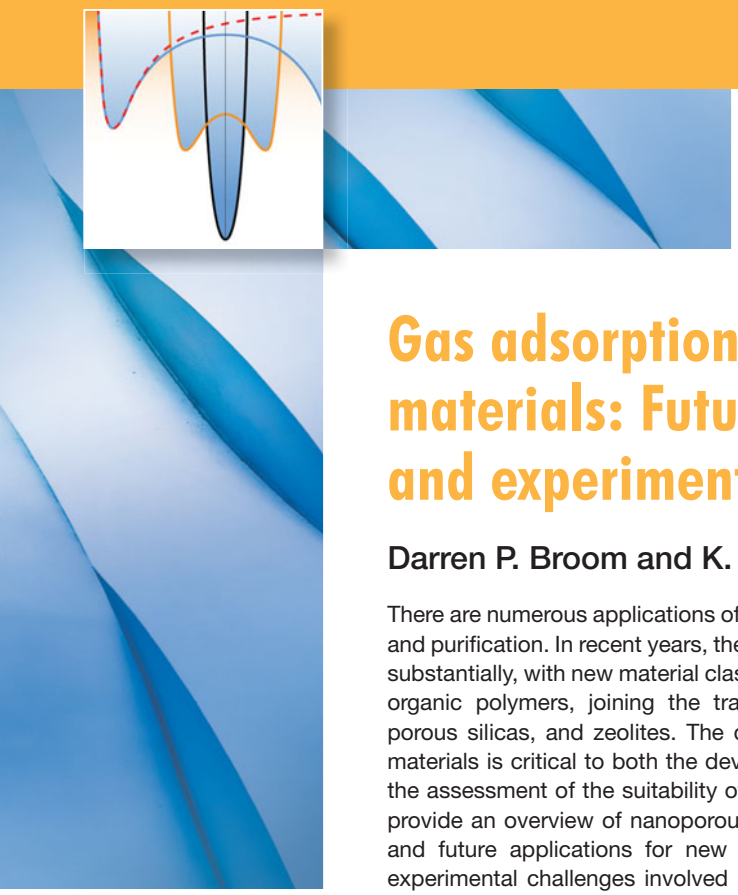


Gas adsorption by nanoporous materials: Future applications and experimental challenges

Darren P. Broom and K. Mark Thomas

There are numerous applications of nanoporous materials, including gas storage, separation, and purification. In recent years, the number of available nanoporous materials has increased substantially, with new material classes, such as metal-organic frameworks and microporous organic polymers, joining the traditional adsorbents, which include activated carbons, porous silicas, and zeolites. The determination of the gas adsorption properties of these materials is critical to both the development of new materials for targeted applications and the assessment of the suitability of a material for a particular technology. In this article, we provide an overview of nanoporous materials and their gas adsorption properties, existing and future applications for new materials, adsorption measurement methods, and the experimental challenges involved in the determination of gas adsorption both at elevated pressures and from multicomponent mixtures.

Introduction

Over the last century or so, the use of synthetic adsorbents in industrial gas separation and purification has become widespread.[1–6] As a result, pressure swing adsorption (PSA), the most common separation method, is now a mature technology. The materials used traditionally in these applications include activated carbons, activated aluminas, silica gels, and zeolites.[4,5,7] In recent years, the number of available adsorbents has increased significantly and now includes ordered mesoporous silicas,[8,9] permanently microporous metal-organic frameworks,[10–14] covalent organic frameworks,[15] and amorphous microporous organic polymers.[16–18] The dramatic growth in the range of materials and our ability to control their properties and characterize them at the nanometer scale, combined with a technological focus on the development of clean energy sources, has led to worldwide research efforts aimed at new gas storage, separation, and purification applications.

Characterizing the adsorption properties of a material under practical conditions is crucial both to assess its suitability for a specific task and to improve our understanding of the processes involved. Gas storage requires elevated pressures due to volumetric capacity considerations and the need to deliver gas at ambient pressure or above. Separation and purification, meanwhile, involve the selective adsorption of particular species from gas mixtures. However, both high pressures and multicomponent adsorption pose significant experimental challenges. In this article, following an introduction to nanoporous materials, we cover some emerging gas adsorption applications and discuss the associated measurement challenges.

Nanoporous materials and their gas adsorption properties

The term *nanoporous* refers to any material with a pore size below ~100 nm. This encompasses both the microporous (<2 nm) and mesoporous (2–50 nm) regimes, as defined by International Union of Pure and Applied Chemistry (IUPAC) guidelines.[19] There are many different types of nanoporous materials currently available.

