A ANNUAL REVIEWS

Annual Review of Chemical and Biomolecular Engineering

Characterization of Nanoporous Materials

M. Thommes and C. Schlumberger

Institute of Separation Science and Technology, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen 91058, Germany; email: matthias.thommes@fau.de

Annu. Rev. Chem. Biomol. Eng. 2021. 12:137-62

First published as a Review in Advance on March 26, 2021

The Annual Review of Chemical and Biomolecular Engineering is online at chembioeng.annualreviews.org

https://doi.org/10.1146/annurev-chembioeng-061720-081242

Copyright © 2021 by Annual Reviews. All rights reserved

ANNUAL CONNECT

www.annualreviews.org

- Download figures
- Navigate cited references
- Keyword search
- Explore related articles
- Share via email or social media

Keywords

physical adsorption, textural characterization, density functional theory, pore condensation, mercury porosimetry, nanopores

Abstract

Detailed analysis of textural properties, e.g., pore size and connectivity, of nanoporous materials is essential to identify correlations of these properties with the performance of gas storage, separation, and catalysis processes. The advances in developing nanoporous materials with uniform, tailor-made pore structures, including the introduction of hierarchical pore systems, offer huge potential for these applications. Within this context, major progress has been made in understanding the adsorption and phase behavior of confined fluids and consequently in physisorption characterization. This enables reliable pore size, volume, and network connectivity analysis using advanced, high-resolution experimental protocols coupled with advanced methods based on statistical mechanics, such as methods based on density functional theory and molecular simulation. If macropores are present, a combination of adsorption and mercury porosimetry can be useful. Hence, some important recent advances in understanding the mercury intrusion/extrusion mechanism are discussed. Additionally, some promising complementary techniques for characterization of porous materials immersed in a liquid phase are introduced.

1. INTRODUCTION

Nanopore:

pore width <100 nm

Micropore: pore width <2 nm

Mesopore: pore width 2–50 nm

Macropore: pore width >50 nm Challenges arising with the necessity of further optimizing applications in the area of gas storage, separation processes, and catalysis (e.g., 1–5) cause a demand in tailoring of textural properties of adsorbents and methodologies for their textural characterization. Within this context, major progress has been made concerning the development of advanced nanoporous materials, such as ordered mesoporous molecular sieves (e.g., M41S materials), ordered carbons (e.g., CMK materials), metal–organic frameworks (MOFs), and related materials (e.g., 6–10). The introduction of hierarchical pore systems in materials such as zeolites, carbons, and silicas has received a lot of attention as well (e.g., 11–16).

For the design and optimization of these challenging processes, we need to investigate the relationship between structural properties and process performance. In particular, pore size, shape, and connectivity are key parameters affecting diffusional rates, adsorption capacity, and selectivity (e.g., 17–20). Advanced textural characterization is crucial to obtain detailed information on surface area, pore size, and network connectivity. Combining this information with studies on process performance will help to correlate structural properties of materials with the performance of these processes. Hierarchical pore structures especially can improve diffusional rates and, hence, process performance (e.g., 17, 18). Additionally, adsorption capacity can often be directly correlated with pore structure (e.g., 21–24). Moreover, molecular simulation and high-throughput screening of possible new porous materials are powerful tools for correlating textural properties with process performance (25–29).

Textural characterization can be based on different techniques, such as gas adsorption, X-ray diffraction, small-angle X-ray and neutron scattering, mercury porosimetry, electron microscopy, and nuclear magnetic resonance (NMR) methods. Each of these methods has a limited application range. Reference 30 provides an overview of the different methods and their application ranges for pore size analysis.

Characterization based on gas adsorption allows for the determination of a wide range of pore sizes in the nanopore size range (up to 100 nm), including the complete range of micropores (pore width smaller than 2 nm) and mesopores (pore width between 2 and 50 nm) (31). In recent years, major progress has been made in the textural characterization of porous materials by physisorption (31–42). To characterize larger nanopores and macropores (pore width >50 nm) up to ~400 μ m, complementary techniques such as mercury porosimetry are needed. Gas adsorption in combination with mercury porosimetry covers a wide range of pore sizes; hence, we focus on these methods for textural characterization in this review.

However, in contrast to textural characterization in the gas phase, far fewer advances have been made in the textural characterization of porous materials immersed in a liquid, although this is essential for the optimization of corresponding processes, e.g., liquid chromatography. This is particularly important for functionalized nanoporous materials, where the interaction with the chosen liquid may affect the accessible surface area and porosity, or in cases in which materials cannot be outgassed or dried without changing their texture.

In this work, we do not attempt to provide a comprehensive general review of recent advances in the field of porous materials characterization but instead focus on selected, important aspects of assessing surface and pore structure of nanoporous materials via physical adsorption. We also briefly discuss recent advances in macropore analysis by mercury porosimetry and the challenges associated with the textural characterization of solvated porous materials.



(*a*) International Union of Pure and Applied Chemistry classification of physisorption isotherms (reproduced with permission from Reference 31) and (*b*) schematic illustration of adsorption potential on a planar, nonporous surface and in a meso- and micropore (based on Reference 34).

2. PHYSICAL ADSORPTION CHARACTERIZATION

In general, adsorption means the enrichment of molecules, atoms, or ions near an interface. The material in the adsorbed phase is known as the adsorbate; the same component in the fluid phase is referred to as the adsorptive. Physical adsorption occurs whenever an adsorptive is brought into contact with the surface of a solid (adsorbent) because of attractive fluid–(pore–)wall interactions (31).

2.1. Adsorption Mechanism

Understanding the adsorption mechanism is essential for a reliable interpretation of adsorption isotherms and hence for obtaining structural information, surface area, pore size, volume, and connectivity of porous materials from gas adsorption experiments. In the case of complex pore networks, analyzing the adsorption mechanism can be challenging.

The shape of the adsorption isotherm reflects the interplay between attractive fluid–fluid and fluid–wall interactions coupled with the effect of confinement. Accordingly, isotherms are classified based on the 2015 International Union of Pure and Applied Chemistry (IUPAC) classifications (31). The classification of physisorption isotherms is illustrated in **Figure 1***a*. **Figure 1***b* schematically shows the characteristic adsorption potentials. In micropores, sorption behavior is dominated almost completely by the interactions between fluid molecules and the pore wall. Hence, micropore filling is, in most cases, a continuous process and occurs at low relative pressures $p/p_0 < 0.15$ (for N₂ and Ar at 77 and 87 K, respectively; p_0 is the saturation pressure of the bulk fluid at a given temperature). In the case of ultramicropores, the pore filling is governed entirely by the

Ultramicropore: pore width <0.7 nm



Schematic (qualitative) illustration of pore geometry effects on the adsorption mechanism. (*a*) Adsorptive molecule inside a slit, cylindrical, and spherical micropore with the same pore width w. (*b*) Adsorption potential depending on the micropore geometry. (*c*) Pore geometry effects on adsorption isotherm; i.e., the relative pressure at which pore filling occurs increases depending on the pore geometry from spherical to cylindrical to slit pores.

enhanced gas–solid interaction, giving rise to a type I(a) isotherm. However, in addition to the strong adsorption potential, a cooperative mechanism plays a role in the pore-filling process of wider micropores (i.e., supermicropores), which occurs in a range of higher relative pressures (e.g., $p/p_0 = 0.01-0.15$ for N₂ and Ar at 77 and 87 K, respectively), leading to a type I(b) adsorption isotherm. Figure 2 illustrates the effect of different micropore geometries for a given pore width on the adsorption potential and the isotherm. The relative pressure at which pore filling occurs for a given pore width increases from spherical to cylindrical to slit pores owing to their different adsorption potentials, whereby the adsorption potential increases from slit- to spherical-pore geometry. Hence, this illustrates the importance of assuming a proper pore geometry for a reliable pore size analysis, as discussed in Section 2.2.3.

Reversible type II isotherms are characteristic for nonporous or macroporous materials with heterogeneous surfaces. In this case, unrestricted monolayer–multilayer formation during adsorption is possible. In the case of a highly uniform nonporous surface, layer-by-layer adsorption occurs, leading to a type VI adsorption isotherm, e.g., Ar and Kr adsorption on graphitized carbon blacks (32). In contrast, type III isotherms can be observed if the fluid does not completely wet the surface because of weak interactions between fluid molecules and the (pore) wall. In this case, the molecules build clusters around preferred sites of the adsorbent owing to stronger interactions between fluid molecules compared with fluid-wall interactions. In the case of type V isotherms, molecular clustering is followed by pore filling (31). For instance, type V isotherms are observed for water adsorption in hydrophobic microporous and mesoporous adsorbents.

Type IV isotherms are characteristic for the adsorption of fluids in mesopores. In fact, the definition of micro- and mesopore size ranges is somewhat arbitrary, and the detailed adsorption mechanism depends on the ratio between molecular size and pore size. However, particularly for simple fluids such as Ar, N_2 , CO_2 , and Kr, which are the key adsorptives for textural characterization, the association of type I isotherms and type IV isotherms with microporous and mesoporous materials, respectively, is phenomenologically true.

In case of Type IV isotherms, adsorbate films completely wet the adsorbent surface. The sorption and phase behavior of fluids in mesopores depend not only on the fluid–wall attraction but also significantly on the attractive fluid–fluid interactions. This leads to the occurrence of multilayer

Supermicropore: pore width 0.7–2 nm

adsorption followed by capillary condensation. Pore condensation represents a phenomenon whereby gas condenses to a liquid-like phase in pores at a pressure lower than the saturation pressure, p_0 , of the bulk fluid. In this sense, pore condensation reflects a first-order phase transition between an inhomogeneous gas configuration, which consists of vapor in the core region of the pore in equilibrium with a liquid-like adsorbate layer, and a liquid configuration, where the pore is filled with liquid (36, 37). At the pore critical point of the confined fluid, these two hitherto-distinct fluid configurations become indistinguishable; i.e., a pore condensation step can no longer be observed (43). The critical temperature of the confined fluid is shifted to lower temperatures; i.e., in contrast to the predictions of the classical Kelvin equation, pore condensation and hysteresis will vanish already at temperatures below the critical temperature of the bulk fluid. The shift of the critical temperature can be rationalized, for instance, by the argument that a fluid in narrow pores is an intermediate between a three-dimensional fluid and a one-dimensional fluid for which no critical point exists at T > 0. Hence, the shift in pore critical temperature (43). Consequently, at a given subcritical temperature, pore condensation is possible only in pores wider than the critical pore size w_c.

