See the unseen: applications of imaging techniques to study adsorption in microporous materials

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Abstract

Chemical processes that incorporate porous solids (adsorbents and catalysts) include transient and spatially localised phenomena. Their thorough understanding requires the development of experimental methods that enable in situ observations made under process conditions. Imaging techniques are providing an unprecedented level of detail in the study of adsorption, both in the gas and liquid phase, including spatiotemporal measurements of adsorption equilibrium, kinetics and dynamics in microporous solids. The available techniques range from microscopy to multidimensional spectroscopy and tomography, and enable the development of so-called digital workflows, where adsorbent properties can be computed from spatially distributed adsorption uptake curves and isotherms. The widespread applicability of these methods is expected to pave the way towards resolving the complex structure of adsorption systems, from nano- to macro-scale, while providing new fundamental understanding of adsorption processes operando.

Keywords: adsorbents, heterogeneity, transport, imaging

1. Introduction

Adsorption is a basic phenomenon underlying the numerous industrial uses of porous solids, including heterogeneous catalysis, separation processes and

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natural gas recovery from sedimentary formations. The presence of a porous solid, whether it is a rock or a synthetic engineered material, introduces heterogeneities in the system over various length-scales, from the nonuniform distribution of pores at the microscale to local differences in the packing of grains or pellets at the macroscale. Making accurate predictions of transport and adsorption in technical adsorbents requires probing the internal structure of the porous solid at the full range of relevant spatial scales, so as to include the effects of the heterogeneities described above.

Most characterisation measurements of adsorption systems provide information on average properties, assuming that the porous solid is a spatially homogeneous object when placed in the measuring chamber. Similarly, the performance of an adsorption column is typically inferred from concentration measurements in the effluent stream, without any validation from direct observations of the internal concentration profiles. In the recent years, these traditional approaches have been increasingly complemented by the use of imaging techniques that can observe phenomena in situ and under process conditions, including micro(spectro)scopy [1, 2] and tomography [3]. With this short review article, we aim at capturing recent developments in the field of imaging techniques to study adsorption in microporous solids, including adsorbents and catalysts. While significant advances have been made in the area of nanoporous materials characterisation by imaging [1, 4–6], we purposely focus our attention on the imaging of the adsorption process itself, thereby covering equilibria, kinetics and dynamics in both gas and liquid phase. Selected examples are presented of recent experimental achievements over the full range of relevant spatial scales, from microporous crystals to fixed-bed adsorption columns.

This novel ability to probe adsorption in space and time creates the missing link between traditional physisorption methods for the textural characterisation of micro-/meso-porous solids [7] and imaging technology. Such developments are key towards the design of improved adsorbent materials and their scale-up into technical bodies (e.g., pellets, monoliths or foams) to be used in large-scale processes. Knowledge of spatiotemporal phenomena in adsorption systems will

pave the way towards the design of robust processes that account for these heterogeneities.

2. Imaging the adsorbent and its heterogeneities

Adsorbent materials used in separation applications draw their functionality from their microstructure, which is made of micro- (pore sizes less than 2 nm), meso- (2 and 50 nm) and macro-pores (> 50 nm). Uniformity in the distribution of size, shape, volume and surface chemistry of the pores is key to achieve superior performances [8]. While zeolites and activated carbons continue to find applications in their traditional areas of use (e.g., air separation and water purification), new classes of materials are attracting substantial attention, including Metal Organic Frameworks (MOFs) [9], as well as both hierarchical [10] and isoreticular zeolites [11]. To be useful for industrial implementation, the adsorbent powders obtained in the laboratory need to be shaped into so-called technical materials, i.e. millimetre-sized bodies with sufficient porosity and mechanical stability. The archetypal example of this formulation process is the commercial preparation of molecular sieve adsorbents [12], where the active microporous zeolite crystals ($1-10$ microns in size) are mixed with a clay binder ($10-20$%wt. in the final product) to form extrudates or pellets. The obtained product is thus a composite material that offers new multi-scale features, such as intra- and extra-crystalline porosity, but that also reveals variations in local pore structure over length-scales that are significantly larger than the pore size [10, 13]. Of particular significance to industrial processes is the unfavourable impact that these heterogeneities have on both micro- [14] and macro-scale transport [15].

