**Digital Adsorption: 3D Imaging of Gas
Adsorption Isotherms by X-ray Computed
Tomography**

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Abstract

We report on a novel approach for the measurement of gas adsorption in microporous solids using X-ray computed tomography (CT) that we refer to as *digital adsorption*. Similar to conventional macroscopic methods, the proposed protocol combines observations with an inert and an adsorbing gas to produce equilibrium isotherms in terms of the truly measurable quantity in an adsorption experiment, namely the surface excess. Most significantly, X-ray CT allows probing the adsorption process in three dimensions, so as to build spatially-resolved adsorption isotherms with a resolution of approximately 10 mm^3 within a fixed-bed column. Experiments have been carried out at 25°C and in the pressure range 1–30 bar using CO_2 on activated carbon, zeolite 13X and glass beads (as control material), and results are validated against literature data. A scaling approach was applied to analyze the whole population of measured adsorption isotherms (~ 7600), leading to single universal adsorption isotherm curves that are descriptive of all voxels for a given adsorbate-adsorbent system. By analyzing the adsorption heterogeneity at multiple length scales (1 mm^3 to 1 cm^3), packing heterogeneity was identified as the main contributor for the larger spatial variability in the adsorbed amount observed for the activated carbon rods as compared to zeolite pellets. We also show that this technique is readily applicable to a large spectrum of commercial porous solids, and that it can be further extended to weakly adsorbing materials with appropriate protocols that reduce measurement uncertainties. As such, the obtained results prove the feasibility of digital adsorption and highlight substantial opportunities for its wider use in the field of adsorptive characterization of porous solids.

1 Introduction

Gas adsorption at the interface to a solid occurs in the presence of porous materials with high surface area, particularly nanoporous solids. This phenomenon is exploited in several processes of the chemical and energy industries; examples of relevant technologies include

gas separation processes, such as air separation,¹ CO₂ capture² and natural gas upgrading,³ heterogeneous catalysis, adsorption based heat pumps for solar cooling systems,⁴ hydrogen storage,⁵ and CO₂ storage in the subsurface with or without the recovery of hydrocarbons, such as during coalbed methane⁶ or shale gas production.⁷ Because it strongly depends on the geometric and chemico-physical properties of pore surfaces, gas adsorption has also developed into a well-established tool for the structural characterization of the porous solids themselves. High-resolution experimental protocols are nowadays available that profitably combine a range of sub-critical gases and that exploit their specific phase-behavior under confinement.^{8,9} From the interpretation of a full adsorption/desorption isotherm, material-specific metrics are extracted (e.g., surface area, pore volume, pore size distribution) that are needed for the design and optimization of the processes described above. Most significantly, progress in materials engineering research continues to trigger advances in this field, such as for the textural characterization of new hierarchical adsorbent materials by physical adsorption¹⁰ and through the development of reliable molecular-scale models for data interpretation.¹¹ Despite these continued efforts, gas adsorption measurements still result in average properties of the given sample and they fail at uncovering variabilities that are known to exist over the continuum of relevant length scales. Recent developments in spectroscopic techniques (*chemical imaging*, see refs.^{12,13} for a comprehensive review on the topic) have uncovered heterogeneities in terms of structure, composition and reactivity among single adsorbent- and catalyst-particles. While these heterogeneities are inevitably linked to both transport and adsorption properties of the porous particle, inter-particle heterogeneities within a particle batch, and batch-to-batch variations are expected to complicate matters even further. In this context, we contend that the ability to couple conventional adsorption experiments with the simultaneous imaging of the densification process could pave the way towards (i) the multi-dimensional, multi-scale characterization of microporous solids and (ii) a comprehensive understanding of the adsorption process over a range of relevant length-scales. We refer to this new technology as *digital adsorption*. The latter is attractive

from mainly two perspectives: on the one hand, because gas adsorption is mostly limited to pores with dimensions of few nanometres, the ability to quantify it would extend the range of operability of those imaging techniques that are limited in their spatial resolution to a few microns and above. On the other hand, the use of the imaging technique itself extends conventional gas adsorption techniques to multiple dimensions, hence providing for an augmented characterization of microporous solids, while enabling *in-situ* and *operando* evaluation of adsorption-based processes.

Among the plurality of available imaging techniques, most advances in the area of adsorption over the last decade have been achieved through the use interference microscopy (IFM).¹⁴ The latter enables observing local 2D concentration maps (where the concentration is averaged along the third direction¹⁵) in single zeotype crystals during transient adsorption/desorption cycles^{16–18} with spatial and temporal resolutions on the order of micrometers and seconds, respectively. While the direct quantification of adsorbed amounts still poses a challenge, the measured relative concentration profiles have allowed for pivotal studies, where evidence was indeed provided for the heterogeneous nature of adsorbent crystals and the corresponding variability in their uptake rate was quantified.¹⁹ Other remarkable attempts at imaging the adsorbed phase have been carried out by X-ray computed tomography (CT). The latter stands out for a number of key features: it is a truly 3D measurement technique; it is an *in-situ* technique that can be applied *operando*²⁰ thanks to its non-invasive nature and the possibility of using actual process gases; and its availability as bench/lab scale setup is widespread, with instruments able to cover a wide range of resolutions and system sizes from the micrometer (crystal size) to the meter (reactor size). In the following, we present a brief review of works that have specifically addressed the study of adsorption by X-ray CT.

1.1 Imaging of gas adsorption with X-rays

The response of X-ray CT measurements depends largely on the bulk density of the imaged object and most CT scanners operate in a way that measurements of the X-ray beam attenu-

ation are taken for multiple sample orientations, which upon reconstruction provides data at various spatial locations (voxels) within the object. The ability to quantify the local density from X-ray CT scans makes it plausible to exploit this technique for the detection of the adsorbed phase, which has a liquid-like density, hence a much larger density as compared to the bulk gas phase. Evidence to this dates back to the mid-70s, when Dubinin et al.²¹ visualized the propagation of the adsorptive front of bromobenzene into zeolite particles with radiographs. The realization that the dense adsorbed phase provides for attenuation contrast has been exploited in more recent works; however, most of these studies were either purposely qualitative^{21–23} or used a strongly attenuating component for imaging (e.g. Krypton,^{24,25} Xenon,^{26,27} brominated²¹ or chlorinated^{22,23} solvent vapors). As shown in Figure S1 (SI), these radio-opaque components provide a 5- to 100-fold increase in attenuation as compared to more conventional process gases (e.g., CO₂). Only a limited number of studies have used X-ray CT measurements to study adsorption quantitatively by providing critical elements that support the use of this technique, such as (i) the validation of the X-ray measurement with an independent adsorption experiment and (ii) the recognition that adsorption data can be measured on a voxel-by-voxel level. Again, the picture is rather incomplete, as some of these studies^{26,28} report solely on the measurement of total loadings, without differentiating between the bulk- and adsorbed-phase, while others^{24,25,27,29} do quantify adsorption, but without referring to the truly measurable quantities in an adsorption experiment, namely net and excess adsorbed amounts. Most significantly, they all lack of the proper estimation of measurement uncertainties, which is a key requirement to justify the use of X-ray CT as a novel tool for 3D adsorption experiments. It is only in a recent communication by Pini³⁰ that these issues were tackled by providing both the operating equations and the experimental protocol to measure excess adsorption using X-rays, and by validating them on a common host-guest system, namely CO₂ on zeolite 13X.