Both type IV(a) isotherms with hysteresis and IV(b) isotherms without hysteresis can be observed for mesoporous materials. Capillary condensation is accompanied by hysteresis if the pore width exceeds a certain critical width, which is dependent on adsorptive and temperature. Hysteresis is attributed to the existence of a metastable state of the pore fluid associated with the nucleation of the liquid phase; i.e., pore condensation is delayed. For instance, hysteresis occurs for nitrogen (77 K) and argon (87 K) adsorption when the pore size exceeds 4.5 nm. For smaller mesopores, no hysteresis is observed. This phenomenon is correlated with the effect of confinement on the phase diagram of a confined fluid, as indicated above. **Figure 3** provides a schematic,



Figure 3

Schematic phase diagram of a bulk and pore fluid confined to different-sized pores of widths $w_1 > w_2$ and resulting isotherm types IV(a) and IV(b). (*a*) T-p-diagram for bulk fluid (*black*) and fluid confined in a pore with width w_1 (*blae*) and width w_2 (*red*), respectively. Pore condensation lines terminate in the pore critical points C₁ and C₂. Near the pore critical point, the hysteresis critical temperature (T_{H1}, T_{H2}), which is the temperature below which experimental hysteresis can be observed, can be defined (based on Reference 34). (*b*) Materials with pore width w_1 exhibit a type IV(a) isotherm at the measurement temperature T_{meas} (T_{meas} < T_{H1}). (*c*) Materials with smaller pores of width w_2 lead to a type IV(b) isotherm (T_{meas} > T_{H2}).



(*a*) Adsorption (points 1 to 4) and desorption points (points 4 to 7) at temperature T_1 in a schematic pressure–density phase diagram of a fluid confined to a mesopore. (*b*) Resulting type IV(a) isotherm with marked points 1 to 5 during adsorption and 4 to 7 during desorption.

simplified illustration of the shifted phase diagram for a fluid confined to slit-like mesopores with two different widths together with the resulting isotherm types IV(a) and IV(b). As illustrated, the critical point of confined fluid shifts to lower pressures and temperatures compared with the bulk critical point (44, 45). The triple point is also shifted to lower temperatures (43–48), in line with experimental observations for simple fluids such as Ar, Kr, and CO_2 (46, 49, 50) confined in mesoporous silica. However, details of the sorption and phase behavior below the bulk triple point, as well as the nature of pore triple points, are still under investigation.

Near the pore critical point, a hysteresis critical temperature T_H can be defined. If the measurement temperature is below T_H for a given pore width, pore condensation with hysteresis occurs [type IV(a) isotherm in **Figure 3***b*], whereas for temperatures above T_H , reversible pore condensation occurs, giving rise to a type IV(b) adsorption isotherm. This is the case for the smaller pores (width w_2), in which a completely reversible type IV(b) isotherm is found (**Figure 3***c*). However, decreasing the measurement temperature could lead again to hysteresis for this pore.

Figure 4a illustrates the detailed mechanism of delayed condensation in case of a type IV(a) isotherm with a schematic pressure-density (here displayed as $1/\rho$) phase diagram for a fluid confined in a mesopore [the phase diagram is shifted to higher densities as compared to the corresponding bulk phase diagram (44, 46, 50-52), but this is not shown here for clarity]. The average density of the pore fluid can be correlated directly with the amount adsorbed, and the resulting type IV(a) isotherm is shown in Figure 4b. The delay in pore condensation is consistent with the classical van der Waals picture, which predicts that the metastable adsorption branch terminates at a vapor-liquid spinodal, where the limit of stability for the metastable states is achieved and the pore fluid spontaneously condenses into a liquid-like state (so-called spinodal condensation; see 53, 54, and references therein). Points 1-4 represent capillary condensation during adsorption, and points 5-7 represent evaporation during desorption. Hence, during the adsorption process, the phase transition does not occur when crossing the binodal (point 2). The delayed phase transition is induced near the spinodal (point 3). In contrast, at the beginning of the desorption process, the pore is filled with liquid-like condensate. Hence, a liquid-vapor interface with the bulk vapor phase is already present. This leads to desorption without nucleation via a receding meniscus (55). The evaporation occurs when crossing the binodal (point 6). Therefore, the desorption process is associated with the equilibrium liquid-vapor transition. At higher temperatures, the width of



Adsorption hysteresis types and their correlation with pore structure, coupled with their underlying adsorption mechanism. (*a*) Type H1 hysteresis; (*b*) type H2(a) hysteresis in materials with wide pore cavity size distribution with marked points 1 and 2 during desorption and corresponding illustration of an example ink-bottle pore during pore blocking; (*c*) type H2(b) hysteresis in materials with a wide pore neck size distribution; and (*d*) type H2(a) hysteresis with marked points 1–3 during desorption, illustrating cavitation in a pore system with very narrow necks, and corresponding illustration of an example ink-bottle pore during cavitation (adapted with permission from Reference 36).

the metastable region becomes smaller. Hence, the hysteresis width also decreases, and hysteresis should disappear at the pore critical temperature (43, 46). However, experimental hysteresis will already disappear at a temperature near the pore critical temperature at the hysteresis critical temperature, as already mentioned (44, 45). At the hysteresis critical temperature, fluctuations are sufficient to overcome the now very small nucleation barrier associated with the narrow metastable region; i.e., the difference between binodals and spinodals becomes smaller as it approaches the critical temperature, where it disappears.

A detailed understanding of the effect of confinement on the sorption and phase behavior of fluids, including their critical behavior, is important not only for advanced physisorption characterization but also for many applications in the area of oil and gas production, where an accurate description of the state of hydrocarbons confined in real nanoporous systems, such as shale reservoirs, is required (51, 56).

To obtain detailed information on the pore (network) structure of a material, the origin of hysteresis and, consequently, the shape of hysteresis loops must be analyzed. The IUPAC (31) categorizes hysteresis loops into five different types. **Figure 5** illustrates some selected hysteresis types. In general, type H1 hysteresis is typical for materials with no pore network effects. Type H1 hysteresis can be found for mesoporous materials with independent cylindrical pores (e.g., MCM-41) and ordered three-dimensional pore networks (e.g., MCM-48, KIT-6 silicas, and controlled pore glass) (50, 57).

In addition to delayed condensation during adsorption, materials with more complex pore networks, e.g., networks with ink-bottle pores, show a shift in liquid–vapor transition during desorption (e.g., porous vycor glass, certain silica gels). Pore blocking or cavitation can cause delayed evaporation (58). The pore neck width determines which of these mechanisms is present for a given adsorptive and temperature. For nitrogen and argon adsorption at 77 K and 87 K, respectively, the critical neck width lies at 5–6 nm (59–61). Pore blocking occurs for pore necks larger than the critical width. In this case, the pore body remains filled until the neck evaporates at a lower relative pressure, and then the fluid from the pore cavity and neck evaporates simultaneously.

Pore blocking usually leads to type H2(a) or H2(b) hysteresis, as illustrated in **Figure 5***b*,*c*. Type H2(a) hysteresis shows a steeper desorption branch compared with the adsorption branch. This can be caused by a relatively wide size distribution of pore cavities compared with the distribution of neck sizes. Another reason for H2(a) hysteresis is percolation effects in pore networks. Hence, the liquid in the cavities evaporates when the largest neck evaporates (42). In this case, the desorption mechanism depends not only on the neck size but also on the connectivity to neighboring pores and their state (62). In contrast, type H2(b) hysteresis can be observed for materials with a narrow pore-cavity size distribution and in the absence of percolation effects (42). In this case, the pore neck size distribution can be obtained by analyzing the desorption branch. In some special cases, H1 hysteresis is possible for materials exhibiting pore blocking, e.g., for 3DOm carbons with spherical pores that are restricted by windows of a uniform size (63).

If the pore neck width is smaller than a certain critical width for a given adsorptive and temperature, desorption occurs via cavitation (58). In this case, the liquid in the pore cavity evaporates, whereas the neck remains filled. In case of cavitation, the neck and cavity remain filled while crossing the metastable region (illustrated in **Figure 4***a*). Near the spinodal of the pore fluid, a spontaneous nucleation of a bubble in the pore cavity followed by a liquid–vapor transition is induced; i.e., cavitation-induced desorption/evaporation represents a spinodal evaporation (64). Cavitation usually leads to type H2(a) hysteresis, as illustrated in **Figure 5***d*. However, for materials with narrow cavity size distribution, type H1 hysteresis can also be observed.

It is important to note that many materials used in various adsorption-based applications are highly disordered and show a wide pore size/volume and shape distribution. Hence, a combination of the above-described phenomena is present for these materials. Consequently, important insights obtained from a systematic investigation of the adsorption and phase behavior of fluids in model porous materials also allow for improving the understanding of the adsorption behavior in disordered materials, which in turn contributes to advancing physisorption-based characterization methodologies. A detailed understanding of the adsorption and desorption mechanisms is essential for reliable pore size distribution, pore size, and pore network analysis, as discussed in the following section.

2.2. Assessment of Surface Area and Pore Size

For textural characterization, the adsorption isotherm should ideally be considered a fingerprint of the pore structure. Hence, adsorption should not be appreciably affected by the adsorbent's surface chemistry for reliable surface area, pore size/volume, and network analysis. The proper choice of adsorptive coupled with the application of advanced data-reduction methods is the basis for accurate textural characterization.

2.2.1. Choice of adsorptive. For surface area and pore structure analysis, choosing the proper adsorptive is critical. Although nitrogen (N_2) adsorption at 77 K was the accepted standard adsorptive for both micropore and mesopore size analysis for many years, nitrogen is not always

appropriate for surface area and micropore size analysis. Nonpolar materials, and specifically nonfunctionalized carbons, can be analyzed accurately using nitrogen at 77 K. However, specific interactions between the quadrupole moment of the nitrogen molecule and various surface functional groups and exposed ions that are present in materials such as MOFs or zeolites lead to inaccurate analysis. This affects both the orientation of the adsorbed nitrogen molecules and the micropore filling pressure. Such specific interactions shift the pore-filling pressure of nitrogen to very low relative pressures (p/p₀ equal to $\sim 10^{-7}$) (e.g., 31, 42). Consequently, the pore-filling pressure is not correlated in a straightforward way with the micropore size.