Conventionally, micro-/meso-porous adsorbents are characterized by physisorption analysis [7], which exploits the sensitivity of gas adsorption to the textural and wetting properties of the solid. Gravimetric or manometric methods are applied to this aim and result in observations of the adsorption equilibrium and kinetics. Specifically, gas adsorption isotherms measured at cryogenic

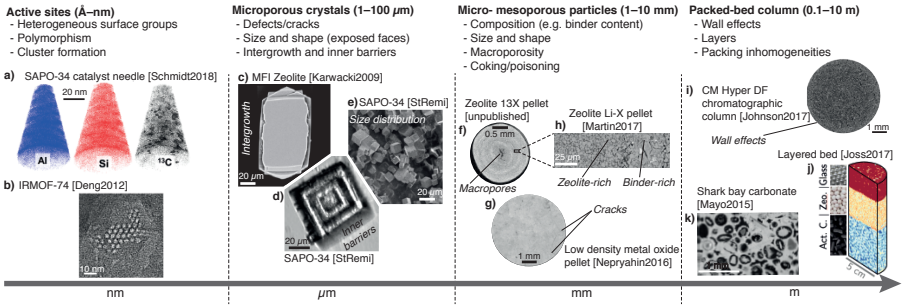

Figure 1: From Ångströms to metres: the length scales at stake in adsorption systems. Four categories are considered: the active sites, microporous crystals, micro-mesoporous particles, and the packed column/reactor, with the associated heterogeneities illustrated by using literature examples. **a.** Variability of chemical composition revealed by atomic probe tomography [16]. **b.** Individual pores of IRMOF-74 revealed by HRTEM [17] **c.** Inter-growth of a MFI zeolite (acquired by SEM, [18]). **d.** Inner barriers in SAPO-34 revealed by interference microscopy and **e.** SEM picture of their crystal size distribution [14]. **f.** X-ray CT scan of one zeolite 13X pellet revealing concentric layering and the presence of a crack in the centre. **g.** Heterogeneous pellet structure obtained by compaction of copper/zinc oxide alumina crystals and visualised by X-ray CT [19]. **h.** SEM micrograph of Li-X zeolite particle showing the presence of binder- and zeolite-rich phases [20]. **i.** X-ray CT of a chromatographic column showing a region of lower porosity close to the wall [21]. **j.** Artificially produced adsorbent layers (zeolite 13X and activated carbon) imaged by X-ray CT [22]. **k.** Heterogeneous grain and intra-granular porosity distribution in an oolitic carbonate imaged by X-ray CT.

temperatures enable the estimation of specific surface area, pore volume and pore size distribution. These represent average properties of the given sample, because the interpretation of the experiment relies on the assumption that the solid (e.g., the pellet or the packing of pellets) is spatially homogeneous when placed in the measurement chamber. It follows that a single experiment made with these conventional methods fails at uncovering variabilities that are known to exist in porous media from the pore- to the continuum-scale. In this context, imaging techniques, from spectroscopy [1] to tomography [10], are providing an unprecedented level of observational detail on the structure and composition of porous media, including adsorbents and catalysts. Most significantly, they have demonstrated the presence of heterogeneities at various length scales, l, in terms of (i) active sites ($\mathcal{O}(l) \sim$ nm)[1, 16, 17, 23], including active site zoning and the presence of different crystal planes or polymorphs (Figure 1a,b); (ii) crystal diversity ($\mathcal{O}(l) \sim \mu$m) [14, 18, 24], referring to size, shape and the presence of defects (Figure 1c-e); and (iii) variation in size, shape and composition of formulated particles ($\mathcal{O}(l) \sim$ mm) [19, 20] (Figure 1f-h).