In this work, we build on these last findings by presenting and discussing digital adsorption experiments carried out for two adsorbate/adsorbent systems, namely CO₂/zeolite 13X

and CO₂/activated carbon in the range of pressure 1–30 bar at 25 °C. Specifically, the aims of this work are (i) to design a workflow for measuring excess adsorption isotherms from X-ray CT scans, including a rigorous uncertainty analysis of the measurements; (ii) to present the first 3D data set of adsorption isotherms measured at a resolution of 10 mm³ on a laboratory fixed-bed adsorption column; (iii) to validate the obtained experimental results by comparison with independent data reported in the literature; and (iv) to assess the applicability of this novel method for the measurement of gas adsorption isotherms on different classes of natural and synthetic porous materials.

2 Theory

The response of a reconstructed X-ray CT image is the local linear attenuation coefficient, μ , which is defined as the product between the bulk density of the scanned object, ρ , and its mass attenuation coefficient, α :³¹ $\mu = \alpha\rho$. In the energy range applied in X-ray CT (30–140 keV), α is composed of the contributions from photoelectric effect (dominant at $E \ll 100$ keV) and Compton scattering (dominant at $E > 100$ keV), and it depends on the photon energy (spectrum) and the atomic properties of the scanned object. When the latter is composed of a mixture of a certain number of phases (P), the overall attenuation coefficient $\bar{\mu}$ is obtained by assuming ideal mixing and by using the attenuation coefficient/density values of each individual phase k :

$$\bar{\mu} = \bar{\rho} \sum_{k=1}^P \frac{w_k}{\rho_k} \mu_k = \sum_{k=1}^P \phi_k \mu_k \quad (1)$$

where $\bar{\rho}$ is the density of the mixture, and w_k and ϕ_k are the weight and the volumetric fractions of phase k in the mixture, respectively. When a porous solid of bulk volume, V_{tot} , with total pore space, V_{pore} , is exposed to an adsorptive “a”, surface forces will result in the densification of the fluid at the interface to the solid phase, thus creating an adsorbed phase with liquid-like density. Hence, the overall attenuation coefficient can be written as the sum

of contributions from the bulk fluid, solid and adsorbed phases:

$$V_{\text{tot}}\bar{\mu}_{\text{a}} = (V_{\text{pore}} - V_{\text{a}})\rho_{\text{f}}\alpha_{\text{a}} + (V_{\text{tot}} - V_{\text{pore}})\rho_{\text{s}}\alpha_{\text{s}} + m^{\text{ads}}\alpha_{\text{a}} \quad (2)$$

where ρ_{f} and ρ_{s} are the densities of the bulk fluid and of the solid, respectively, and m^{ads} is the absolute adsorbed mass. Note that because the fluid phase is a pure component, the same proportionality constant, α_{a} , is used for both the bulk fluid and adsorbed phase. Eq. 2 is rearranged by introducing an excess adsorption term, η^{ex} :

$$\bar{\mu}_{\text{a}} = \phi_{\text{tot}}\mu_{\text{a}} + (1 - \phi_{\text{tot}})\mu_{\text{s}} + \eta^{\text{ex}} \quad (3)$$

where $\phi_{\text{tot}} = V_{\text{pore}}/V_{\text{tot}}$ is the total void fraction, and η^{ex} is directly related to the truly measurable quantity in an adsorption experiment, namely the surface excess³² $m^{\text{ex}} = m^{\text{ads}} - \rho_{\text{f}}V^{\text{ads}}$. It follows that:

$$\eta^{\text{ex}} = \frac{m^{\text{ex}}\alpha_{\text{a}}}{V_{\text{tot}}} = m_v^{\text{ex}}\alpha_{\text{a}} \quad (4)$$

where m_v^{ex} is the excess adsorbed amount per unit volume. The overall attenuation coefficient of the same volume of porous solid exposed to an inert gas “i” is given by:

$$\bar{\mu}_{\text{i}} = \phi_{\text{tot}}\mu_{\text{i}} + (1 - \phi_{\text{tot}})\mu_{\text{s}} \quad (5)$$

Upon subtraction of Eqs. (3) and (5) and rearranging, the following expression is obtained:

$$\eta^{\text{ex}}(p, T) = \bar{\mu}_{\text{a}}(p, T) - \bar{\mu}_{\text{i}}(p^*, T^*) - \phi_{\text{tot}} [\mu_{\text{a}}(p, T) - \mu_{\text{i}}(p^*, T^*)] \quad (6)$$

where it can readily be observed that excess adsorption can be determined by combining independent measurements (i.e., CT scans) of the porous solid exposed to the adsorptive and inert gas, respectively, with prior knowledge of the attenuation of the pure fluids and of the total void fraction³⁰. In Eq. 6, the (p, T) conditions were made explicit to emphasize

that they may differ between the measurements with the adsorptive and the inert gas. In this study, the latter are carried out for a single set of reference pressure ($p^* = 5$ bar) and temperature ($T^* = 25$ °C). Hereby, the sole assumption is that the linear attenuation coefficient of the solid phase, μ_s , takes the same value at both reference and experimental conditions.

Some instruments, more particularly medical CT scanners, provide images reconstructed in Hounsfield units (HU), or CT numbers, which are obtained from a linear combination of the measured linear attenuation coefficients with values known from a calibration of the instrument with suitable phantoms (e.g., water and air):

$$CT = \frac{\mu - \mu_{\text{water}}}{\mu_{\text{water}} - \mu_{\text{air}}} 1000 \quad (7)$$

Eq. 6 can thus be rewritten in terms of CT numbers:

$$H^{\text{ex}}(p, T) = \overline{CT}_{\text{a}}(p, T) - \overline{CT}_{\text{i}}(p^*, T^*) - \phi_{\text{tot}} [CT_{\text{a}}(p, T) - CT_{\text{i}}(p^*, T^*)] \quad (8)$$

The excess adsorbed mass can then be computed as:

$$m_v^{\text{ex}} = H^{\text{ex}}/a_{\text{a}} \quad (9)$$

where $a_{\text{a}} = 1000 \alpha_{\text{a}}/(\mu_{\text{water}} - \mu_{\text{air}})$, can also be conveniently found from the slope of the calibration curve, $CT_{\text{a}} = a_{\text{a}}\rho_{\text{f}} + b$ (see Experimental section). Eq. 8 and 9 provide the working equations to determine adsorbed amounts from X-ray CT scans in terms of the typical units used in conventional adsorption experiments. It is worth noting that these equations are not restricted to a specific energy range provided that a negligible beam hardening is present (sample exposed to a homogeneous energy spectrum), nor are they restricted to any resolution. They are thus applied for each voxel in the system, whereas slice- or sample-averaged properties are calculated using slice- or sample-averaged CT numbers. We also

note that when working with commercial adsorbents, such as in this study, it is reasonable to assume that the attenuation of the solid component takes a constant value, as these materials are homogeneous in terms of skeletal density and composition at the spatial resolution of medical CT scanners (mm and above). Because the average sample porosity can be measured from independent experiments, the CT number of the solid can be estimated from Eq. 5 written in terms sample-averaged CT numbers:

$$CT_s = \frac{\overline{CT}_{i,avg}(p^*, T^*) - \phi_{tot,avg} CT_i(p^*, T^*)}{1 - \phi_{tot,avg}} \quad (10)$$

