous solids can be considered as the building blocks for more complex porous structures, including hierarchical adsorbents [37] or disordered materials (e.g. activated carbons), which feature pores across the entire spectrum of sizes. As such, they also represent important reference materials for the textural characterisation of industrial adsorbents by physisorption [8] and for the development of rigorous models with predictive ability at high pressures [12].

With analogy to the classic IUPAC classification [42], we propose to group supercritical adsorption isotherms into three types (Fig. 8). In this endeavour we have solely considered the excess adsorbed amount, because it remains by and large the most widely adopted formulation to report supercritical adsorption isotherms. In this context, we agree with the recommendation that the adsorbent skeletal volume (and its uncertainty) should always be reported alongside the excess adsorption data, so as to enable their conversion to net adsorption [3, 23].

The Type E1 isotherm is given by microporous solids and is the direct counterpart of the Type I isotherm in the original classification of sub-critical isotherms. The adsorption process is governed by the filling of the accessible micropore volume. The enhanced adsorbent-adsorptive interactions in narrow micropores results in the steep initial uptake and micropore filling at \(\rho_b/\rho_c \ll 1\). The isotherm is thus characterised by an early maximum (M) followed by a linear descending part (starting at point L) with a slope approximately equal to \(\rho_c v_{\text{tot}} \phi_2\). Materials featuring a distribution of wider micropores and narrow mesopores (< \(\sim 2.5\) nm), e.g. activated carbons, also belong to this category, albeit they may show slight deviations from linearity (see Fig. 2).

The Type E2 isotherm is given by mesoporous adsorbents and is the direct counterpart of the Type IV isotherm in the original classification of sub-critical isotherms, albeit without the appearance of a hysteresis loop. Compared to Type E1, the isotherm’s maximum (M) is shifted towards higher bulk density values and its location depends on the average pore size, approaching \(\rho_b/\rho_c = 1\) for large mesopores (>\(\sim 20\) nm) [33]. For measurements at near-critical conditions \((T - T_c = 10\) K), the isotherm shows the distinctive features of multilayer adsorption on the mesopore walls, namely an inflection point (B) and a marked dependence of

![Fig. 8](image)

Fig. 8 Classification of supercritical isotherms in terms of the excess amount adsorbed, \(m_{\text{ex}}\), plotted as a function of the reduced density, \(\rho_b/\rho_c\).
the maximum excess adsorption on temperature [36]. The descending part of the isotherm beyond the maximum is curved; as such, the determination of the adsorbed phase properties is not as straightforward as for Type E1 and a rigorous quantitative discussion of the excess adsorption isotherm would require knowledge of the density profile in the mesopores of the material.

The Type E3 isotherm is given by the adsorption of supercritical gases on micro-mesoporous materials with fairly large mesopores (>~20 nm) and has been observed in this study for the dual-porosity MZ. The isotherm shows features of both Type E1 and E2: it is characterised a steep initial uptake at $\rho_c/\rho_c \ll 1$ followed by a broad maximum (located somewhere between Type E1 and Type E2) and a curved descending part. At sufficiently large bulk density values, the isotherm falls linearly with density with a slope of value $\geq \rho_c V_{\text{tot}} \phi_2$.

7 Concluding remarks

The analysis of net and excess adsorption isotherms measured on morphologically distinct adsorbents shows that these two formulations offer consistent, yet complementary insight on the supercritical adsorption process. While net adsorption provides for a more direct and non-ambiguous means to report adsorption data, excess adsorption is inherently more sensitive to the behaviour of supercritical adsorbed phase, which is adsorbent-specific. Yet, the ability to measure the adsorbent’s skeletal volume accurately is at the basis of its definition and can represent a source of uncertainty in high-pressure adsorption measurements. We have presented in this paper a detailed step-by-step analysis of high-pressure adsorption experiments, with the aim of providing some useful guidance on good reporting practice of adsorption data and their uncertainty.

We have also discussed that there is a profound analogy between unary adsorption isotherms measured at sub- and super-critical conditions, when the latter are acquired at a temperature not too far from the critical point ($T - T_c < 10$ K). The ability to unravel pore-size dependent adsorption behaviour from supercritical adsorption isotherms represents an exciting prospect for the textural characterisation of porous solids. Arguments in favour of extending this practice beyond low-pressure cryogenic adsorption experiments include the need to mimic the conditions of the specific industrial application and to validate the obtained pore-structural information over a range of thermodynamic conditions.

Supplementary Information The online version of this article (https://doi.org/10.1007/s10450-021-00313-z) contains supplementary material, which is available to authorized users.

Acknowledgements We thank Mariya Shamzh (Czech Academy of Sciences, J. Heyrovsky Institute of Physical Chemistry, Czech Republic) for supplying the mesoporous zeolite used in this study. HA is grateful for the financial support provided by the Marit Mohn Scholarship at the Department of Chemical Engineering, Imperial College London. JH was funded by a departmental scholarship from the Department of Chemical Engineering, Imperial College London.