While the current trend of imaging porous solids is that to increase spatial resolution to resolve individual pores [16, 25], this can only be achieved at the expense of sample size. In fact, the field-of-view that can be probed is typically in the order of 1000 times the voxel resolution, resulting in sample sizes that are significantly smaller than a cubic millimetre, thereby limiting the statistical significance of the dataset. One alternative is to exploit quantitative imaging methods that provide a space-resolved macroscopic measurement of the adsorption of a fluid in the nanopore space. The benefits of combining imaging techniques with conventional physisorption methods have been demonstrated for Magnetic resonance imaging (MRI) [26] and X-ray Computed Tomography (X-ray CT) [22], where protocols have been devised to result in spatial maps of microstructure properties, such as the specific surface area and locally-averaged mean pore size [27, 38]. Because they can accommodate much larger objects (e.g., a fixed-bed reactor), these techniques can resolve the complex architecture of adsorbent systems at larger length-scales ($\mathcal{O}(l) \sim$ mm $-$ m), thereby revealing

heterogeneities related to the nonuniform material degradation or poisoning [28] and to the packing structure [29], including wall effects [21, 30, 31] and artificially produced layers in adsorbent columns [22, 38] (Figure 1i-k).

3. Imaging techniques to probe adsorption

The first successful attempts in the imaging of the adsorbed phase in microporous solids have been achieved in the late 1970s by using X-rays [32] and nuclear magnetic resonance (NMR) [33]. These two techniques have since experienced significant improvements in both their temporal and spatial resolution, while new methods have appeared, namely positron emission tomography (PET) and several light microscopy techniques, including fluorescence- (FM), interference- (IFM) and infrared microscopy (IRM). We proceed to give a brief overview of these techniques below, while the main features are summarised in Table 1.

In an *X-ray CT* experiment, the measured quantity is the integral attenuation of the X-ray beam. By taking attenuation measurements for multiple sample orientations, a map (tomogram) of the local attenuation coefficients can be reconstructed, whose values depend on the voxel-averaged electron density and atomic number. For adsorption studies, two approaches have been followed to monitor the concentration of guest molecules, namely (i) by using strongly attenuating fluids (e.g., Xenon [36], brominated [32] and chlorinated [40] solvent vapours, or aqueous solutions of iodine salts [42]) or (ii) by exploiting directly the attenuation contrast provided by the dense adsorbed phase [37]. More recent developments enable the quantification of the excess adsorbed amount by using difference images acquired with and inert and adsorbing gas [3, 22]. A major highlight of X-ray CT is that the same principle enables probing a wide range of object sizes and spatial resolutions, from mm-size samples (μm-resolution using synchrotron sources or a laboratory microCT instrument) to metre-size samples (mm-resolution using a medical instrument).

In a *PET* experiment, the adsorptive is labelled with a positron-emitting isotope (e.g., ^{11}C [43, 46] or ^{18}F [66]) and its activity is monitored in space and

Table 1: Imaging techniques to probe adsorption. List of sample size and spatio-temporal resolution reported for different imaging techniques used to study adsorption, alongside key references where the study of adsorption equilibrium, kinetics, dynamics from a single component or a mixture has been demonstrated in the gas (G) or liquid (L) phase.

Technique[b]	Sample size (mm)	Spatial resolution (mm)	Time resolution	Equilibrium	Kinetics and dynamics	Mixtures
X-ray CT	0.01–100	0.2–2	2 min–1 h[c]	G: [3, 22, 34–38] L: –	G: [32, 39, 40] L: [31, 41, 42][d]	G: [29][e] L: –
PET	4–60	1–3	0.5 s (1D) 10 s (3D)	G: – L: –	G: [43–46] L: [47]	G: – L: [47]
IFM	0.05–0.1	5×10^{-4}	10 s	G: – L: –	G: [2, 14, 48–51, 68] L: –	G: [52] L: –
IRM	0.05–0.1	3×10^{-3}	2 s	G: – L: –	G: [2, 53, 54] L: –	G: [54, 55] L: –
FM	0.02–0.1	5×10^{-4} [f]	5 s [f]	G: – L: –	G: – L: [23, 71]	G: – L: [24]
MRI	0.3–50	0.1–5	5–10 min (2D) 0.1–10 s (1D)	G: [27, 56] L: –	G: [33, 57–63] L:[64]	G: [60] [65][g]

[a] – indicates that no study of that specific case has been reported, to the best of the authors' knowledge.

[b] X-ray CT: X-ray computed tomography (CT); PET: positron emission tomography or profiling; IFM: interference microscopy; IRM: infrared microscopy; FM: fluorescence microscopy; MRI magnetic resonance imaging.