The local porosity can then readily be estimated from Eq. 10 solved for each voxel in the system:

$$\phi_{tot} = \frac{CT_s - \overline{CT}_i(p^*, T^*)}{CT_s - CT_i(p^*, T^*)} \quad (11)$$

When spatial variations in composition are expected, such as with natural porous solids or beds with mixed adsorbents, the assumption above needs to be relaxed and local porosity values can be estimated from the subtraction of scans of the porous solid saturated with zero-excess fluids, as is typically done with air and water for the determination of the porosity map of rocks.^{33,34}

3 Materials and methods

3.1 Materials and apparatus

The adsorption experiments were performed using the experimental setup depicted in Figure 1. A custom-made aluminum sample-holder (wall thickness: 1.35 cm) has been used that can accommodate a cylindrical sample of 5 cm in diameter and of variable length. While it is fairly translucent to X-rays, aluminum provides for the required mechanical strength and reduces beam-hardening artifacts.³⁵ The sample is located between two aluminum end-plates with embedded circular grooves for enhanced fluid distribution upon injection. The sample-

holder is placed horizontally on the bed of the scanning instrument (Universal Systems HD-350 X-ray CT scanner) and is connected to the gas lines by means of 1/16" PEEK tubing. Two high-accuracy pressure transducers (Keller UK, model PA-33X) are connected through tubing ported directly to the inlet and outlet faces of the sample. These are continuously logged throughout the experiment in a data acquisition PC (DAQ PC). Two microporous

Figure 1: Schematic of the apparatus (not to scale) used for gas adsorption experiments by X-ray computed tomography (CT). The sample is a multi-layered fixed-bed consisting of glass beads, zeolite 13X pellets and activated carbon rods (properties listed in Table 1). Total bed length, $L = 11$ cm; column inner diameter, $d = 5$ cm. 3D reconstruction of the layered adsorbent column saturated with helium (bottom).

solids, namely Zeolite 13X beads (batch Z10-03, bead diameter ≈ 1.6 – 2.5 mm, supplied by Zeochem AG, Switzerland) and activated carbon rods (Norit RB3, diameter ≈ 3 mm, supplied by Sigma Aldrich), and non-porous (non-adsorbing) glass beads (Assistent/AR-Glas[®], diameter ≈ 2 mm, supplied by Glaswarenfabrik Karl Hecht, Germany) were used in the experiments. Helium ($M_m = 4.00$ g/mol) and carbon dioxide ($M_m = 44.01$ g/mol) gases were purchased at CP grade from BOC (99.999% and 99.995% for He and CO₂, respectively).

3.2 Experimental procedure and X-ray imaging

The experiments were carried out at room temperature (25 °C) and using dry adsorbents. Prior to the measurements, the solids were regenerated by heating during at least 4 hours (150 °C for the activated carbon and the glass beads, and 290 °C for the zeolites). A multi-

Table 1: Properties of the adsorbent materials and of the layered fixed-bed. The bed density (ρ_{bed}) was calculated based on the mass of material and the measured volume (AL) occupied within the adsorbent column. The adsorbent material (skeletal) density (ρ_s) was obtained from the literature in the case of zeolites,³⁰ and from a helium gravimetric measurement in the case of activated carbon (10–135 bar, 25 °C in a Rubotherm Magnetic Suspension Balance). The total porosity of each layer is estimated as $\phi_{\text{tot,avg}} = 1 - \rho_{\text{bed}}/\rho_s$. The attenuation of the solid is computed from Eq.10 applied to each layer of adsorbent, independently.

	Glass beads	Zeolite 13X	Activated carbon
L (cm)	2.5 ± 0.3	3.4 ± 0.3	4.8 ± 0.3
ρ_{bed} (g/cm ³)	1.69 ± 0.13	0.672 ± 0.038	0.435 ± 0.018
ρ_s (g/cm ³)	2.65 ± 0.02	2.567 ± 0.040	2.16 ± 0.34
$\phi_{\text{tot,avg}}$ (–)	0.36 ± 0.05	0.74 ± 0.02	0.80 ± 0.03
CT_s (HU)	2142 ± 292	1905 ± 164	1056 ± 315

layered bed was prepared by packing the adsorbents (glass beads / zeolites / activated carbon) in the cylindrical sample holder under a gentle flow of helium, so as to avoid any excessive contact of the materials with air, and subsequently kept under helium atmosphere (ca. 5 bar). Each layer (2–4 cm in length) was separated by a stainless steel mesh, achieving a total bed length $L = 11$ cm (properties listed in Table 1). After positioning it in the scanner gantry, a full X-ray scan of the layered bed was taken (referred to as ‘Helium scan’) and the sample holder was no longer moved for the whole duration of the experiment. The gas adsorption experiments (referred to as ‘CO₂ scans’) were carried out by both increasing (1 bar, 3 bar, 6 bar, 10 bar, 15 bar, 20 bar and 30 bar) and decreasing (20 bar, 10 bar and 1 bar) the gas pressure in the sample holder; this was achieved by setting the inlet pressure regulator to the desired level, while using the back-pressure valve to maintain a low CO₂ flow through the bed, which was also kept during the scans. The flow rate was adjusted so as to result in a negligible pressure drop along the bed. Adsorption equilibrium was achieved after about 30 min and was followed by the acquisition of a full X-ray scan of the layered bed. For each adsorbent-layer and at each pressure step, an additional set of 10 repeated scans were taken at selected locations (slices); as described in Pini and Madonna³⁴, repeated scans are very useful to assess image noise and to estimate the uncertainties in the computed

adsorbed amounts. All images were acquired by applying a tube voltage of 120 kV, a current of 200 mA, a scan time of 1 s per slice and a (120×120) mm field of view (further details on the CT setup are provided in section 2 the SI). Images were reconstructed with a (xyz) resolution of $(0.234 \times 0.234 \times 1)$ mm³ without applying any filter. Scanning of the entire bed (11 cm) required ca. 10 min, so that approximately 8 hours were required to measure the 3D adsorption isotherms with 8 points. Image analysis and data processing were carried out using in-house MATLAB codes.