In contrast to the issues with nitrogen adsorption, argon adsorption at 87 K (the boiling temperature of argon) displays no specific interactions with surface functionality or uncertainty in orientation and is the IUPAC's recommended choice for micropore characterization (31). In addition to using liquid argon, a variety of commercially available cryostats and cryocoolers enable high-precision control of experimental temperature at 87 K. Because in many cases argon (87 K) adsorption fills micropores at significantly higher p/p_0 than nitrogen, it is possible to reliably resolve small differences in micropore size (65, 66). However, nanoporous carbons may contain significant amounts of ultramicropores (i.e., often active carbons exhibit pores <0.5 nm), and diffusion further limits access to these micropores. To address this problem, the use of CO₂ as adsorptive was proposed for adsorption measurements at temperatures close to 273 K. It had been shown that carbon dioxide, with slightly smaller kinetic diameter and high adsorption temperature, enables higher diffusion rates, ultimately producing better ultramicropore resolution (67, 68). Because of these experimental advantages, CO₂ adsorption at 273 K has become a standard tool for the assessment of microporous carbons (32, 55, and references therein).

Coupling of CO₂ (273 K) adsorption with N₂ and Ar adsorption to obtain the combined micromesopore analysis (69) is needed because at 273 K and atmospheric pressure (i.e., the maximum pressure in conventional adsorption equipment used for physisorption characterization), CO₂ is restricted to filling pores narrower than \sim 1 nm (atmospheric pressure corresponds to a relative pressure of 10⁻²). Hence, expanding the pore size analysis of carbon based on CO₂ adsorption at 273 K would require use of high-pressure CO₂ adsorption data, measured up to saturation pressure (\sim 35 bar) (52).

Moreover, compared with N_2 , CO_2 exhibits an even stronger quadrupole moment, which affects the adsorption behavior on surfaces with polar surface functionality and hence prohibits the use of CO_2 as adsorptive for reliable pore size analysis of materials such as zeolites and MOFs. Also, caution must be applied in characterizing carbons containing appreciable amounts of oxygen surface functionalities.

2.2.2. Assessment of surface area. Despite its well-known limitations (32, 34, 41), the Brunauer–Emmett–Teller (BET) method (70) continues to be widely used to evaluate surface areas of micro- and mesoporous adsorbents, including nanoporous carbons. Indeed, under certain, carefully controlled conditions, the BET area of a nonporous, macroporous, or mesoporous solid giving rise to type II or type IV(a) isotherms can be regarded as the probe-accessible area or the effective area available for the adsorption of specified adsorptives. The 2015 IUPAC recommendations (31) provide a concise critical appraisal of the BET method. In addition to problems arising from the chemical and geometrical heterogeneity of the surface, porosity (i.e., existence of micro- and/or mesopores) plays an important role in determining the applicability of the BET equation. In the presence of micropores (i.e., type I isotherms and combinations of type I and II or type I and IV isotherms, which are characteristic of many micromesoporous materials), application of the BET method leads only to an apparent surface area (i.e., BET area). This is also correlated with the fact that the processes of monolayer–multilayer adsorption and

micropore filling are impossible to separate. Within the same context, it also appears that the BET method is inaccurate for estimating the surface area of mesoporous materials exhibiting a type IV(b) isotherm. Here, pore condensation is observed at pressures very close to the pressure range in which monolayer–multilayer formation on the pore walls occurs: This may lead to a significant overestimation of the monolayer capacity in a BET analysis.

As already indicated, the BET theory is not applicable in the presence of micropores, and by applying the BET method, the linear BET range is often shifted to significantly lower relative pressures (41, 71, 72). As a result, for predominantly microporous materials, linear BET plots are typically found at relative pressures of 0.1 and even lower. In fact, locating the relative pressure range for the linear BET plot can be challenging. Rouquerol and colleagues (71) introduced a useful procedure for determining the linear BET range that allows one to overcome this difficulty and determine the linear BET range in an unambiguous way for purely microporous materials. However, the BET area derived from an isotherm obtained on a microporous adsorbent should be treated not as a realistic probe-accessible surface area but rather as an apparent surface area, which, however, still may serve as a useful fingerprint of the adsorbent (31).

Furthermore, the heterogeneous nature of many surfaces causes another problem. As mentioned in the previous section, the quadrupole moment of the nitrogen molecule leads to specific interactions with potential polar surface sites (such as hydroxyl groups), causing an orienting effect on the adsorbed nitrogen molecule (31, 42). Consequently, the effective cross-sectional area is smaller than the customary value of 0.162 nm^2 . For a completely hydroxylated surface, a crosssectional area of 0.135 nm² was proposed, which was obtained by measuring the volume of N_2 adsorbed on silica spheres of known diameter (31, 34, and references therein). Accordingly, these uncertainties concerning the assumption of a proper cross-sectional area may affect the accuracy of BET areas obtained from N_2 (77 K) adsorption by up to 20–25%. Hence, as discussed above, argon adsorption (at 87 K) may be a useful alternative adsorptive for surface-area determination. Argon is monatomic, and far less reactive than the diatomic nitrogen molecule mainly because of the absence of a quadrupole moment. Hence, the cross-sectional area of argon $(0.142 \text{ nm}^2 \text{ at})$ 87 K) is also less sensitive to structural differences of the adsorbent surface. Consequently, as also discussed in the 2015 IUPAC recommendations, argon has significant advantages compared with nitrogen as a probe for the textural characterization of powders and porous materials. Alternative methods to obtain a specific surface area from gas adsorption are based on the application of the standard isotherm concept, e.g., t- and alpha-s methods (including the high resolution alpha-s analysis). In this connection, the alpha-s method has been found helpful because under certain conditions it allows one to obtain and approximate both the internal and external available areas (32).

In summary, the above-discussed points concerning the proper choice of adsorptive are crucial for a reliable surface assessment, and if not taken into account, this may lead to inaccuracies in surface area determination of 20–30%. Hence, this is important for the design of adsorption-based separation processes and applications in catalysis.

2.2.3. Pore size analysis. To obtain reliable information about pore size, pore size distribution, pore volume, and porosity from adsorption data, proper models that describe the underlying adsorption mechanism must be applied. For materials containing only micro- and mesopores, type I, type IV, or a combination of type I and IV isotherms can be observed. In this case, the nearly horizontal plateau near the bulk saturation pressure indicates that the pores are completely filled with adsorbate. Therefore, the pore volume can be calculated based on the amount of gas adsorbed near the saturation pressure, e.g., $p/p_0 = 0.95$, assuming the density of the adsorbate corresponds to the bulk liquid density [Gurvich rule (34)]. This method is not applicable for

materials containing macropores, as are, for instance, present in isotherms exhibiting hysteresis of type H3 where no plateau can be observed.

The validity of classical, macroscopic, thermodynamic methods for mesopore size analysis, such as the widely used BJH (Barrett, Joyner, Halenda) method (32), which is based on the modified Kelvin equation, becomes questionable for narrow mesopores. In fact, the effect of confinement on the state of the pore fluid cannot be described accurately via macroscopic, thermodynamic approaches (35, 55, 73), leading to large errors in pore size analysis for narrower pores of a diameter <20 nm. It was found that the BJH method– and related Kelvin equation–based procedures may underestimate the pore size by up to 20–30% for narrow mesopores smaller than 10 nm (34, 36, 55) if not properly corrected (74, 75). However, these calibrated methods are valid over only a limited pore size range.

Very often, microporous materials contain additional mesoporosity, and in this case, the micropore volume can be obtained by applying standard and comparison isotherm concepts (t-method, alpha-s method). These empirical methods allow one to determine micropore volume, external surface area, and, in principle, information about the average pore size (34, 76).

Similar to the situation of mesopore analysis, classical methods for micropore analysis based on the Dubinin–Radushkevich and the Horvath and Kawazoe methods (32, 77–79) often underestimate the pore size.

Applying microscopic methods based on molecular simulation [grand canonical Monte Carlo and density functional theory (DFT)] for pore size analysis addresses the above-mentioned problems of the macroscopic, thermodynamic methods. These advanced methods yield the thermodynamic and density profiles of confined fluids (80); describe molecular-level details of the adsorbed phase; and capture the essential features of the underlying mechanism for micropore filling, pore condensation, and hysteresis (37, 55, 81, 82). Use of DFT and molecular simulation–based methods allows for the determination of pore size distributions for the complete micro- and mesopore range. This is demonstrated in **Figure 6**, which shows the pore size distribution of hierarchically structured ZSM-5 zeolite determined with a nonlocal DFT (NLDFT) analysis of the argon (87 K) adsorption data (13).



Figure 6

Characterization of hierarchically structured ZSM-5 zeolite by argon (87 K) adsorption and nonlocal density functional theory (NLDFT) analysis. (*a*) High-resolution transmission electron microscopy image of a self-pillared pentasil (SPP) lamella. (*b*) Argon (87 K) isotherm for the silica SPP zeolite with the NLDFT (cylindrical pore model) fit. (*c*) Pore size distributions up to 10 nm for silica, aluminosilicate SPP zeolite, and commercial MFI zeolite (reproduced with permission from Reference 13).

DFT-based methods, in particular NLDFT, can be regarded as a standard method for pore size/volume analysis of nanoporous materials (for a review, see 55). Commercial software is now available for many adsorption systems, and the DFT method is also featured in international standards (such as ISO 15901–3). Recent advances include the development of 2D-NLDFT approaches (83–85) and quenched solid DFT (QSDFT), which consider the heterogeneity of real carbon surfaces (86). With these advanced DFT methods, much more realistic pore size analysis of disordered carbons can be obtained as compared to NLDFT. The NLDFT approach is based on the assumption of a molecularly smooth surface leading to pronounced layering in the theoretical adsorption isotherms and consequently to artifacts in the obtained pore size distribution (87, 88).

With these advanced DFT methods, it is now possible to obtain reliable information from both the adsorption and desorption branches of the hysteresis loop. In fact, DFT methods can take quantitatively into account the delay in condensation owing to metastable adsorption films in case of mesopores. This allows one to accurately calculate the pore size distribution from the adsorption branch by using a dedicated metastable adsorption branch kernel (89, 90). The application of metastable adsorption branch kernels is essential for the textural characterization of porous materials exhibiting pore blocking or cavitation; i.e., this is the only way to obtain a reliable pore size analysis for such materials, because classical approaches based on the Kelvin equation do not correctly describe the origin of hysteresis owing to delayed condensation.