Data availability The experimental net and excess adsorption isotherms associated with this work may be obtained from the Imperial College London Research Data repository using the following link: https://doi.org/10.14469/hpc/7543 (embargoed until paper acceptance).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Ansari, H., Joss, L., Hwang, J., Trusler, J.M., Maitland, G., Pini, R.: Supercritical adsorption in micro-and meso-porous carbons and its utilisation for textural characterisation. Microporous Mesoporous Mater. 308, 110537 (2020)
2. Blankenship, T.S., H., Balahmar, N., Mokaya, R.: Oxygen-rich microporous carbons with exceptional hydrogen storage capacity. Nat. Commun. 8(1), 1–12 (2017)
3. Brandani, S., Mangano, E., Sarkisov, L.: Net, excess and absolute adsorption and adsorption of helium. Adsorption 22(2), 261–276 (2016)
4. Busch, A., Bertier, P., Gensterblum, Y., Rother, G., Spiers, C., Zhang, M., Wentinck, H.M.: On sorption and swelling of co$_2$ in clays. Geomech. Geophy. Geo-energy Geo-resources 2(2), 111–130 (2016)
5. Casas, N., Schell, J., Joss, L., Mazzotti, M.: A parametric study of a PSA process for pre-combustion co$_2$ capture. Sep. Purif. Technol. 104, 183–192 (2013)
6. Chareonsuppanimit, P., Mohammad, S.A., Robinson, R.L., Jr., Gase, K.A.: High-pressure adsorption of gases on shales: measurements and modeling. Int. J. Coal Geol. 95. 34–46 (2012)
7. Connolly, B.M., Aragones-Anglada, M., Gandara-Loe, J., Danaf, N.A., Lamb, D.C., Mehta, J.P., Vulpe, D., Wuttke, S., Silvestre-Albero, J., Moghadam, P.Z.: Tuning porosity in macroscopic monolithic metal-organic frameworks for exceptional natural gas storage. Nat. Commun. 10(1), 1–11 (2019)
8. Cychosz, K.A., Guillet-Nicolas, R., García-Martínez, J., Thommes, M.: Recent advances in the textural characterization of
1. Di Giovanni, O., Dörfler, W., Mazzotti, M., Morbidelli, M.: Adsorption of supercritical carbon dioxide on silica. Langmuir 17(14), 4316–4321 (2001)

10. Do, D., Do, H.: Appropriate volumes for adsorption isotherm studies: the absolute void volume, accessible pore volume and enclosing particle volume. J. Colloid Interface Sci. 316(2), 317–330 (2007)

11. Dreisbach, F., Lösch, H.: Magnetic suspension balance for simultaneous measurement of a sample and the density of the measuring fluid. J. Therm. Anal. Calorim. 62(2), 515–521 (2000)

12. Fang, H., Findley, J., Muraro, G., Ravikovitch, P.I., Sholl, D.S.: A strong test of atomically detailed models of molecular adsorption in zeolites using multilaboratory experimental data for co$_2$S adsorption in ammonium ZSM-5. J. Phys. Chem. Lett. 11(2), 471–477 (2019)

13. Gumma, S., Talu, O.: Gibbs dividing surface and helium adsorption. Adsorption 9(1), 17–28 (2003)

14. Gumma, S., Talu, O.: Net adsorption: A thermodynamic framework for supercritical gas adsorption and storage in porous solids. Langmuir 26(22), 17013–17023 (2010)

15. Hocker, T., Rajendran, A., Mazzotti, M.: Measuring and modeling supercritical adsorption in porous solids. Carbon dioxide on 13X zeolite and on silica gel. Langmuir 19(4), 1245–1267 (2003)

16. Hwang, J., Joss, L., Pini, R.: Measuring and modelling supercritical adsorption of co$_2$S and ch$_4$S on montmorillonite source clay. Microporous Mesoporous Mater. 273, 107–121 (2019)

17. Maggs, F., Schwabe, P., Williams, J.: Adsorption of helium on carbons: influence on measurement of density. Nature 186(4729), 956–958 (1960)

18. Malbrunot, P., Vidal, D., Vermesse, J., Chahine, R., Bose, T.K.: Adsorbent helium density measurement and its effect on adsorption isotherms at high pressure. Langmuir 13(3), 539–544 (1997)

19. Mazzotti, M., Pini, R., Storti, G.: Enhanced coal bed methane recovery. J. Supercrit. Fluids 47(3), 619–617 (2009)

20. Menon, P.G.: Adsorption at high pressures. Chem. Rev. 68(3), 277–294 (1968)

21. Micromeritics: ASAP 2020 Operator’s Manual, 4.01 edn (2011)

22. Moon, D.K., Lee, D.G., Lee, C.H.: H$_2$ pressure swing adsorption experiments and theoretical models. Langmuir 13(11), 4316–4321 (2001)