3.2.1 Calibration and measurement uncertainty

As anticipated in the previous section, knowledge of the attenuation of each operating gas (He and CO₂) at experimental conditions (pressure and temperature) is needed to compute adsorbed amounts using Eq. 8. To this aim, the empty sample-holder was filled with gas-phase only and was imaged by acquiring 10 repeated scans at a given location using the same imaging parameters applied for the adsorption experiments. Images were taken at various pressures and over the same pressure range covered in the adsorption experiments. As expected (and shown in Figure S2 of the SI), the attenuation in Hounsfield units is linearly correlated to the density of the gas, i.e., $CT_k = a_k \rho_f + b$, where the constant parameters a_k and b were estimated by fitting to the respective sets of calibration experiments ($k = \{\text{He}, \text{CO}_2\}$, values given in Table 2) and the density values at each measured pressure were obtained from the NIST database.³⁶ We note that this calibration procedure has to be carried out only once (for a given sample-holder) and is somewhat analogous to the acquisition of a reference measurement that is commonly needed for gravimetric or manometric adsorption experiments. To estimate measurement uncertainties, the protocol described in Pini and Madonna³⁴ was followed and details specific to the experiments reported here are presented in the SI. Briefly, because the noise observed in CT images is random and uncorrelated for voxel sizes larger than 500 μm^3 (see Figure S3), classic rules of error propagation apply and measurement error is estimated from the standard deviation observed in the (normal)

Table 2: Calibration of the CT number as a function of density ($CT_k = a_k \rho_f + b$) for the pure component gases at 25 °C and over the pressure range 1–30 bar. CT numbers were obtained by averaging readings for all voxels within a 5 mm $\times$ 1 mm circular mask ($\approx$ 75 voxels). Parameters are reported as the best least-square estimator and the corresponding 95% confidence interval. Note that differences in the parameter b are within measurement error and the value (899 ± 1) HU will be used throughout the study.

	$a_k, (\text{HU m}^3 \text{ kg}^{-1})$	$b, (\text{HU})$
CO ₂	0.871 ± 0.008	-898.9 ± 0.4
He	0.73 ± 0.04	-899.1 ± 0.9

distribution of values obtained upon subtracting two images taken at identical locations. As shown in Figure S4, the uncertainty associated with the measured CT number depends on (i) average CT number (Figure S4a) and (ii) the voxel size (Figure S4b), and it can be described by the following general equation (Figure S4c):

$$\sigma_{\overline{CT}} = (c_1 \overline{CT} + c_2) v_{\text{vox}}^{c_3} \tag{12}$$

where the coefficients $c_1 = (3.18 \pm 0.04) \times 10^{-3}$, $c_2 = 6.36 \pm 0.03$, $c_3 = -0.331 \pm 0.003$ were fitted to the CT noise obtained from the analysis of the repeated scans at various voxel resolutions (1–10³ mm³). The uncertainty on the measured excess adsorption, $\sigma_{m_v^{\text{ex}}}$, ranges between 2%rel. and 5%rel. for voxel sizes of 10 mm³, and it is negligible for slice- and layer-averaged values ($\sigma_{m_v^{\text{ex}}} < 1\%$ rel.). We note that the estimated values include a contribution from the uncertainty in the estimated porosity ($\sigma_{\phi_{\text{tot}}}$, see Eqs. S3 and S4 in the SI) of ± 0.02 and ± 0.03 for the zeolite and activated carbon layer, respectively.

4 Results

4.1 X-ray images of adsorption

The results of this work comprise a set of 4D data in the form of three dimensional scans of a layered bed at different partial pressures of CO₂. For the sake of clarity, results are first presented using X-ray CT units in Figures 2 (2D maps) and 3 (1D profiles), together with a summary of layer-averaged data in Table 3. Figure 2 shows 2D attenuation maps of a selected

Figure 2: 2D maps of CT attenuation for a selected slice within each layer saturated with helium (5 bar), and CO₂ at 1 bar, 15 bar and 30 bar and 25 °C. (a) Slice of glass beads taken at 15 mm from the inlet; (b) slice of zeolite 13X pellets taken at 45 mm from the inlet; (c) slice of activated carbon pellets taken at 80 mm from the inlet. Voxel dimensions are $(0.234 \times 0.234 \times 1) \text{ mm}^3$.

slice within the (a) glass bead, (b) zeolites and (c) activated carbon layer, as obtained during the helium and CO₂ scans (with pressures given in the figure). While the xy resolution of the tomograms, $(0.234 \times 0.234) \text{ mm}^2$, enables outlining the characteristic structural features of each adsorbent layer, their most striking feature is the distinct attenuation (i.e. “coloring”) pattern. On the one hand, pore space (blue) and solid phase (red) can be easily distinguished for the images with nonporous glass beads, due to the strong density contrast between the two phases; helium and CO₂ maps are also practically identical and so are the CO₂

Figure 3: Equilibrium slice average CT number along the adsorption bed obtained from scans acquired with helium (triangles, 5 bar) and CO_2 at 1 bar, 6 bar, 15 bar and 30 bar (circles from darker to lighter grey) and at 25°C . The arrows indicate the slice shown in Figure 2 for each material, and the colored areas correspond to the regions considered for the calculation of the layer-averaged values given in Table 3.

results at various pressures. On the other hand, zeolite pellets and activated carbon rods contain a significant amount of intra-particle porosity ($\sim 60\%$ vol.), which leads to much lower attenuation values. Most significantly, for these adsorbent particles the attenuation increases substantially with CO_2 pressure, thus providing means to image the phenomenon of adsorption and to resolve it spatially.

Figure 3 shows the equilibrium slice-averaged CT number along the whole adsorbent column for measurements with helium ($p^* = 5$ bar) and CO_2 at various pressures (1 bar, 6 bar, 15 bar and 30 bar). The former (triangles) allow identifying three layers characterized by distinct (but uniform) attenuation, which reflects the expected change in the bed density (see Table 1). Upon increasing the pressure of CO_2 (circles), the CT number increases uniformly in both the zeolite and activated carbon layers, while changes within the glass bead layer are very small. The latter are associated with an increase in the gas-phase density with pressure, as confirmed by the corresponding layer-averaged numerical values reported in Table 3. In fact, the computed excess adsorption term is negligibly small and does not

change with pressure ($H^{\text{ex}} \approx 2.8$ HU, corresponding to ≈ 0.07 mmol/cm³). In contrast, the change in attenuation of the zeolite and activated carbon layers is significantly larger and increases with pressure (zeolites: $H^{\text{ex}} = 112$ – 142 HU, corresponding to 2.9 – 3.7 mmol/cm³; activated carbon: $H^{\text{ex}} = 46$ – 146 HU, corresponding to 1.2 – 3.8 mmol/cm³). This behavior can be explained by the presence of a denser, liquid-like phase in the micropores of the two materials, as would be indeed expected from the occurrence of CO₂ adsorption.

Table 3: Layer-averaged CT attenuation expressed as difference between CO₂ and helium scans, and obtained from the experiments with, $\overline{CT}_{\text{a}} - \overline{CT}_{\text{i}}$, and without adsorbent in the sample holder, $-\phi_{\text{tot}}(CT_{\text{a}} - CT_{\text{i}})$. The latter represents the contribution of the bulk phase in an adsorption experiment and the excess term (H^{ex}) is obtained as their sum. Layer-averaged CT numbers are given in Hounsfield units [HU] and are computed by averaging all voxel readings within a section that is at least 20 mm thick (shaded regions in Figure 3).