An interesting example is given in **Figure 7**, which shows the nitrogen (77 K) adsorption isotherm of a typical carbide-derived carbon (91, 92). The isotherm reveals a type H4 hysteresis loop indicating the presence of micro- and mesopores. The steep stepdown in the isotherm around a relative pressure of 0.4 indicates the presence of cavitation in this sample. In this case, an accurate pore size distribution must be calculated from the adsorption branch of the isotherm. Hence, a hybrid QSDFT method, which assumes slit-pore geometry for the micropores and a cylindrical pore model to correctly describe the adsorption/condensation mechanism in the mesopores and considers the delay in condensation owing to metastable adsorption fluids, was applied. **Figure 7***a* demonstrates that this model fits the experimental adsorption isotherm, and the resulting pore size distribution is shown in **Figure 7***b*. In addition, the pore size distribution was obtained from the desorption branch by applying a slit/cylinder QSDFT equilibrium transition model. The obtained pore size distribution agrees with the pore size distribution derived from the adsorption branch



Figure 7

(*a*) Nitrogen (77 K) adsorption isotherm on carbide-derived carbon with quenched solid density functional theory (QSDFT) fit. (*b*) Pore size distribution (PSD) calculated from the desorption branch using a QSDFT equilibrium kernel illustrating the artifact owing to cavitation at \sim 5 nm and pore size distribution calculated from the adsorption branch using a QSDFT metastable adsorption branch kernel (reproduced with permission from Reference 40).



Pore model effect on the calculation of the pore size distribution of KLE silica (61). (*a*) N₂ (77 K) adsorption isotherm. (*b*) Pore size distribution calculated by applying nonlocal density functional theory on the N₂ (77 K) adsorption branch using a cylindrical pore model and a hybrid pore model consisting of cylindrical micropores and spherical mesopores. Because KLE silica pore structure consists of spherical mesopores, mesopore size can be readily determined with the hybrid (cylindrical/spherical) model. The cylindrical model causes a significant underestimation (~35%) of the mesopore size.

with the exception of the artificial peak at 5 nm, which is due to cavitation-induced evaporation, indicating that some larger pores are accessible only through necks/entrances that are smaller than a critical width [\sim 5–6 nm for N₂ (77 K) adsorption] (40).

As explained in Section 2.1, the pore geometry affects the adsorption potential. Hence, a certain pore geometry must be assumed for calculating a reliable pore size distribution. For instance, in classical models, a slit-pore geometry is often assumed for microporous carbons, whereas the Kelvin equation-based methods for mesopore analysis usually assume a cylindrical pore model. The effect of assuming an incorrect pore model for the pore size analysis is demonstrated in Figure 8 for a micro- and mesoporous KLE silica (61). The pore size distributions were calculated based on N_2 (77 K) adsorption by applying NLDFT with a cylindrical pore model and a hybrid model assuming cylindrical micropores and spherical mesopores. Owing to cavitation effects, the NLDFT model was applied on the N₂ adsorption branch. However, the micropores of the KLE silica are cylindrical and connected to spheroidal mesopores. Hence, the pore size distribution calculated with the cylindrical/spherical model represents a realistic description of the pore size (61). However, assuming only cylindrical pores clearly underestimates the mesopore size by approximately 35%. Assuming a spherical model gave here the mesopore size in agreement with small-angle X-ray scattering and TEM analysis (61, 93). This clearly demonstrates the importance of choosing the right pore model for calculating pore size distributions. An accurate evaluation of the pore size distribution is possible only if the adsorptive/adsorbent system and the nanopore structure are compatible with the chosen DFT kernel. Hence, a good fit between experimental and theoretical isotherm is a necessity but not a sufficient criterion.

Obtaining detailed complementary information on pore network connectivity requires advanced adsorption experiments coupled with state-of-the-art approaches based on DFT and molecular simulation. Coupling of various adsorptives at different temperatures in addition to hysteresis scanning experiments enables the identification of the underlying mechanisms of observed hysteresis. This provides the basis for analyzing details of the pore network characteristics (42, 61, 94, 95). During hysteresis scanning, partial adsorption/desorption curves are measured in the relative pressure range in which hysteresis occurs by changing the direction of the gas



Argon and nitrogen adsorption on mesostructured zeolite Y. (*a*) Ar (87 K) and N₂ (77 K) adsorption isotherms. (*b*) Nonlocal density functional theory pore size distribution calculated from Ar and N₂ isotherms. (*c*) Ar isotherms at 77 K and 65 K. (*d*) Hysteresis scanning isotherms with argon (77 K) (adapted with permission from Reference 98).

pressure variation during the adsorption/desorption process. For example, a desorption scan is started at a relative pressure at which pores are only partially filled. Within this context, a recently developed statistical theory describes adsorption/desorption hysteresis including scanning curves in one-dimensional pore structures with structural disorder (96, 97). A quantitative description of scanning curves obtained in 3D pore networks has been suggested by percolation models coupled with methods based on molecular simulation (e.g., 94, 95, and references therein).

An example is given in Figure 9, which shows advanced physisorption experiments on C16 mesostructured zeolite Y to verify the hierarchical structure of the material (98). For both nitrogen and argon adsorption isotherms at 77 and 87 K, respectively, hysteresis associated with pore condensation was observed (Figure 9a). The width of the hysteresis loops for argon and nitrogen is different, indicating different states of the mesopore fluid [i.e., nitrogen at 77 K is here much closer to its pore critical temperature (35)]. Figure 9b exhibits a bimodal pore size distribution obtained by applying dedicated NLDFT hybrid methods, assuming, in accordance with the underlying pore structure, a spherical pore model for the micropores and a cylindrical pore model for the mesopore range. Additional argon adsorption experiments at 77 and 65 K (Figure 9c) helped to further elucidate structural details about the micromesopore network characteristics of this mesoporous zeolite. Lowering the analysis temperature affects the state of the confined phase; i.e., the fluids even in narrow mesopores (i.e., the pores in the range from 3-4 nm) are now also below their hysteresis critical temperature (see Section 2.1 and Figure 3) and therefore contribute, contrary to 87 K, to the shape of the hysteresis loop. As Figure 9c shows, type H5 hysteresis, according to the IUPAC classification, is observed for argon adsorption isotherms at 65 and 77 K. This hysteresis loop is associated with the presence of both open and partially blocked pores, whereby the majority of mesopores are freely accessible without constriction, whereas access to a smaller amount of mesopores is affected by constrictions in the form of pore necks; i.e., most likely these pores are accessible only via the narrow zeolitic micropore channels. The emptying of these constricted pores is associated with cavitation, as confirmed by analysis of hysteresis scanning measurements performed for the argon (77 K) isotherm and shown in Figure 9d. Advanced analysis of these data obtained with the described procedure allows one to differentiate between different types of interconnected pore networks and to quantify the accessible pore volume. In this case, approximately 33% of pores are restricted, whereas the remaining mesopores are fully accessible and lead to the micropores of the zeolite, as had been demonstrated by the application of complementary techniques based on electronic tomography (98). However, despite the amount of restricted pores, this hierarchically structured mesoporous zeolite Y performs better in catalysis (14).

3. MACROPORE ANALYSIS

Although gas adsorption can be used to assess the pore network characteristics of porous materials exhibiting micro- and mesopores, major challenges are still associated with assessing macroporosity. In 2012, the IUPAC (99) provided an overview of various techniques that can be used for macropore analysis, including liquid-intrusion methods such as contact porosimetry, capillary flow porometry, and mercury porosimetry. Mercury porosimetry is still considered to be the state-ofthe-art method for textural analysis of macroporosity (99). The main attraction of this technique is that it allows pore size analysis over a wide range of mesopore-macropore widths (from \sim 3 nm up to >400 μ m) in a fast and highly reproducible way (100). In contrast to physical adsorption of fluids such as nitrogen and argon at their boiling temperatures, where the adsorbed phase completely wets the pore walls, liquid metals such as mercury do not wet the majority of materials at or close to room temperature. Hence, (hydraulic) pressure must be applied to force liquid metals into pores. By using the Washburn equation, the pore size distribution can be calculated from the intrusion data. In recent years, a more detailed understanding of the phase behavior of mercury in nanoconfinement has been achieved via systematic experiments on porous materials with welldefined meso- and macropore structure coupled with approaches based on statistical mechanics such as DFT and molecular simulation (101-106).

Further insights on mercury sorption and phase behavior were enabled very recently through the discovery that KIT-6 silica (an ordered mesoporous molecular sieve exhibiting an ordered 3D pore network) can (in contrast to MCM-41 or MCM-48) withstand the high pressures in mercury intrusion/extrusion experiments. These studies on KIT-6 silicas also allowed investigation of the analogies between condensation/evaporation mechanisms of wetting (N_2 at 77 K) and nonwetting (Hg at 298 K) fluids as a function of pore size, confirming the thermodynamic consistency between Hg intrusion/extrusion and capillary evaporation/condensation (105). This is demonstrated in Figure 10*a*, which shows the N_2 at 77 K isotherm on one of the KIT-6 in comparison with the corresponding mercury adsorption/desorption isotherm (i.e., the hydraulic pressure needed to push mercury into the pores is correlated with the pressure of mercury vapor that coexists with the liquid mercury inside the porous material). The reversed symmetry observed between the two sets of curves is striking. Whereas capillary condensation of N2 occurs at pressures smaller than the saturation pressures, the vapor-liquid phase transition for the nonwetting fluid mercury occurs at pressures larger than the saturation pressure. The effect of pore size on both the vapor-liquid phase transition of the wetting adsorptive (N₂, 77 K) and the nonwetting fluid (Hg) could also be investigated, and the results are summarized in the schematic phase diagram in Figure 10b. These experiments on the highly ordered mesoporous molecular sieves KIT-6 confirm the analogy between mercury intrusion/extrusion and gas adsorption (pore condensation/evaporation). Hence, one is now in a potential position to transfer and adapt methodologies developed for assessing the pore network characteristics by physisorption (e.g., scanning of hysteresis loop) to interpret intrusion/extrusion data of nonwetting fluids such as mercury. However, more work is needed to arrive at proper methodologies.

4. CHARACTERIZATION IN THE LIQUID PHASE

The main drawback of gas adsorption, liquid intrusion, and complementary methods based on electron microscopy, such as scanning and transmission electron microscopy, stems from their



Equivalence of mercury porosimetry and gas sorption: phase behavior of wetting and nonwetting fluids in mesopores. (*a*) Adsorption and desorption isotherms for KIT-6C of wetting (N₂, 77 K) and the corresponding equivalent gas sorption isotherms of a nonwetting fluid (Hg, 298 K) converted from the mercury porosimetry data. (*b*) Schematic phase diagram of bulk and confined fluid showing the symmetry between pore condensation/evaporation and Hg intrusion/extrusion (adapted with permission from Reference 105).

inability to test wet materials (i.e., in presence of the liquid/mobile phase), thus providing no direct information concerning the state of the nanoporous materials immersed in a liquid phase. This is particularly important for functionalized nanoporous materials for which the interaction with the chosen liquid may affect the effective surface chemistry, as well as accessible surface area and porosity, or in case the materials cannot be outgassed or dried without changing the material's texture. Hence, for the optimization of processes in the liquid phase, e.g., liquid chromatography, characterization based only on gas adsorption and complementary techniques may not be sufficient.