[c] 5 s/slice with a medical CT; 1 h for a 3D micro-CT scan.

[d] These studies only considered the hydrodynamics in a chromatography column by using an inert KI tracer in methanol.

[e] Multicomponent measurements with X-ray CT have only been demonstrated by exploiting the K-edge of Xenon.

[f] Space- and time-resolution can be reduced to a few nm and 0.2 s using a single molecule localization and tracking approach [72].

[g] While adsorption is not the focus of this study, it provides a very nice example of how MRI can be used to differentiate chemical compounds present in microporous solids.

time by detecting the gamma rays that are emitted during radioactive decay. This is achieved by means of a cylindrical array of detectors, thereby enabling the three-dimensional reconstruction of the adsorptive distribution in the porous medium. Major highlights of PET are the high molecule-specificity (enabling the study of e.g., chromatographic separations [47]), the high-temporal resolution (seconds) and the penetrating power of gamma rays (enabling the monitoring of processes occurring within dense porous materials and inside stainless-steel reactors [43, 46]). Positron-emitting isotopes with half-life of a few minutes to a few days are typically used [67], and therefore PET facilities must include a radionuclide generator, or be in proximity of a cyclotron facility.

IFM is based on the detection of the phase shift emerging from the superposition of a light beam passing through a porous crystal and another one passing through the surrounding atmosphere [68]. Because the magnitude of this change is proportional to that of the change in the local adsorbate concentration, direct visualisation of the adsorption/desorption process is possible. When the time scale of uptake (or release) is too fast, IFM is complemented by IRM that records IR spectra by a focal plane array detector to yield the time dependence of the total molecular uptake on individual crystals [68]. Both methods are applicable to crystals of regular geometry and that are transparent to the applied wavelength, whereby the measured variable is the integral of the local relative concentration in the direction of light propagation (2D imaging) [2]. Absolute sorbate concentrations are determined by comparison with independent adsorption isotherm measurements or simulations. By acquiring molecule-specific absorption bands, IRM also enables the study of multicomponent adsorption, co- and counter-diffusion [55]. Time-resolved and molecule-specific concentration profiles in micrometre-sized single crystals can also be monitored by fluorescence micro(spectro)scopy (FM), thereby using a much higher intensity light source to excite a suitable (model) fluorescing dye that diffuses through the sample [4].

In MRI, a defined pulse sequence in a spatially varying magnetic field is applied to determine images of the local spin density, which can be transferred

into concentration maps by assuming direct proportionality. For adsorption studies in nanoporous materials, MRI has been applied to ^{1}H [60], ^{13}C [62] and ^{129}Xe [59] nuclei. Of particular interest to adsorption studies is the ratio of NMR relaxation times T_1/T_2 (spin-lattice/spin-spin), which provides an indication of the relative surface affinities of adsorbates [69, 70]. Moreover, the resonance frequency provides information on the chemical composition in the case of mixtures, and the use of pulsed magnetic field gradients allows labelling and tracking the position of the nuclei for characterising transport processes [61]. MRI is highly versatile, although the acquisition of three-dimensional images remains time consuming [70]. Specific pulse sequences have been devised for fast acquisition, but identifying the correct measurement protocol for studying a specific system remains hardly accessible to non-specialists.

4. Adsorption equilibria, kinetics and dynamics visualised

The ability to image adsorption processes in nanoporous solids has been demonstrated by various techniques, covering the range of length-scales from single crystals ($\mathcal{O}(l) \sim 100$ μm) to adsorbent beds ($\mathcal{O}(l) \sim 10$ cm). Examples of such achievements are summarised in Figure 2 and include measurements of adsorption equilibria, kinetics and dynamics.