CO ₂ pressure	1 bar	15 bar	30 bar
Glass			
$\overline{CT}_{\text{a}} - \overline{CT}_{\text{i}}$	2.82 ± 0.15	12.1 ± 0.2	24.7 ± 0.2
$-\phi_{\text{tot}}(CT_{\text{a}} - CT_{\text{i}})$	-0.04 ± 0.12	-9.7 ± 1.6	-21.5 ± 3.6
H^{ex}	2.78 ± 0.20	2.4 ± 1.6	3.2 ± 3.6
Zeolite 13X			
$\overline{CT}_{\text{a}} - \overline{CT}_{\text{i}}$	111.72 ± 0.12	156.5 ± 0.1	185.6 ± 0.1
$-\phi_{\text{tot}}(CT_{\text{a}} - CT_{\text{i}})$	-0.08 ± 0.25	-19.8 ± 0.5	-43.6 ± 0.9
H^{ex}	111.60 ± 0.28	136.8 ± 0.5	142.0 ± 0.9
Activated Carbon			
$\overline{CT}_{\text{a}} - \overline{CT}_{\text{i}}$	46.06 ± 0.11	149.7 ± 0.1	192.7 ± 0.1
$-\phi_{\text{tot}}(CT_{\text{a}} - CT_{\text{i}})$	-0.09 ± 0.27	-21.4 ± 0.9	-47.2 ± 1.9
H^{ex}	45.98 ± 0.29	128.3 ± 0.9	145.5 ± 1.9

4.2 Adsorption isotherms

Equilibrium adsorption isotherms are shown in Figure 4 that have been obtained upon application of Eqs. 8 and 9 to the X-ray tomograms acquired at various CO₂ pressures. These have been obtained upon averaging all voxels values within a 20 mm-long section of each adsorbent layer (~ 4000 voxels) and are reported in terms of molar excess adsorbed amount per unit mass of adsorbent, $n^{\text{ex}} = m_v^{\text{ex}}/(\rho_{\text{bed}}M_{\text{m}})$. For all materials, differences

between measurements taken in adsorption (filled symbols) and desorption mode (empty symbols) are very small and well within the predicted measurement uncertainty. The latter is represented by the error bars (one standard deviation from the mean) and amounts to about 5%rel. and 3%rel. for zeolite and activated carbon data, respectively (see Section 5.1 in the SI). We note that the observed uncertainty is dominated by the error on the estimated bed density (see Table 1), which is needed to convert adsorbed amounts from volume- to mass- specific values.

Figure 4: Equilibrium excess adsorption isotherms of CO₂ as a function of pressure at 25 °C, as measured by X-ray CT in both adsorption (filled symbols) and desorption (empty symbols) mode for glass beads, zeolite 13X and activated carbon. Adsorption data have been calculated from the average of CT numbers within a 20 mm-thick section of the adsorbent column (corresponding to roughly 4000 voxels). A selection of literature data is also shown (shown by the crosses; 13X refs.^{37–42}, AC refs.^{42–46}).

As anticipated in the previous section, the non-porous glass beads show negligible adsorption over the pressure range investigated ($p = 1\text{--}30$ bar). On the contrary, the measured CO₂ adsorption data on zeolites and activated carbon follow a type I isotherm that is indeed often observed on microporous materials.⁴⁷ Nevertheless, the two sets of isotherms differ significantly, thus reflecting distinct the material’s specific pore structure and surface chemistry: zeolites (orange-colored symbols) possess almost exclusively micropores of uniform size (1.2 nm for zeolite 13X⁴⁸) and extra-framework cations (e.g. Na⁺ions), which contribute to

the early uptake of gas and, accordingly, to a very steep isotherm that flattens out upon reaching saturation. On the contrary, activated carbons (violet-colored symbols) possess a distribution of pore sizes, with a significant fraction of both micro- ($< 2\text{ nm}$) and mesoporosity ($2\text{--}50\text{ nm}$);⁴⁷ accordingly, their adsorption isotherms are characterized by a more gradual rise. Most significantly, the adsorption isotherms obtained in this study by X-ray imaging are in good agreement with data reported in the literature at similar p, T conditions and obtained using conventional techniques, such as the manometric and gravimetric methods (references provided in Table 4). In the figure, the latter are represented by the crosses, which, for both materials, outline a fairly wide area, as indicated through color-shading. This variability highlights once more issues presented in the Introduction, such as batch-to-batch heterogeneities, differences in material suppliers and selection of regeneration conditions. However, the general agreement between results from this study and the trends reported in the literature in terms of both isotherm shape and adsorption loadings strongly supports the reliability of our measurements and the suitability of X-ray CT for gas adsorption studies on microporous solids. We note that while previous studies have indicated the potential of this and other imaging techniques for measuring adsorption in porous materials, this is the first time that isotherms have been fully resolved on commercial adsorbents using X-ray CT.

4.3 Multi-dimensional, multi-scale adsorption isotherms

In Figure 5, isotherms are shown for selected voxels within the central horizontal cross section of the layered adsorbent bed (filled symbols) and that have been calculated by considering three different voxel volumes, namely (a) 10^1 mm^3 , (b) 10^2 mm^3 and (c) 10^3 mm^3 . The isotherms are reported in terms of molar excess adsorbed amount per unit bulk volume, $n_v^{\text{ex}} = m_v^{\text{ex}}/M_m$, and are compared to the corresponding layer-averaged curves discussed previously (empty symbols, average of ~ 4000 voxels). Error bars are also shown in each plot and are only visible for the data acquired at the highest resolution. In agreement with the results discussed in the previous section, it can be seen that isotherms measured on the two

Table 4: Adsorbed amount of CO₂ at 25 °C and 1 bar on zeolite 13X and activated carbon. Data from the literature are compared to results from this study (X-ray CT).

Reference	Supplier	Regeneration	Method	$n_{1\text{bar}}^{\text{ex}}$ [mol/kg]
Zeolite 13X				
Siriwardane et al. ³⁸	Zeochem	298 K	volumetric	3.6
Hyun and Danner ³⁷	Linde	467 K	volumetric	3.9
Delgado et al. ⁴²	Union Carbide	593 K	volumetric	4.1
Cavenati et al. ³⁹	CECA	593 K	gravimetric	4.6
Bezerra et al. ⁴⁰	Klostrolith	623 K	gravimetric	5.1
Hefti et al. ⁴¹	Zeochem	673 K	gravimetric	5.4
This work	Zeochem	563 K	X-ray CT	4.5 ± 0.3
Activated Carbon				
Schell et al. ⁴⁵	Chemviron	423 K	gravimetric	1.6
Delgado et al. ⁴²	BPL 4X10	423 K	volumetric	1.8
Dreisbach et al. ⁴³	Norit R1	353 K	volumetric	2.2
Millward and Yaghi ⁴⁴	Norit RB2	573 K	gravimetric	2.5
Singh and Kumar ⁴⁶	Norit RB3	373 K	volumetric	3.0
This work	Norit RB3	423 K	X-ray CT	2.8 ± 0.1

materials differ significantly, thus reflecting their distinct adsorptive properties. Notably, while they follow the same qualitative behavior as the layer-averaged data, the local (voxel-specific) adsorption isotherms are relatively distinct from each other, thus indicating a degree of variability in the adsorption properties of the packed bed at the mm-scale. The latter decreases with increasing voxel size and the isotherms within each adsorbent become almost indistinguishable for voxels with volume $V_{\text{vox}} = 1 \text{ cm}^3$. This result can be understood by considering that also the void fraction in each voxel differs, and that in a random pack this variability decreases upon increasing the volume of the spatial domain of interest.⁴⁹