One traditional approach is to study adsorption from the liquid phase via the standard immersion method, in which one adds a known mass of the adsorbent to a measured amount of the solution of known concentration and follows the change in solute concentration by proper analytical techniques (107–110). Within this context, immersion calorimetry has also been applied. The obtained heat of immersion (or heat of wetting) can be correlated with surface and textural properties (surface area and micropore size distribution) of the system under investigation (66, 111). Immersion calorimetry has been employed mainly for the textural characterization of microporous carbons for estimating the accessible surface area and for pore size analysis (66). Rouquerol et al. (112) provide more details on the theoretical background and experimental aspects of this technique.

However, one technique that can be applied to assess textural properties such as pore size and volume distribution of meso- and macroporous chromatographic adsorbents over a wide range of pore widths (i.e., from 1–400 nm) is inverse size exclusion chromatography (ISEC) (113–121). ISEC is performed in the liquid phase and uses a set of molecular probes with defined sizes to determine pore dimensions; i.e., ISEC is based on the relationship between retention volumes and sizes of polymer standards with known molecular mass and narrow mass distribution. Various theoretical approaches for deriving pore size and porosity information have been developed based on the assumption of independent cylindrical pores, complex agglomerates of spheres, and



Spin–spin (T_2) nuclear magnetic resonance relaxation of water in comparison to 10 wt% silica particles with different surface area in water.

other models (113, 118–120, 122). However, major challenges still exist with regard to rigorous validation of the accuracy and resolution of ISEC for the pore size assessment of porous materials, particularly if they exhibit bimodal or multimodal pore size distributions.

An important challenge in liquid-phase characterization is a reliable and fast assessment of surface area. The application of NMR relaxometry for textural characterization has received a lot of attention recently. This method is based on the fact that the relaxation behavior of molecules in contact with a surface is different from that of the bulk phase ("free" liquid) because molecules near a surface exhibit a reduced relaxation time compared with the bulk liquid. Hence, the higher the surface area of a material immersed in a liquid phase, the shorter the relaxation time as more liquid is bound to the surface (123-137). This phenomenon can be observed for both spin-lattice relaxation (T₁) and spin-spin relaxation (T₂). For example, **Figure 11** shows the spin-spin relaxation of silica particles with different specific surface area immersed in water compared with pure water. From an analysis of these relaxation data, information on the specific surface area can be obtained (129, 134–137). NMR relaxation measurements have already been applied on various material types, including silicas and titania, carbons (129, 136, 137), and even MOF materials (134, 135), to assess surface area in the liquid phase. However, a rigorous and systematic validation of the method using materials with true surface area benchmark data has not yet been reported.

Moreover, NMR relaxation measurements not only can provide valuable information about the surface area but also can be used to assess pore volume, pore size, and pore size distributions (e.g., 124, 126, 127, 130–132, 138, 139). However, similar to the situation with assessing surface area, a systematic, rigorous validation of the technique for pore size analysis based on model materials is missing.

5. SUMMARY AND CONCLUSION

Detailed information on pore size and connectivity can help to identify correlations between these textural properties and the performance of gas storage, separation, and catalytic processes. Within this context, major advances have been made during the last 25 years with regard to the physisorption characterization of nanoporous materials. The 2015 IUPAC technical report (31) summarized corresponding recommendations for surface and pore size analysis. Performing reliable adsorption experiments requires the choice of an appropriate adsorptive leading to an adsorption isotherm that ideally can be considered a fingerprint of the adsorbent texture. Here, argon adsorption at 87 K is the recommended adsorptive for assessing both surface and pore size characteristics. In

contrast to nitrogen, for instance, argon does not exhibit a quadrupole moment that shows specific interactions with polar surface functionality. Microscopic treatments such as DFT and molecular simulation can be regarded as a standard method for pore size/volume analysis of nanoporous materials. Commercial software is now available for many adsorption systems, and the DFT method is also featured in international standards (such as ISO 15901-2/ISO 15901-3). With these advanced methods, it is now also possible to obtain reliable information from both the adsorption and desorption branches of the hysteresis loop, which is crucial for pore size characterization of materials consisting of an interconnected micro-mesoporous network.

Advanced experimental physisorption methodologies, including the combination of different adsorptives, measurements at various temperatures, and hysteresis scanning, allow one to differentiate between different types of interconnected pore networks and even quantify the amount of open and restricted mesopores. If macropores are present, it is useful to combine adsorption with complementary techniques such as mercury porosimetry, and we discussed some important recent advances in our understanding of the underlying mechanisms of mercury intrusion/extrusion (see Section 3). These results confirm the analogy between condensation–evaporation mechanisms of a wetting fluid (e.g., argon and nitrogen at their boiling temperatures) and of a nonwetting fluid (mercury at room temperature). Based on these new insights, it is now possible to transfer and adapt methodologies developed for assessing the pore network characteristics by physisorption (e.g., scanning of hysteresis loop) for the interpretation of mercury intrusion/extrusion data; however, more systematic work is needed here.

Although the nature of connectivity of the restricted mesopores follows directly from advanced gas adsorption studies (and mercury intrusion/extrusion experiments), only limited information about the connectivity of the freely accessible mesopores can be obtained by physisorption analysis alone. For this, a combination of advanced physisorption experiments with complementary techniques such as digital image analysis, small angle scattering, e.g., small angle X-ray scattering, or even techniques such as positronium annihilation lifetime spectroscopy is possible (140, 141). In fact, more efforts are needed to combine and integrate such complementary experimental techniques with the development of enhanced experimental protocols and simulations. Within this context, it is crucial to develop data-reduction methods based on more realistic porous materials models (e.g., 3D reconstructed pore networks) to address the many open questions associated with the investigation and identification of structural descriptors, which exhibit a strong correlation with transport phenomena. Understanding the relation between porous materials morphology and key transport properties is crucial for optimizing the application of disordered porous materials in many industrial applications including catalysis, adsorption, and separation (142, 143). Within the same context, there are challenges associated with the assessment of surface heterogeneity/surface chemistry, although some progress has been made here, also by introducing roughness into DFT models (e.g., QSDFT, 2D-NLDFT methods). Major advances are needed with regard to surface area and pore size characterization of MOFs and related nonrigid materials, particularly when the adsorbent undergoes a phase or structural change during the adsorption process (144-147).

The advances made in textural characterization allow us to enhance existing (industrial) characterization protocols for assessing the textural properties of adsorbents used in many industrial processes, including catalysis and adsorption-based separation processes.

The inclusion of advanced methodologies for surface area and pore size analysis in characterization protocols will allow for the investigation of the correlation between textural properties of adsorbents and the resulting process performance in more detail, i.e., to define the underlying structure–property–performance relationship. This is a key factor for the optimization of existing processes but is also essential for the design of new processes in catalysis and separation using novel materials with tailor-made textural properties (e.g., 2, 3). The introduction of hierarchical pore structures promises huge improvements in catalysis (e.g., 148–155) and may also lead to improvements in adsorption-based separation processes such as wastewater treatment, adsorption-based removal of volatile organic compounds, and CO₂ capture (e.g., 18, 104, 156–163). However, the underlying structure–property–performance relationships are in many cases not well understood yet, and more research is absolutely required here.

To optimize processes in a liquid phase (e.g., liquid chromatography), the characterization of materials immersed in a liquid phase can be required. Some promising methods for characterization of porous materials immersed in a liquid phase exist, such as NMR relaxometry or ISEC. However, further advancement of these methods is necessary to enable reliable textural characterization in the case of complex pore networks and hierarchical materials.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—Project-ID 416229255 - SFB 1411.

LITERATURE CITED

- Zanco S, Joss L, Hefti M, Gazzani M, Mazzotti M. 2017. Addressing the criticalities for the deployment of adsorption-based CO2 capture processes. *Energy Procedia* 114:2497–505
- Brandani S. 2017. Determining the properties of novel nanoporous materials for the evaluation of process performance in carbon capture applications. *Adv. Sci. Lett.* 23:6012–14
- 3. Pullumbi P, Brandani F, Brandani S. 2019. Gas separation by adsorption: technological drivers and opportunities for improvement. *Curr. Opin. Chem. Eng.* 24:131–42
- 4. Brandani S, Mangano E, Brandani F, Pullumbi P. 2020. Carbon dioxide mass transport in commercial carbon molecular sieves using a volumetric apparatus. *Sep. Purif. Technol.* 245:116862
- 5. Chen Z, Li P, Anderson R, Wang X, Zhang X, et al. 2020. Balancing volumetric and gravimetric uptake in highly porous materials for clean energy. *Science* 368:297–303
- 6. Zhao D, Wan Y. 2007. The synthesis of mesoporous molecular sieves. Stud. Surf. Sci. Catal. 168:241-300
- Kleitz F. 2008. Ordered mesoporous materials. In *Handbook of Heterogeneous Catalysis*, ed. G Ertl, H Knözinger, F Schüth, J Weitkamp, pp. 178–219. Atlanta: Am. Cancer Soc.
- Kresge CT, Roth WJ. 2013. The discovery of mesoporous molecular sieves from the twenty year perspective. Chem. Soc. Rev. 42:3663–70
- Li H, Eddaoudi M, O'Keeffe M, Yaghi OM. 1999. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* 402:276–79
- 10. Férey G. 2007. Hybrid porous solids: past, present, future. Chem. Soc. Rev. 37:191-214
- Serrano DP, Aguado J, Morales G, Rodríguez JM, Peral A, et al. 2009. Molecular and meso- and macroscopic properties of hierarchical nanocrystalline ZSM-5 zeolite prepared by seed silanization. *Chem. Mater.* 21:641–54
- Pérez-Ramírez J, Mitchell S, Verboekend D, Milina M, Michels NL, et al. 2011. Expanding the horizons of hierarchical zeolites: beyond laboratory curiosity towards industrial realization. *ChemCatChem* 3:1731–34
- Zhang X, Liu D, Xu D, Asahina S, Cychosz KA, et al. 2012. Synthesis of self-pillared zeolite nanosheets by repetitive branching. *Science* 336:1684–87
- Li K, Valla J, Garcia-Martinez J. 2014. Realizing the commercial potential of hierarchical zeolites: new opportunities in catalytic cracking. *ChemCatChem* 6:46–66