23. Myers, A.L., Monson, P.A.: Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis. Adsorption 20(4), 591–622 (2014)

24. Neimark, A.V., Ravikovitch, P.I.: Calibration of pore volume in adsorption experiments and theoretical models. Langmuir 13(19), 5148–5160 (1997)

25. Nguyen, H.G.T., Espinal, L., van Zee, R.D., Thomess, M., Toman, B., Hudson, M., Mangan, E., Brandani, S., Broom, D., Benham, M.J., Dailly, A., Dreisbach, F., Edubilli, S., Gumma, S., Möllmer, J., Lange, M., Mays, T.J., Shigeoka, T., Yamakita, S., Hakuman, M., Nakada, Y., Nakai, K., Hwang, J., Pini, R., Jiang, H., Ebner, A.D., Nicholson, M.A., Ritter, J.A., Farrando-Pérez, J., Cuadrado-Collados, C., Silvestre-Albero, J., Tampaxis, C., Steriotis, T., Římnáčová, D., Švábová, M., Vorokhta, M., Wang, H., Bovens, E., Heymans, N., De Weireld, G.: A reference high-pressure CH$_4$S adsorption isotherm for zeolite y: results of an interlaboratory study. Adsorption 26(8), 1253–1266 (2020)

26. NIST: NIST Chemistry WebBook. http://webbook.nist.gov/chemistry (2018)

27. Pini, R.: Interpretation of net and excess adsorption isotherms in microporous adsorbents. Micropor. Mesoporous Mater. 187, 40–52 (2014)

28. Quantachrome Instruments: Autosorb iQ/ASiQwin Operating Manual, 2.0 edn (2011)

29. Reiser, S., Türk, M.: Influence of temperature and high-pressure on the adsorption behavior of scco$_2$S on MCM-41 and SBA-15. J. Supercrit. Fluids 144, 122–133 (2019)

30. Rosi, N.L., Eckert, J., Eddaoudi, M., Vodak, D.T., Kim, J., O’Keeffe, M., Yaghi, O.M.: Hydrogen storage in microporous metal-organic frameworks. Science 300(5622), 1127–1129 (2003)

31. Rother, G., Krukowski, E.G., Wallacher, D., Grimm, N., Bodnar, R.J., Cole, D.R.: Pore size effects on the sorption of supercritical co$_2$S in mesoporous CPG-10 silica. J. Phys. Chem. C 116(11), 917–922 (2012)

32. Sigma Aldrich: (2020). https://www.sigmaaldrich.com/catalog/product/ALDRICH/699640

33. Sircar, S.: Measurement of gibbsian surface excess. AIChE J. 47(5), 1169–1176 (2001)

34. Specovius, J., Findenegg, G.: Study of a fluid/solid interface over a wide density range including the critical region. i. surface excess of ethylene/graphite. Berichte der Bunsgesellschaft für physikalische Chemie 84(7), 690–696 (1980)

35. Szczepniak, B., Choma, J., Jaroniec, M.: Major advances in the development of ordered mesoporous materials. Chem. Commun. 56(57), 7836–7848 (2020)

36. Talu, O., Myers, A.L.: Molecular simulation of adsorption: Gibbs dividing surface and comparison with experiment. AIChE J. 47(5), 1160–1168 (2001)

37. Tao, L., Xiao, P., Qader, A., Webley, P.A.: Co$_2$S capture from high concentration co$_2$S natural gas by pressure swing adsorption at the co2crc otway site, australia. Int. J. Greenh. Gas Control 83, 1–10 (2019)

38. Tatsuda, N., Goto, Y., Setoyama, N., Fukushima, Y.: Adsorption of carbon dioxide on mesoporous silicas near the critical temperature. Adsorp. Sci. Technol. 23(9), 763–776 (2005)

39. Thommes, M., Findenegg, G.H.: Pore condensation and critical-point shift of a fluid in controlled-pore glass. Langmuir 10(11), 4270–4277 (1994)

40. Thommes, M., Kaneko, K., Neimark, A.V., Olivier, J.P., Rodriguez-Reinoso, F., Rouquerol, J., Sing, K.S.: Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure Appl. Chem. 87(9–10), 1051–1069 (2015)

41. Ustinov, E.A., Do, D.D., Herbst, A., Staudt, R., Harting, P.: Modelling of gas adsorption equilibrium over a wide range of pressure: A thermodynamic approach based on equation of state. J. Colloid Interface Sci. 250(1), 49–62 (2002)

42. Zhou, Y., Zhou, L.: Fundamentals of high pressure adsorption. Langmuir 25(23), 13461–13466 (2009)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.