The analysis presented above is extended by probing the variability in the adsorption properties of the two adsorbents across a continuum of length scales, i.e. in the range 10^{-1} – 10^5 mm^3 . This is illustrated in Figure 6 in the form of so-called representative elementary volume (REV) curves⁵⁰ that have been obtained here by calculating the adsorbed amount at 30 bar within a volume that is grown from a single voxel (with volume $(0.5 \times 0.5 \times 1) \text{ mm}^3$) up to the total volume of the adsorbent layer. In the figure, eleven REV curves with randomly

Figure 5: 3D reconstruction of the adsorbent column in terms of adsorbed amount at 30 bar and different voxel volumes, namely (a) 10 mm^3 , (b) 10^2 mm^3 and (c) 10^3 mm^3 . The corresponding CO₂ adsorption isotherms are shown in each plot; these have been extracted for selected voxels within the horizontal central section of the column ($y-z$ plane, two pairs for each adsorbent shown by the filled symbols) and are compared to layer-averaged isotherms (empty symbols) measured for both materials.

distributed starting points are shown alongside boxplots that display distributions at specific voxel sizes, namely 1 mm^3 , 10^1 mm^3 , 10^2 mm^3 and 10^3 mm^3 (line: median, box: interquartile range, whiskers: 95% range). For both materials, the REV curves and the boxplots indicate a very similar behavior. For small voxel sizes ($<10\text{ mm}^3$), local variations in the adsorbed amount are large: at 1 mm^3 , n_v^{ex} ranges between 2–5.5 mmol/cm³ for zeolite 13X (45% relative deviation from the mean) and between 1.2–6.5 mmol/cm³ for activated carbon (65% relative deviation from the mean). As the voxel size increases, the distribution becomes narrower until it entirely falls in a range that lies within 5% deviation from the mean (indicated by the color-shaded regions). For zeolite 13X, this point is attained at a voxel size of 10^2 mm^3 , while voxel sizes of at least 10^3 mm^3 are required to observe uniform adsorption in activated carbon. For both materials these distinct voxel sizes correspond to 3–4 particles per voxel edge, as indicated by the secondary x -axis. This number agrees very well with the attainment of a REV for the porosity of a random pack of uniform glass beads.⁴⁹ Packing effects are thus expected to contribute to a greater extent in the variability of the adsorbed amount at scales for which the voxel size is comparable to the size of the adsorbent pellets.

5 Discussion

Gas adsorption has established itself as a practical and reliable tool for the structural characterization of microporous solids. Over the years, experimental protocols have been developed that allow the practitioner to make use of a variety of gases and organic vapors to selectively probe the pore-space of the material under investigation. Accordingly, approaches are available nowadays that enable extracting parameters, such as pore volumes, pore-size distribution and surface areas, which serve as a fingerprint of the adsorbent. The coupling of these standard approaches with the simultaneous imaging of adsorption by X-ray CT adds a new dimension to adsorption-based techniques by providing an unprecedented level of observational detail on both material properties and the adsorption process itself. In the following,

Figure 6: Spatial variability of adsorption: the adsorbed amount measured at 30 bar is plotted as a function of the elementary (i.e., voxel) volume. The solid lines represent REV curves starting at eleven different random locations within the adsorbent layer. These are constructed by expanding the voxel symmetrically in the xy direction, while maintaining a unitary aspect ratio through the growth in the z direction. Color-shaded regions are shown to represent 5% deviation from the layer-averaged adsorbed amounts. Boxplots are also shown for selected voxel sizes: 1 mm^3 , 10^1 mm^3 , 10^2 mm^3 and 10^3 mm^3 (line: median, box: interquartile range, whiskers: 95% range). The secondary axis represents the number of particles per edge length, ΔL , where the particle hydraulic diameter, d_h , is used as the characteristic length (1.8 mm for the spherical pellets of zeolite 13X and 2.7 mm for the cylindrical pellets of activated carbon).

we discuss two technical developments: (i) the measurement of spatially resolved adsorption isotherms and their use for quantifying adsorption heterogeneity; (ii) the extension of the X-ray CT technique to a range of porous solids, including weakly adsorbing materials, such as microporous rocks.

5.1 Adsorption heterogeneity

5.1.1 Voxel-by-voxel adsorption isotherms and scaling

One of the benefits arising from the application of a tomographic technique for measuring adsorption is the ability to make observations over multiple spatial dimensions and, accordingly, to access spatially resolved adsorption isotherms and parameters. Figure 7a shows the whole population of adsorption isotherms measured within the zeolite (3060 isotherms) and activated carbon layers (4540 isotherms) at a resolution of 10 mm³. These are plotted alongside the adsorption isotherms representative of each adsorbent layer (empty symbols), outlining a type I isotherm, which is typically described by the Langmuir isotherm model (black lines in the figure):⁴⁷

$$n_v^{\text{ex}} = \frac{n^\infty Kp}{1 + Kp} \quad (13)$$

where the parameters n^∞ and K are the saturation capacity and the affinity coefficient, respectively, both of which depend on the adsorbent type (fitted parameters values are provided in the figure caption). At any given pressure and for both materials, the spread of adsorption loadings at the voxel-scale is significant: at 20 bar, n_v^{ex} ranges between 2.8–4.2 mmol/cm³ for zeolite 13X (20% relative deviation from the mean) and between 1.8–2.5 mmol/cm³ for activated carbon (50% relative deviation from the mean). These variations are significantly larger than the predicted uncertainty in the measured adsorbed amount at the same scale (3% and 5% relative deviation from the mean for zeolite 13X and activated carbon, respectively) and reflect therefore true spatial variabilities in the adsorption properties of the adsorbent bed. Nevertheless, all isotherms retain the characteristic shape outlined by the

layer-averaged curve and Eq. 13 can thus be used to describe each isotherm by fitting the set of parameters n_j^∞ and K_j for each voxel j independently. As a validation of this approach, all isotherms are again plotted in Figure 7b in terms of a scaled adsorbed amount, $n_{v,j}^{\text{ex}}(p)/n_j^\infty$, and by using $K_j p$ as the new independent variable; to facilitate comparison with the unscaled data, units are re-established by multiplication with the layer-averaged isotherm parameters n_{avg}^∞ and $1/K_{\text{avg}}$, respectively. It can be seen that all data points now collapse around two distinct curves that describe activated carbon and zeolite adsorption data; the effectiveness of the scaling is quantified through the Spearman rank correlation, which increases from ≈ 0.8 for the unscaled data to > 0.95 for the scale data, and through the value of the sum of squared residuals with respect to the fitted Langmuir isotherms, which is reduced to only 11% (for zeolites) and 4% (for activated carbon) of the value for the unscaled data. In practice, this result indicates that, within each adsorbent layer, voxels can be considered *similar* (with reference to the early work by Miller and Miller⁵¹) in terms of their adsorptive properties, which in this case are fully characterized through pairs of spatially distributed scaling factors, namely $n_{\text{avg}}^\infty/n_j^\infty$ and K_j/K_{avg} . Accordingly, the scaling exercise yields two separate universal adsorption isotherm curves, $\Gamma^{\text{ex}}(\xi)$, that are descriptive of all voxels in the given adsorbate-adsorbent system and that take the following form:

$$\Gamma^{\text{ex}} = \frac{\xi}{1 + \xi} \quad (14)$$

where $\Gamma^{\text{ex}} = n_{v,j}^{\text{ex}}(p)(n_{\text{avg}}^\infty/n_j^\infty)$ and $\xi = p(K_j/K_{\text{avg}})$. We note that the scaling approach applied here to spatially distributed isotherms is analogous to the adoption of the so-called generalized (or characteristic) adsorption curve that correlate adsorption isotherms of a given adsorbate/adsorbent pair at different temperatures⁵² or of different adsorbates onto one adsorbent.⁵³