- Schwieger W, Machoke AG, Weissenberger T, Inayat A, Selvam T, et al. 2016. Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity. *Chem. Soc. Rev.* 45:3353–76
- Hartmann M, Schwieger W. 2016. Hierarchically-structured porous materials: from basic understanding to applications. *Chem. Soc. Rev.* 45:3311–12
- Hasan FA, Xiao P, Singh RK, Webley PA. 2013. Zeolite monoliths with hierarchical designed pore network structure: synthesis and performance. *Chem. Eng.* 7. 223:48–58
- Liu J, Yang X, Wang C, Ye L, Sun H. 2019. Synthesis of hierarchical 5A zeolites to improve the separation efficiency of n-paraffins. *Adsorpt. Sci. Technol.* 37:530–44
- 19. Chanut N, Ghoufi A, Coulet MV, Bourrelly S, Kuchta B, et al. 2020. Tailoring the separation properties of flexible metal-organic frameworks using mechanical pressure. *Nat. Commun.* 11:1216
- Seidel-Morgenstern A. 2020. Schnelle Abschätzung des Durchbruchsverhaltens von konkurrierend adsorbierenden Komponenten. Chem. Ing. Tech. 92:323–30
- Ashourirad B, Arab P, Islamoglu T, Cychosz KA, Thommes M, El-Kaderi HM. 2016. A cost-effective synthesis of heteroatom-doped porous carbons as efficient CO₂ sorbents. *J. Mater. Chem. A* 4:14693–702
- Sevilla M, Sangchoom W, Balahmar N, Fuertes AB, Mokaya R. 2016. Highly porous renewable carbons for enhanced storage of energy-related gases (H₂ and CO₂) at high pressures. ACS Sustain. Chem. Eng. 4:4710–16
- Jordá-Beneyto M, Suárez-García F, Lozano-Castelló D, Cazorla-Amorós D, Linares-Solano A. 2007. Hydrogen storage on chemically activated carbons and carbon nanomaterials at high pressures. *Carbon* 45:293–303
- Hu X, Radosz M, Cychosz KA, Thommes M. 2011. CO₂-filling capacity and selectivity of carbon nanopores: synthesis, texture, and pore-size distribution from quenched-solid density functional theory (QSDFT). *Environ. Sci. Technol.* 45:7068–74
- Bae YS, Snurr RQ. 2011. Development and evaluation of porous materials for carbon dioxide separation and capture. *Angew. Chem. Int. Ed.* 50:11586–96
- Wilmer CE, Farha OK, Bae YS, Hupp JT, Snurr RQ. 2012. Structure–property relationships of porous materials for carbon dioxide separation and capture. *Energy Environ. Sci.* 5:9849–56
- 27. First EL, Hasan MMF, Floudas CA. 2014. Discovery of novel zeolites for natural gas purification through combined material screening and process optimization. *AICbE J*. 60:1767–85
- Farmahini AH, Krishnamurthy S, Friedrich D, Brandani S, Sarkisov L. 2018. From crystal to adsorption column: challenges in multiscale computational screening of materials for adsorption separation processes. *Ind. Eng. Chem. Res.* 57:15491–511
- Farmahini A, Friedrich D, Brandani S, Sarkisov L. 2020. Exploring new sources of efficiency in processdriven materials screening for post-combustion carbon capture. *Energy Environ. Sci.* 13:1018–37
- 30. Rouquerol J, Avnir D, Fairbridge CW, Everett DH, Haynes JM, et al. 1994. Recommendations for the characterization of porous solids (Technical Report). *Pure Appl. Chem.* 66:1739–5831
- Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, et al. 2015. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* 87. https://doi.org/10.1515/pac-2014-1117
- 32. Gregg SJ, Sing KSW. 1982. Adsorption, Surface Area, and Porosity. London/New York: Academic
- Woo HJ, Sarkisov L, Monson P. 2002. Understanding adsorption hysteresis in porous glasses and other mesoporous materials. *Stud. Surf. Sci. Catal.* 144:155–62
- 34. Lowell S, Shields JE, Thomas MA, Thommes M. 2004. *Characterisation of Porous Solids and Powders: Surface Area, Pore Size and Density.* Dordrecht, Neth.: Kluwer Acad. Publ.
- Thommes M. 2004. Physical adsorption characterization of ordered and amorphous mesoporous materials. In *Nanoporous Materials: Science and Engineering*, ed. GQ Lu, XS Zhao, pp. 317–64. Ser. Chem. Eng. 4. London: World Sci. Publ.
- Thommes M, Cychosz KA. 2014. Physical adsorption characterization of nanoporous materials: progress and challenges. *Adsorption* 20:233–50
- Monson P. 2012. Understanding adsorption/desorption hysteresis for fluids in mesoporous materials using simple molecular models and classical density functional theory. *Microporous Mater*. 160:47–66

- Thommes M. 2010. Physical adsorption characterization of nanoporous materials. *Chem. Ing. Tech.* 82:1059–73
- Kaneko K, Itoh T, Fujimori T. 2012. Collective interactions of molecules with an interfacial solid. *Chem. Lett.* 41:466–75
- Thommes M, Cychosz KA, Neimark AV. 2012. Advanced physical adsorption characterization of nanoporous carbons. In Novel Carbon Adsorbents, ed. JMD Tascón, pp. 107–45. Oxford, UK: Elsevier
- 41. Rouquerol F, Rouqerol J, Llewellyn P, Maurin G, eds. 2013. *Adsorption by Powders and Porous Solids*. London: Academic. 2nd ed.
- 42. Cychosz KA, Guillet-Nicolas R, García-Martínez J, Thommes M. 2017. Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem. Soc. Rev.* 46:389–414
- Ball PC, Evans R. 1989. Temperature dependence of gas adsorption on a mesoporous solid: capillary criticality and hysteresis. *Langmuir* 5:714–23
- Thommes M, Findenegg GH. 1994. Pore condensation and critical-point shift of a fluid in controlledpore glass. *Langmuir* 10:4270–77
- Morishige K, Fujii H, Uga M, Kinukawa D. 1997. Capillary critical point of argon, nitrogen, oxygen, ethylene, and carbon dioxide in MCM-41. *Langmuir* 13:3494–98
- Gelb LD, Gubbins KE, Radhakrishnan R, Sliwinska-Bartkowiak M. 1999. Phase separation in confined systems. *Rep. Progress Phys.* 62:1573–659
- Burgess CGV, Everett DH, Nuttall S. 1989. Adsorption hysteresis in porous materials. Pure Appl. Chem. 61:1845–52
- de Keizer A, Michalski T, Findenegg GH. 1991. Fluids in pores: experimental and computer simulation studies of multilayer adsorption, pore condensation and critical-point shifts. *Pure Appl. Chem.* 63:1495– 502
- Duffy JA, Wilkinson NJ, Fretwell HM, Alam MA, Evans R. 1995. Phase transitions of CO₂ confined in nanometer pores as revealed by positronium annihilation. *J. Phys.* 7:L713–17
- Thommes M, Köhn R, Fröba M. 2002. Sorption and pore condensation behavior of pure fluids in mesoporous MCM-48 silica, MCM-41 silica, SBA-15 silica and controlled-pore glass at temperatures above and below the bulk triple point. *Appl. Surf. Sci.* 196:239–49
- Barsotti E, Tan SP, Piri M, Chen JH. 2018. Phenomenological study of confined criticality: insights from the capillary condensation of propane, *n*-butane, and *n*-pentane in nanopores. *Langmuir* 34:4473–83
- Dantas S, Struckhoff KC, Thommes M, Neimark AV. 2019. Phase behavior and capillary condensation hysteresis of carbon dioxide in mesopores. *Langmuir* 35:11291–98
- Neimark AV, Ravikovitch PI. 2001. Capillary condensation in MMS and pore structure characterization. Microporous Mesoporous Mater. 44–45:697–707
- 54. Neimark AV, Ravikovitch PI, Vishnyakov A. 2000. Adsorption hysteresis in nanopores. *Phys. Rev. E* 62:R1493–96
- Landers J, Gor GY, Neimark AV. 2013. Density functional theory methods for characterization of porous materials. *Colloids Surf. A* 437:3–32
- Qiu X, Tan SP, Dejam M, Adidharma H. 2019. Simple and accurate isochoric differential scanning calorimetry measurements: phase transitions for pure fluids and mixtures in nanopores. *Phys. Chem. Chem. Phys.* 21:224–31
- 57. Thommes M, Köhn R, Fröba M. 2000. Sorption and pore condensation behavior of nitrogen, argon, and krypton in mesoporous MCM-48 silica materials. *J. Phys. Chem. B* 104:7932–43
- Sarkisov L, Monson PA. 2001. Modeling of adsorption and desorption in pores of simple geometry using molecular dynamics. *Langmuir* 17:7600–4
- Ravikovitch PI, Neimark AV. 2002. Density functional theory of adsorption in spherical cavities and pore size characterization of templated nanoporous silicas with cubic and three-dimensional hexagonal structures. *Langmuir* 18:1550–60
- Ravikovitch PI, Neimark AV. 2002. Experimental confirmation of different mechanisms of evaporation from ink-bottle type pores: equilibrium, pore blocking, and cavitation. *Langmuir* 18:9830–37
- 61. Thommes M, Smarsly B, Groenewolt M, Ravikovitch PI, Neimark AV. 2006. Adsorption hysteresis of nitrogen and argon in pore networks and characterization of novel micro- and mesoporous silicas. *Langmuir* 22:756–64