Kärger and coworkers have successfully applied IFM and IRM to observe the temporal and spatial evolution of light hydrocarbons, alcohols and their mixtures during adsorption/desorption in a number industrially-relevant zeolite crystals, such as ZSM-5 [48], FER [49], SAPO STA-7 [50], MFI [2], SAPO-34 [14] and MOFs [54]. As an example of general validity, Figure 2a shows one- and two-dimensional transient concentration profiles acquired during propylene uptake in a cubic crystal of zeolite AlPO-LTA [68]. Upon comparison of the experimental profiles with the solution of a suitable mathematical model of the uptake process, important transport parameters can be estimated, such as the diffusivity and surface permeability. Because it directly records intra-crystalline concentration, microimaging by IFM has revealed novel insight into the nature

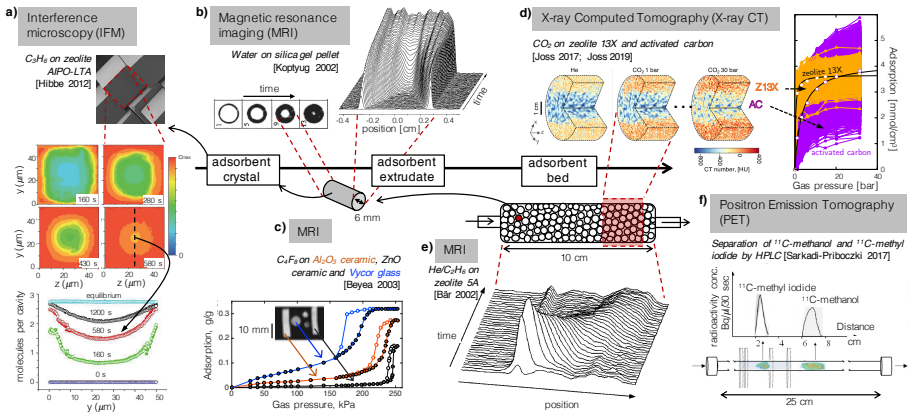

Figure 2: The digital adsorption lab: selected literature examples, where adsorption equilibria, kinetics and dynamics are measured using imaging techniques. **a.** 2D transient concentration maps acquired by IFM during propylene uptake at 295 K by a single crystal of zeolite AIPO-LTA (shown on the SEM image) and the corresponding profiles through the crystal centre (bottom plot) [68]. **b.** Transient concentration profiles acquired by MRI during adsorption of water in a single pellet of silica gel and the corresponding 2D radial concentration maps [63]. **c.** Adsorption (filled symbols) and desorption isotherms (empty symbols) acquired by MRI using C_4F_8 at 291 K on a composite porous test material composed of ZnO ceramic (bottom curves), Al_2O_3 ceramic (middle curves) and Vycor glass (top curves) [27]. **d.** Three-dimensional X-ray CT maps of the attenuation (in Hounsfield units, HU) of a composite zeolite/activated carbon adsorbent bed when exposed to helium and at increasing pressures of CO_2 ($1-3$ MPa) at room temperature. The measured local adsorption isotherms are shown on the adjacent plot for zeolite (3060 isotherms, orange triangles) and activated carbon (4540 isotherms, violet circles) [22]. **e.** Evolution of the concentration profile of an ethane pulse injected into a 3-cm diameter, 10-cm long column packed with 5A zeolite pellets (helium is the carrier gas flowing at 500 mL/min at room temperature) [60]. **f.** Radio-chromatographic peaks of ^{11}C-methyl iodide and ^{11}C-methanol acquired by PET along the length of a 25 cm-long HPLC column and the corresponding tomograms [47].

of transport resistances in nanoporous crystals [2], thereby providing direct evidence for diffusion anisotropy [51], for the presence of internal structural defects [49] and for the variability in surface permeability among crystals of similar origin [14]. Similar observations have been made by FM on individual crystals of layered double hydroxides [71] and ZSM-5 [24]. By profitably combining observations with selected dye molecules, FM can also discriminate between different pore systems (straight and sinusoidal) and enables the visualisation of intracrystalline mesoporous defects through dye adsorption [23]. An interesting development of the technique is the ability to track the trajectory of a single luminescent dye molecule at the nanometre scale and to calculate local diffusion coefficients, as demonstrated for mesoporous silica [72].