Figure 7: (a) Voxel-by-voxel adsorption isotherms ($n_{v,j}^{\text{ex}}$ vs. p) for zeolite 13X (3060 isotherms, triangles) and activated carbon (4540 isotherms, circles). The Langmuir isotherm fits of the layer-average data (empty symbols) are shown by the solid black line (13X: $n_{\text{avg}}^{\infty} = 3.71$ mmol/cm³, $K_{\text{avg}} = 3.32$ bar⁻¹; AC: $n_{\text{avg}}^{\infty} = 4.18$ mmol/cm³, $K_{\text{avg}} = 0.30$ bar⁻¹). (b) Scaled adsorption data (Γ^{ex} vs. ξ), where the fitted Langmuir-parameters are used as scaling factors, namely $\Gamma^{\text{ex}} = n_{v,j}^{\text{ex}}(p)(n_{\text{avg}}^{\infty}/n_j^{\infty})$ and $\xi = p(K_j/K_{\text{avg}})$. Voxel size: 10 mm³.

5.1.2 Parameterization of adsorption heterogeneity

Histograms representing the distribution of the Langmuir isotherm parameters obtained from the previous fitting exercise are shown in Figure 8. Symmetric and skewed distributions are observed for the saturation capacity, n_j^{∞} , and the affinity coefficients, K_j , respectively (note that in the latter case a logarithmic scale is used for plotting). Gaussian curves are additionally shown that have been fitted to the binned data; they provide further support that the obtained saturation capacity and the affinity coefficient follow normal and lognormal distributions, respectively (with the corresponding parameter values, mean and standard deviation, reported in the figure caption). Several interesting observations can be made. The distribution of saturation capacities is significantly wider than the range of values reported in the literature for the same parameter (and indicated as colored bars at the top of the plot); this is particularly true for the activated carbon data, where the latter is about half of the width of the distribution observed in this study (95% confidence interval). The affinity

coefficients also possess a wide distribution, although the width of the distribution observed in this study is of similar magnitude as the corresponding literature range. As anticipated above, the saturation capacity is reported here for voxels with a volume of 10 mm^3 and the observed spread of values is therefore likely to ensue from the variation in pellet density per voxel, which in turn affects the number of available adsorption sites per voxel. The stronger heterogeneity observed for activated carbon is also expected, as the ratio between voxel edge length ($\approx 2.15 \text{ mm}$) and the particle hydraulic diameter indicates that each voxel can accommodate less than two zeolite particles per edge, and less than one activated carbon particle per edge (see also Figure 6).

Figure 8: Distribution of the Langmuir parameters fitted onto the adsorption isotherms at the voxel scale (voxel size 10 mm^3). (a) Saturation capacity n^∞ : the mean and standard deviations of the fitted Gaussian curves are $n^\infty = (3.679 \pm 0.006) \text{ mmol/cm}^3$, $\sigma_{n^\infty} = (0.354 \pm 0.008) \text{ mmol/cm}^3$ for zeolite 13X and $n^\infty = (4.27 \pm 0.02) \text{ mmol/cm}^3$, $\sigma_{n^\infty} = (1.05 \pm 0.03) \text{ mmol/cm}^3$ for activated carbon. (b) Affinity coefficient K : the mean and standard deviations of the fitted Gaussian curves are $\ln K = 1.239 \pm 0.002$, $\sigma_{\ln K} = 0.327 \pm 0.005$ for zeolite 13X and $\ln K = -1.23 \pm 0.01$, $\sigma_{\ln K} = 0.72 \pm 0.02$ for activated carbon. The stars indicate the values of the respective parameter fitted to the layer-averaged isotherms (n_{avg}^∞ and K_{avg} , see Figure 7). The bars at the top of the figures represent the range spanned by the respective parameters fitted to the literature isotherms shown in Figure 4.

The observed variability in the affinity coefficient is more intriguing, because this parameter is expected to be independent of packing density. In fact, a lognormal distribution in the

affinity coefficient could arise from a random distribution of the free energy of adsorption, ΔG_{ads}^* . As shown through the mathematical derivation provided in section 5 of the SI, the latter is directly related to the thermodynamic affinity coefficient K' , which for an ideal gas and an ideal adsorbed phase is equal to the Langmuir affinity coefficient, K :⁵⁴

$$\Delta G_{\text{ads}}^* = -RT \ln(K') \equiv -RT \ln(K) \quad (15)$$

Thus, while we cannot exclude a priori that it is an artifact arising from the non-linear fit to uncertain data⁵⁵, the observed distribution may also be reflecting the true physical variability of the adsorbent particles themselves, as it would be expected from physico-chemical variations among or within the pellets. Support to this hypothesis is also the fact that a variation of similar extent in the affinity coefficient is obtained upon analyzing isotherms reported in the literature on the same materials, which are very likely due to discrepancies in modes of adsorbent regenerations and/or batch-to-batch heterogeneities. Further investigations on this topic are necessary to thoroughly understand the origin and scale of the physico-chemical heterogeneity of the adsorbent material and particles. A first step in this direction could follow from the interpretation of 3D digital adsorption experiments carried out at higher resolution, e.g. with the use of a micro-CT, thus allowing to decouple the effect of packing (or bed heterogeneity) from material heterogeneity by resolving individual particles, and computing adsorption isotherms for individual particles.

5.2 Digital adsorption: applicability to different materials

Because gas adsorption still represents the gold standard for the characterisation of microporous solids, advancements are continuously being made to refine measurement protocols and interpretation of the obtained adsorption isotherms.⁹ Experiments typically involve measuring the excess adsorption of small gases, e.g. N_2 , Ar, Kr and/or CO_2 , under sub-critical conditions, and at pressures ranging from vacuum to 1 bar. These measurements, from

which pore volume, specific surface area and pore size distribution can be obtained, have become routine practice in the characterization of novel adsorbent materials,¹⁰ catalysts⁵⁶ and natural microporous materials, including coals,⁵⁷ carbonates,^{58,59} clays and shales.⁶⁰ To assess the applicability of X-ray CT for measuring gas adsorption isotherms on a variety of materials, we discuss in the following the expected measurement uncertainties that have been estimated by considering the adsorption of CO₂ on a generic nanoporous material at conditions representative of sub-critical adsorption measurements (0 °C and $p = 1$ bar). The analysis is intended to help the adsorption practitioner to design an experiment using a conventional medical CT scanner, so as to achieve the required precision at given spatial resolution.