- Morishige K, Tateishi M, Hirose F, Aramaki K. 2006. Change in desorption mechanism from pore blocking to cavitation with temperature for nitrogen in ordered silica with cagelike pores. *Langmuir* 22:9220–24
- Cychosz KA, Guo X, Fan W, Cimino R, Gor GY, et al. 2012. Characterization of the pore structure of three-dimensionally ordered mesoporous carbons using high resolution gas sorption. *Langmuir* 28:12647–54
- Rasmussen CJ, Vishnyakov A, Thommes M, Smarsly BM, Kleitz F, Neimark AV. 2010. Cavitation in metastable liquid nitrogen confined to nanoscale pores. *Langmuir* 26:10147–57
- Lässig D, Lincke J, Moellmer J, Reichenbach C, Moeller A, et al. 2011. A microporous copper metalorganic framework with high H₂ and CO₂ adsorption capacity at ambient pressure. *Angew. Chem. Int. Ed.* 50:10344–48
- 66. Silvestre-Albero J, Silvestre-Albero A, Rodríguez-Reinoso F, Thommes M. 2012. Physical characterization of activated carbons with narrow microporosity by nitrogen (77.4K), carbon dioxide (273K) and argon (87.3K) adsorption in combination with immersion calorimetry. *Carbon* 50:3128–33
- Garrido J, Linares-Solano A, Martin-Martinez JM, Molina-Sabio M, Rodriguez-Reinoso F, Torregrosa R. 1987. Use of N₂ vs. CO₂ in the characterization of activated carbons. *Langmuir* 3:76–81
- Cazorla-Amorós D, Alcañiz-Monge J, Linares-Solano A. 1996. Characterization of activated carbon fibers by CO₂ adsorption. *Langmuir* 12:2820–24
- 69. Zhu Y, Murali S, Stoller MD, Ganesh KJ, Cai W, et al. 2011. Carbon-based supercapacitors produced by activation of graphene. *Science* 332:1537–41
- Brunauer S, Emmett PH, Teller E. 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* 60:309–19
- Rouquerol J, Llewellyn P, Rouquerol F. 2007. Is the bet equation applicable to microporous adsorbents? Stud. Surf. Sci. Catal. 160:49–56
- 72. Keii T, Takagi T, Kanetaka S. 1961. A new plotting of the BET method. Anal. Chem. 33:1965
- Neimark AV, Ravikovitch PI, Vishnyakov A. 2003. Bridging scales from molecular simulations to classical thermodynamics: density functional theory of capillary condensation in nanopores. *J. Phys.* 15:347–65
- Kruk M, Jaroniec M, Sayari A. 1997. Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements. *Langmuir* 13:6267–73
- 75. Jaroniec M, Solovyov LA. 2006. Improvement of the Kruk-Jaroniec-Sayari method for pore size analysis of ordered silicas with cylindrical mesopores. *Langmuir* 22:6757–60
- Sing KS, Rouquerol F, Llewellyn P, Rouquerol J. 2013. Assessment of microporosity. See Reference 41, pp. 219–36
- Horváth G, Kawazoe K. 1983. Method for the calculation of effective pore size distribution in molecular sieve carbon. J. Chem. Eng. Jpn. 16:470–75
- Saito A, Foley HC. 1991. Curvature and parametric sensitivity in models for adsorption in micropores. AIChE J. 37:429–36
- Cheng LS, Yang RT. 1994. Improved Horvath–Kawazoe equations including spherical pore models for calculating micropore size distribution. *Chem. Eng. Sci.* 49:2599–609
- Monson P. 2011. Fluids confined in porous materials: towards a unified understanding of thermodynamics and dynamics. *Chem. Ing. Tech.* 83:143–51
- Seaton NA, Walton JPRB, Quirke N. 1989. A new analysis method for the determination of the pore size distribution of porous carbons from nitrogen adsorption measurements. *Carbon* 27:853–61
- Lastoskie C, Gubbins KE, Quirke N. 1993. Pore size distribution analysis of microporous carbons: a density functional theory approach. J. Phys. Chem. 97:4786–96
- Jagiello J, Olivier JP. 2009. A simple two-dimensional NLDFT model of gas adsorption in finite carbon pores. Application to pore structure analysis. *J. Phys. Chem. C* 113:19382–85
- Jagiello J, Ania C, Parra JB, Cook C. 2015. Dual gas analysis of microporous carbons using 2D-NLDFT heterogeneous surface model and combined adsorption data of N₂ and CO₂. *Carbon* 91:330–37
- Jagiello J, Kenvin J, Celzard A, Fierro V. 2019. Enhanced resolution of ultra micropore size determination of biochars and activated carbons by dual gas analysis using N₂ and CO₂ with 2D-NLDFT adsorption models. *Carbon* 144:206–15

- Ravikovitch PI, Neimark AV. 2006. Density functional theory model of adsorption on amorphous and microporous silica materials. *Langmuir* 22:11171–79
- 87. Olivier JP. 1998. Improving the models used for calculating the size distribution of micropore volume of activated carbons from adsorption data. *Carbon* 36:1469–72
- Ravikovitch PI, Vishnyakov A, Russo R, Neimark AV. 2000. Unified approach to pore size characterization of microporous carbonaceous materials from N₂, Ar, and CO₂ adsorption isotherms. *Langmuir* 16:2311–20
- Ravikovitch PI, Neimark AV. 2001. Characterization of nanoporous materials from adsorption and desorption isotherms. *Colloids Surf. A* 187–188:11–21
- Thommes M, Guillet-Nicolas R, Cychosz KA. 2015. Physical adsorption characterization of mesoporous zeolites. In *Mesoporous Zeolites: Preparation, Characterization and Applications*, ed. J García-Martínez, K Li, pp. 349–84. Hoboken, NJ: John Wiley & Sons
- 91. Gogotsi Y, Nikitin A, Ye H, Zhou W, Fischer JE, et al. 2003. Nanoporous carbide-derived carbon with tunable pore size. *Nat. Mater.* 2:591–94
- Oschatz M, Borchardt L, Thommes M, Cychosz KA, Senkovska I, et al. 2012. Carbide-derived carbon monoliths with hierarchical pore architectures. *Angew. Chem. Int. Ed.* 51:7577–80
- Thomas A, Schlaad H, Smarsly B, Antonietti M. 2003. Replication of lyotropic block copolymer mesophases into porous silica by nanocasting: learning about finer details of polymer self-assembly. *Langmuir* 19:4455–59
- 94. Everett DH. 1967. Adsorption hysteresis. In *The Solid-Gas Interface*, ed. EA Flood, pp. 1055–113. New York: Dekker
- Cimino R, Cychosz KA, Thommes M, Neimark AV. 2013. Experimental and theoretical studies of scanning adsorption-desorption isotherms. *Colloids Surf. A* 437:76–89
- Schneider D, Valiullin R. 2019. Capillary condensation and evaporation in irregular channels: sorption isotherm for serially connected pore model. *J. Phys. Chem. C* 123(26):16239–49
- Kikkinides ES, Monson PA, Valiullin R. 2020. Sorption isotherm reconstruction and extraction of pore size distributions for serially connected pore model (SCPM) structures employing algorithmic and statistical models. *J. Phys. Chem. C* 124(39):21591–607
- Garcia-Martinez J, Xiao C, Cychosz KA, Li K, Wan W, et al. 2014. Evidence of intracrystalline mesostructured porosity in zeolites by advanced gas sorption, electron tomography and rotation electron diffraction. *ChemCatChem* 6:3110–15
- Rouquerol J, Baron G, Denoyel R, Giesche H, Groen J, et al. 2012. IUPAC Technical Report: liquid intrusion and alternative methods for the characterization of macroporous materials. *Pure Appl. Chem.* 84:107–36
- 100. Giesche H. 2006. Mercury porosimetry: a general (practical) overview. Part. Part. Syst. Charact. 23:9-19
- Porcheron F, Monson PA, Thommes M. 2004. Modeling mercury porosimetry using statistical mechanics. *Langmuir* 20:6482–89
- Porcheron F, Monson PA. 2005. Dynamic aspects of mercury porosimetry: a lattice model study. *Lang-muir* 21:3179–86
- 103. Porcheron F, Thommes M, Ahmad R, Monson PA. 2007. Mercury porosimetry in mesoporous glasses: a comparison of experiments with results from a molecular model. *Langmuir* 23:3372–80
- 104. Thommes M, Skudas R, Unger KK, Lubda D. 2008. Textural characterization of native and *n*-alkybonded silica monoliths by mercury intrusion/extrusion, inverse size exclusion chromatography and nitrogen adsorption. *J. Chromatogr: A* 1191:57–66
- 105. Guillet-Nicolas R, Ahmad R, Cychosz KA, Kleitz F, Thommes M. 2016. Insights into the pore structure of KIT-6 and SBA-15 ordered mesoporous silica—recent advances by combining physical adsorption with mercury porosimetry. N. J. Chem. 40:4351–60
- Galarneau A, Lefèvre B, Cambon H, Coasne B, Valange S, et al. 2008. Pore-shape effects in determination of pore size of ordered mesoporous silicas by mercury intrusion. *J. Phys. Chem. C* 112:12921–27
- 107. Rockmann R, Kalies G. 2007. Liquid adsorption of *n*-octane/octanol/ethanol on SBA-16 silica. *J. Colloid Interface Sci.* 315:1–7
- Heuchel M, Jaroniec M. 1995. Comparison of energy distributions calculated for active carbons from benzene gas/solid and liquid/solid adsorption data. *Langmuir* 11:1297–303