MRI can also be used to monitor sorption kinetics in adsorbent materials, albeit at lower resolution and on larger samples. Figure 2b shows the transient water diffusion profiles within a single cylindrical silica gel pellet [63]. Similar diffusion experiments have been successfully conducted with water and propane on 13X zeolite extrudates [60], and with Xenon on mm-sized aerogel fragments [58]. This approach has enabled the exploration of the rich variety of diffusional behaviour that can be observed in microporous solids and that depends on (i) the form of the adsorption isotherm and (ii) the concentration-dependency of diffusivity, which leads to the asymmetry between adsorption and desorption concentration profiles [60]. The ability to measure concentration profiles in-situ reveals effects that arise from variations in the local voidage properties within individual adsorbent pellets and that can be quantified through spatially-resolved diffusion coefficients [73, 74]. Efforts in this direction are justified by the need of developing more realistic structural models of technical pellets, including adsorbents and catalysts [75].

Spatially-resolved measurements of equilibrium adsorption isotherms have been successfully carried out on mm-sized samples using both MRI (Figure 2c) and X-ray CT (Figure 2d). Studies with MRI have largely focused on mesoporous ceramics and by using a thermally polarized gas (e.g., C_4F_8) [27, 56]. Early attempts with X-ray CT used a strongly attenuating gas for imaging,

such as Krypton [39] and Xenon [35, 36], while more recently adsorption experiments with CO_2 have been reported [3, 22, 37]. The applicability of X-ray CT is demonstrated by the wide range of materials investigated in these studies, including both natural (coal and shale) and industrial sorbents (activated carbons and zeolite). Notably, high resolution can be achieved by synchrotron-based sources [29], thereby providing access to microstructure properties and their spatial distribution over the continuum of length scales from the micrometre to the metre. In fact, by interpreting adsorption isotherms measured locally by standard physisorption analysis, maps can be constructed that describe the distribution of the average pore-size and the specific surface area [27].

Although qualitative attempts using X-ray CT have been reported [40], MRI and PET appear to be more suitable for the study of adsorption dynamics on the scale of a packed adsorbent bed, because, when imaging along a single dimension, they provide high temporal resolution. Systems that have been studied by MRI include water/4A zeolite [57], CO_2/5A zeolite [62] and light hydrocarbons/5A zeolite [60]. As shown in Figure 2e, this technique enables the direct measurement of the transient concentration profiles within the column, which can be used to compute mass transport rates and adsorption properties. A notable application of the imaging approach is that spatial heterogeneities in mass transport properties can be identified by the local adsorption behaviour in the packed bed, which can be caused by coke formation [76] or by intra-batch pellet variability [59]. PET represents an interesting alternative to MRI, because it enables real-time in-situ monitoring of liquid- and gas-phase processes, albeit at a lower spatial resolution ($\mathcal{O}(l) \sim$ mm) [43]. However, because it detects spontaneous decay activity originating from the sample without the need for continuous excitation, PET can be used to investigate separation processes in three-dimensions, while retaining fast acquisition times ($\sim$10 s, Figure 2f) [47]. Moreover, its very high molecule-specific sensitivity enables the study of multicomponent adsorption. It is worth noting that although all these tomographic techniques enable the study of adsorption dynamics in adsorbent beds over multiple dimensions, so far quantitative analyses have largely been limited

to one-dimension only.

5. Conclusion

The ability to image adsorption in nanoporous materials provides not only a verification of our understanding of fluid-behaviour and mass transfer in these systems, but the required insight for the rational design of the materials themselves and the chemical processes deploying them. As discussed in this short review, a range of advanced characterisation methods exist to probe adsorption processes over the continuum of relevant length-scales. The presented examples illustrate the potential for studying the equilibrium, kinetic and dynamic properties of adsorption systems, and demonstrate the impact of heterogeneities on the behaviour of these systems. In this context, while tremendous progress has been made in the field of catalyst characterisation, significant opportunities still exist in the study adsorption processes, as evidenced by the gaps identified in Table 1. The behaviour of mixtures is still largely unexplored, despite most adsorption-based processes involve multiple components. Physisorption-based characterisation will greatly benefit from high-throughput screening analyses, because of the inherent capability of imaging techniques to measure a multitude of different materials concurrently. The continuous advances in imaging technology, together with the increasing availability of computational power for both image analysis and simulation will enable to fully take advantage of these advanced characterisation methods.

Conflict of interest statement

Nothing declared.

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