If the pressure is sufficiently low, the gas behaves ideally and the second term in Eq. 8 can be dropped (i.e., $\phi_{\text{tot}}(CT_{\text{a}} - CT_{\text{i}}) \approx 0$ ³⁰), hence the estimation of uncertainties in the measured adsorbed amount is greatly simplified (see Eqs. S5 and S6 in the SI). For the calculations, we consider a packed bed ($\phi_{\text{bed}} = 0.37$) of a given adsorbent material with uniform and constant attenuation of the solid component ($CT_{\text{s}} = 2000$ HU). We note that for some of the “lighter” materials (e.g., carbons), this assumption will lead to an overestimation of the measurement uncertainty and the results reported below are thus to be considered as upper bounds. We further assume that the intraparticle porosity is composed of a fraction of micro-/meso-pores (ϕ_{m}) that contribute to adsorption, and a fraction of larger meso-/macro-pores (ϕ_{M}) with negligible surface area, such that the total porosity is given by $\phi_{\text{tot}} = \phi_{\text{bed}} + (1 - \phi_{\text{bed}})(\phi_{\text{m}} + \phi_{\text{M}})$. The variability among different classes of adsorbent materials is introduced by considering typical pore volumes reported in the literature, which are linked to the adsorption capacity by assuming a constant value for the density of the adsorbed phase (21.1 mol/L, taken as the liquid density of CO₂ at 0 °C³⁶). The amount of macroporosity is obtained by assuming a ratio $\phi_{\text{m}} : \phi_{\text{M}}$ of 60 : 40, which is typical for materials produced in pelletized form, such as commercial zeolites.⁴⁸

A contour plot is presented in Figure 9 for the obtained total relative error as a function

of the adsorbed amount and of the voxel size. Not surprisingly and for a given voxel size, the relative error decreases with increasing adsorption. Similarly, for a given amount adsorbed, the error decreases with increasing voxel size, due to the averaging associated with image coarsening. In the figure, various classes of materials are also represented by considering their characteristic pore volumes ($\phi_m(1 - \phi_{bed})$, scale shown on top of the figure). It can be seen that commercial adsorbent materials (MOF, AC and zeolites) fall in a range where the predicted relative error is fairly small (ca. 1–5%rel., for any voxel size), while the measurement of adsorption isotherms on natural porous materials is affected by a larger uncertainty. Specifically, the error for clays is maintained below 10%rel. for voxel sizes that are larger than 10 mm^3 , while much larger voxels are required for coal and shales ($> 100\text{ mm}^3$). The reason for this is twofold: first, high-density materials are prone to a larger measurement uncertainty, because CT noise is proportional to the attenuation of the packed bed, hence to its density. Owing to their large volumetric capacity and low bed density, commercial materials therefore tend to be more suited for adsorption measurements by X-ray CT. Second, materials such as clays or shales have lower porosity and hence a smaller adsorption capacity, which translate into a larger relative error on the measured adsorbed amount, an issue that is shared with the most common adsorptive characterization techniques.⁶¹ We note that in such cases, the averaging of N repeated scans acquired at identical locations would decrease the measurement error significantly without increasing the experiment complexity. Hence, the predicted measurement errors shown in Figure 9 would decrease by a factor $\sqrt{N}$, as suggested by standard rules of error propagation, which apply to variables that are normally distributed (such as the CT noise³⁴). These observations suggest that the X-ray CT method can indeed be applied to a range of microporous materials and provide reliable estimates of the adsorbed amount over a continuum of relevant length-scales. It is worth noting that the presented uncertainty figures are specific for the imaging settings used in this work (X-ray tube voltage, resolution, and core holder), and for the considered operating conditions (0°C and $p = 1\text{ bar}$). However, because the applied methodology and the considerations above

are quite general, we anticipate that a similar conclusion can be drawn for experiments carried out with different imaging setting, and also at larger pressures where most gases are supercritical.

Figure 9: Predicted total relative error (Eqs. S5 and S6 of the SI) of the adsorbed amount of CO_2 at 1 bar and 0°C from X-ray CT measurements as a function of the voxel size and the adsorbed amount for a generic porous solid ($CT_s = 2000$, $\phi_{\text{bed}} = 0.37$). Different classes of materials are listed on the top of the figure that are characterized by given micro-/meso-pore volumes. The latter are linked to amounts adsorbed by assuming a value for the density of the adsorbed phase of CO_2 (21.1 mol/L) as well as the material's specific skeletal density, ρ_s , and macroporosity, ϕ_M (details and references in Table S1).

6 Conclusions

Gas adsorption experiments using X-ray CT have been carried out at 25°C and in the pressure range 1–30 bar using CO_2 on two commercial adsorbents. The validation of the obtained results against literature data supports the application of this non-destructive technique for the characterization of adsorption equilibrium in terms of the truly measurable quantity in an adsorption experiment, namely the surface excess. The experimental approach allows

probing the adsorption process in three dimensions and these data are the first of a kind to directly and non-destructively measure spatially-resolved adsorption isotherms on commercial adsorbents. This novel ability was exploited to investigate adsorption heterogeneity within the fixed-bed at a spatial resolution of 10 mm^3 . A scaling approach was applied to analyze the whole population of measured adsorption isotherms (7600), leading to a single universal adsorption isotherm curve that is descriptive of all voxels for a given adsorbate/adsorbent pair. From the scale dependent analysis of the adsorption heterogeneity (in the range of 1 mm^3 to 1 cm^3), packing heterogeneity was identified as the main contributor to the observed spatial variability, which was larger for the activated carbon rods as compared to the zeolite pellets. Yet, significant variations in the affinity coefficient were observed for both adsorbents, which could indicate true physico-chemical variations among the adsorbent particles.

A peculiarity of this study is that the experiments have been carried out using a ‘classic’ setting, namely a probing gas (CO_2) that is not radio-opaque, and a packed column with dimensions representative of a typical lab-scale fixed bed operating up to 30 bar. Its applicability to different classes of materials was assessed by quantification of the expected measurement uncertainty. Thereby, we have shown that the technique is readily applicable to a large spectrum of commercial porous solids and that it can be extended to weakly adsorbing materials with appropriate protocols that reduce measurement uncertainties. As such, the obtained results encourage a wider use digital adsorption and we see three areas in which it could contribute to the field of adsorptive characterization of porous solids. Firstly, the proven ability to measure a multitude of different materials concurrently enables high-throughput screening analyses, where the number of pressure sensors is decoupled from the number of materials. Second, the non-invasive, multidimensional nature of the technique enables probing the adsorption process *operando* and could be applied to reveal packing deficiencies, the occurrence and location of adsorbent poisoning within a fixed-bed setup, or the extent of propagation of an adsorption front during a dynamic experiment. Finally, the ability to couple conventional sub-critical gas adsorption experiments and interpretation

with X-ray CT imaging could pave the way towards the 3D characterization of porous systems at resolutions spanning multiple length-scales – from the micro-meter to the meter. Such experiments are needed for the systematic design of formulation processes and scale-up of nanoporous solids into shaped structures, such as pellets, monoliths or foams.

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Supporting Information Available

Attenuation coefficients of relevant gases; Imaging parameters; Calibration curves; Analysis of the CT noise; Measurement uncertainty quantification. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Graphical TOC Entry