- Jaroniec M, Choma J, Burakiewicz-Mortka W. 1991. Correlation between adsorption of benzene from dilute aqueous solutions and benzene vapor adsorption on microporous active carbons. *Carbon* 29:1294– 96
- Ismadji S, Bhatia SK. 2000. Investigation of network connectivity in activated carbons by liquid phase adsorption. *Langmuir* 16:9303–13
- Silvestre-Albero J, Gómez de Salazar C, Sepúlveda-Escribano A, Rodríguez-Reinoso F. 2001. Characterization of microporous solids by immersion calorimetry. *Colloids Surf. A* 187–188:151–65
- Rouquerol F, Rouquerol J, Sing K. 1999. Adsorption at the liquid–solid interface: thermodynamics and methodology. See Reference 41, pp. 117–63
- 113. Halász I, Martin K. 1978. Pore sizes of solids. Angew. Chem. Int. Ed. 17:901-8
- Knox JH, Scott HP. 1984. Theoretical models for size-exclusion chromatography and calculation of pore size distribution from size-exclusion chromatography data. *J. Chromatogr. A* 316:311–32
- Knox JH, Ritchie HJ. 1987. Determination of pore size distribution curves by size-exclusion chromatography. J. Chromatogr: A 387:65–84
- Goto M, McCoy BJ. 2000. Inverse size-exclusion chromatography for distributed pore and solute sizes. *Chem. Eng. Sci.* 55:723–32
- Yao Y, Lenhoff AM. 2004. Determination of pore size distributions of porous chromatographic adsorbents by inverse size-exclusion chromatography. J. Chromatogr: A 1037:273–82
- Bacskay I, Sepsey A, Felinger A. 2014. The pore size distribution of the first and the second generation of silica monolithic stationary phases. J. Chromatogr: A 1359:112–16
- Sepsey A, Bacskay I, Felinger A. 2018. Inverse size-exclusion chromatography. In Advances in Chromatography, ed. N Grinberg, PW Carr, pp. 205–27. Boca Raton, FL: CRC Press
- Grimes BA, Skudas R, Unger KK, Lubda D. 2007. Pore structural characterization of monolithic silica columns by inverse size-exclusion chromatography. *J. Chromatogr: A* 1144:14–29
- 121. Bayram-Hahn Z, Grimes BA, Lind AM, Skudas R, Unger KK, et al. 2007. Pore structural characteristics, size exclusion properties and column performance of two mesoporous amorphous silicas and their pseudomorphically transformed MCM-41 type derivatives. *J. Sep. Sci.* 30:3089–103
- Sepsey A, Bacskay I, Felinger A. 2014. Molecular theory of size exclusion chromatography for wide pore size distributions. *J. Chromatogr: A* 1331:52–60
- Brownstein KR, Tarr CE. 1979. Importance of classical diffusion in NMR studies of water in biological cells. *Phys. Rev. A* 19:2446–53
- Gallegos DP, Munn K, Smith DM, Stermer DL. 1987. A NMR technique for the analysis of pore structure: application to materials with well-defined pore structure. *J. Colloid Interface Sci.* 119:127–40
- Gallegos DP, Smith DM. 1988. A NMR technique for the analysis of pore structure: determination of continuous pore size distributions. *J. Colloid Interface Sci.* 122:143–53
- 126. Gallegos DP, Smith DM, Brinker CJ. 1988. An NMR technique for the analysis of pore structure: application to mesopores and micropores. *J. Colloid Interface Sci.* 124:186–98
- 127. Li X, Li Y, Chen C, Zhao D, Wang X, et al. 2015. Pore size analysis from low field NMR spin–spin relaxation measurements of porous microspheres. *J. Porous Mater.* 22:11–20
- Thoma SB, Smith DM, Boughton J, Davies R. 1993. On-line surface area measurement of concentrated slurries using low field spin-lattice relaxation NMR. *Part. Part. Syst. Charact.* 10:246–51
- Davis PJ, Gallegos DP, Smith DM. 1987. Rapid surface area determination via NMR spin-lattice relaxation measurements. *Powder Technol.* 53:39–47
- Munn K, Smith DM. 1987. A NMR technique for the analysis of pore structure: numerical inversion of relaxation measurements. *J. Colloid Interface Sci.* 119:117–26
- Davies S, Kalam MZ, Packer KJ, Zelaya FO. 1990. Pore-size distributions from nuclear magnetic resonance spin-lattice relaxation measurements of fluid-saturated porous solids. II. Applications to reservoir core samples. *7. Appl. Phys.* 67:3171–76
- Meyer M, Buchmann C, Schaumann GE. 2018. Determination of quantitative pore-size distribution of soils with 1H NMR relaxometry. *Eur. J. Soil Sci.* 69:393–406
- Kinn BE, Myers TR, Allgeier AM. 2019. Surface enhanced nuclear magnetic resonance relaxation mechanisms and their significance in chemical engineering applications. *Curr. Opin. Chem. Eng.* 24:115–21

- Chen JJ, Kong X, Sumida K, Manumpil MA, Long JR, Reimer JA. 2013. Ex situ NMR relaxometry of metalorganic frameworks for rapid surface-area screening. *Angew. Chem. Int. Ed.* 52:12043–46
- Chen JJ, Mason JA, Bloch ED, Gygi D, Long JR, Reimer JA. 2015. NMR relaxation and exchange in metalorganic frameworks for surface area screening. *Microporous Mesoporous Mater*. 205:65–69
- 136. Fairhurst D, Cosgrove T, Prescott SW. 2016. Relaxation NMR as a tool to study the dispersion and formulation behavior of nanostructured carbon materials. *Magn. Reson. Chem.* 54:521–26
- Elliott LN, Bourne RA, Hassanpour A, Edwards JL, Sutcliffe S, Hunter TN. 2018. Salt enhanced solvent relaxation and particle surface area determination via rapid spin-lattice NMR. *Powder Technol.* 333:458– 67
- Davies S, Packer KJ, Roberts DR, Zelaya FO. 1991. Pore-size distributions from NMR spin-lattice relaxation data. *Magn. Reson. Imaging* 9:681–85
- 139. Jaeger F, Bowe S, As HV, Schaumann GE. 2009. Evaluation of 1H NMR relaxometry for the assessment of pore-size distribution in soil samples. *Eur. J. Soil Sci.* 60:1052–64
- Kube SA, Turke K, Ellinghaus R, Wallacher D, Thommes M, Smarsly BM. 2020. Pore size gradient effect in monolithic silica mesopore networks revealed by in-situ SAXS physisorption. *Langmuir* 36(40):11996– 99
- Mitchell S, Pinar AB, Kenvin J, Crivelli P, Kärger J, Pérez-Ramírez J. 2015. Structural analysis of hierarchically organized zeolites. *Nat. Commun.* 6:8633
- Müllner T, Unger KK, Tallarek U. 2016. Characterization of microscopic disorder in reconstructed porous materials and assessment of mass transport-relevant structural descriptors. *New J. Chem.* 40(5):3993–4015
- 143. Svidrytski A, Rathi A, Hlushkou D, Ford DM, Monson PA, Tallarek U. 2018. Morphology of fluids confined in physically reconstructed mesoporous silica: experiment and mean field density functional theory. *Langmuir* 34(34):9936–45
- 144. Neimark AV, Coudert FX, Boutin A, Fuchs AH. 2010. Stress-based model for the breathing of metalorganic frameworks. *J. Phys. Chem. Lett.* 1:445–49
- Dantas S, Sarkisov L, Neimark AV. 2019. Deciphering the relations between pore structure and adsorption behavior in metal–organic frameworks: unexpected lessons from argon adsorption on copperbenzene-1,3,5-tricarboxylate. *J. Am. Chem. Soc.* 141:8397–401
- 146. Cychosz Struckhoff K, Thommes M, Sarkisov L. 2020. On the universality of capillary condensation and adsorption hysteresis phenomena in ordered and crystalline mesoporous materials. *Adv. Mater. Interfaces* 7(12). https://doi.org/10.1002/admi.202000184
- 147. Bon V, Brunner E, Pöppl A, Kaskel S. 2020. Unraveling structure and dynamics in porous frameworks via advanced in situ characterization techniques. *Adv. Funct. Mater.* 30(41). https://doi.org/10.1002/ adfm.202070272
- 148. Schwieger W, Machoke AG, Reiprich B, Weissenberger T, Selvam T, Hartmann M. 2017. Hierarchical zeolites. In *Zeolites in Catalysis*, ed. J Čejka, RE Morris, P Nachtigall, pp. 103–45. Cambridge, UK: R. Soc. Chem.
- García-Martínez J, Li K, Krishnaiah G. 2012. A mesostructured Y zeolite as a superior FCC catalyst from lab to refinery. *Chem. Commun.* 48(97):11841–43
- Blakeman PG, Burkholder EM, Chen H-Y, Collier JE, Fedeyko JM, et al. 2014. The role of pore size on the thermal stability of zeolite supported Cu SCR catalysts. *Catal. Today* 231:56–63
- Michels N-L, Mitchell S, Pérez-Ramírez J. 2014. Effects of binders on the performance of shaped hierarchical MFI zeolites in methanol-to-hydrocarbons. ACS Catal. 4(8):2409–17
- 152. Vogt ETC, Weckhuysen BM. 2015. Fluid catalytic cracking: recent developments on the grand old lady of zeolite catalysis. *Chem. Soc. Rev.* 44(20):7342–70
- 153. Caldeira VPS, Peral A, Linares M, Araujo AS, Garcia-Muñoz RA, Serrano DP. 2017. Properties of hierarchical Beta zeolites prepared from protozeolitic nanounits for the catalytic cracking of high density polyethylene. *Appl. Catal. A* 531:187–96
- 154. Ren S, Meng B, Sui X, Duan H, Gao X, et al. 2019. Preparation of mesoporous zeolite Y by fluorine– alkaline treatment for hydrocracking reaction of naphthalene. *Ind. Eng. Chem. Res.* 58(19):7886–91

- 155. Kerstens D, Smeyers B, Waeyenberg JV, Zhang Q, Yu J, Sels BF. 2020. State of the art and perspectives of hierarchical zeolites: practical overview of synthesis methods and use in catalysis. *Adv. Mater*. 32(44):2004690
- Al-Jubouri SM, Curry NA, Holmes SM. 2016. Hierarchical porous structured zeolite composite for removal of ionic contaminants from waste streams and effective encapsulation of hazardous waste. *J. Hazard. Mater.* 320:241–51
- 157. Liu Q, He P, Qian X, Fei Z, Zhang Z, et al. 2017. Enhanced CO₂ adsorption performance on hierarchical porous ZSM 5 zeolite. *Energy Fuels* 31(12):13933–41
- Besser B, Tajiri HA, Mikolajczyk G, Mo J, Odenbach S, Glas R. 2016. Hierarchical porous zeolite structures for pressure swing adsorption applications. ACS Appl. Mater. Interfaces 8(5):3277–86
- Titinchi SJJ, Piet M, Abbo HS, Bolland O, Schwieger W. 2014. Chemically modified solid adsorbents for CO₂ capture. *Energy Procedia* 63:8153–60
- Yu W, Deng L, Yuan P, Liu D, Yuan W, Chen F. 2015. Preparation of hierarchically porous diatomite/MFI-type zeolite composites and their performance for benzene adsorption: the effects of desilication. *Chem. Eng.* 7, 270:450–58
- Li R, Chong S, Altaf N, Gao Y, Louis B, Wang Q. 2019. Synthesis of ZSM-5/siliceous zeolite composites for improvement of hydrophobic adsorption of volatile organic compounds. *Front Chem.* 7:505
- Lee KX, Valla JA. 2019. Adsorptive desulfurization of liquid hydrocarbons using zeolite-based sorbents: a comprehensive review. *React. Chem. Eng.* 4(8):1357–86
- Skudas R, Grimes BA, Thommes M, Unger KK. 2009. Flow-through pore characteristics of monolithic silicas and their impact on column performance in high-performance liquid chromatography. *J. Chromatogr. A* 1216(13):2625–36