Activated carbons are highly porous amorphous carbonaceous materials with large surface areas, and their properties are strongly dependent on the activation method and conditions used. They can possess a wide pore size distribution ranging from macropores down to micropores, although the carbon molecular sieves used for air separation typically have narrow pore constrictions (≈0.4 nm), which give them molecular sieving properties.[20] Zeolites, which are crystalline aluminosilicates formed from AlO_4 and SiO_4 tetrahedra, and other zeolitic materials, sometimes known as zeotypes that include aluminophosphates, borosilicates, and gallogermanates,[21] are

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microporous, although mesoporosity can be introduced into their structure.[22,23] Silicas, including gels and surfactant-templated materials, such as MCM-41 (Mobil crystalline material),[8,9] tend to be mesoporous. Silica xerogels and aerogels[24] have a disordered pore structure,[8,9] whereas surfactant-templated materials have highly uniform pore networks that are determined by the surfactant micelles used in their synthesis.[8,9]

New materials include metal-organic frameworks (MOFs), which are formed from metal complexes, known as secondary building units, joined by organic linkers.[13,14] They can be formed, for example, from first row transition elements and multidentate carboxylic and pyridinic ligands and are generally microporous,[25] although a significant number of mesoporous MOFs are now known.[26,27] The different types of microporous organic polymers (MOPs) include polymers of intrinsic microporosity,[16] hyper-cross-linked polymers,[17] and conjugated microporous polymers, which are all noncrystalline.[18] Covalent organic frameworks (COFs) are another type of MOP, which are crystalline, and can also be mesoporous.[28] More specifically, COFs are organic analogues of MOFs, formed from light elements such as H, B, C, O, and Si.[28–30]

There are also many naturally occurring porous materials, including clays, shales,[31] coals,[32–34] and natural zeolites.[35] Clays and zeolites tend to be microporous, while coals and shales are highly heterogeneous and possess a wide pore size distribution.

Nanoporous materials are of interest for adsorption applications because of the properties related to their porous structure, such as high surface area, large pore volume, and specific surface chemistry. However, some classes of nanoporous materials possess other properties that can also affect their adsorption behavior, such as framework (or structural) flexibility in the case of MOFs.[36] Surface functional groups may be added or modified by chemical treatment in the case of porous carbons,[37,38] and MOFs are also amenable to post-synthetic modification.[39]

Gas adsorption is defined as the enhancement of the density of a particular species at the gas-solid interface. Physical adsorption, or physisorption, occurs as a result of van der Waals and electrostatic interactions and can be enhanced in micropores due to the overlap of the potential energy fields from the pore walls, which are known as adsorption potentials. However, adsorption in mesopores can also be significant, even in the absence of significant adsorption potential overlap, due to changes in the phase behavior of confined fluids.[40,41] This can lead to capillary condensation, in which a liquid-like phase forms under subcritical conditions at a pressure significantly below the saturation pressure. The change in adsorption potential with pore size is illustrated in **Figure 1**.

In terms of adsorption performance, there is typically a trade-off between the surface area, pore volume, and pore size. For example, in principle, a large total pore volume or surface area provides a significant region for adsorption, but materials containing mesopores might satisfy this condition while not possessing the high degree of microporosity required for enhanced adsorption. A balance must therefore be obtained between the pore size, pore volume, and surface area of a material in order to combine the benefits of each property. As a result, attempts to increase gas adsorption capacity by only increasing the pore size have limitations. The pore size is particularly crucial for some applications, for example, cavities and pore windows close to the dimensions of some adsorptives can lead to molecular sieving, in which the entry of certain species into the pores is either prevented entirely or is kinetically controlled. This effect has applications for gas separation.[5,44]

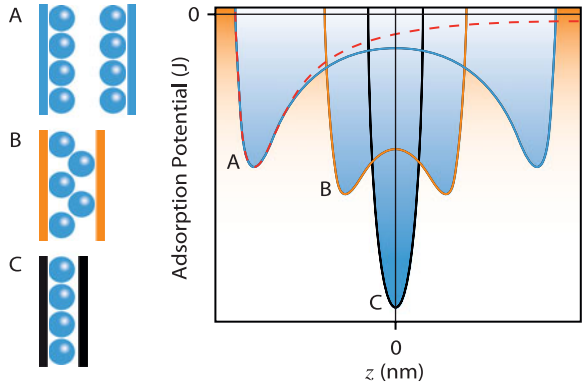


Figure 1. A schematic representation of the adsorption potentials for different width (graphitic) slit micropores (<2 nm), based on calculations using a 10–4 potential,[42,43] which can be obtained from the integration, over two dimensions, of a 12–6 (Lennard-Jones) potential, to represent the intermolecular interactions between an adsorbate molecule and the surface carbon atoms in a graphite surface. The pore size, which is defined by the distance between the two graphite surfaces, decreases from A to C, while *z* expresses the distance from the central plane between the two surfaces. It can be seen that the potentials become deeper with decreasing pore size. The dashed red line shows the adsorption potential for a single graphite surface.

Applications for gas adsorption by nanoporous materials

Adsorption plays a pivotal role in many applications, including catalysis, gas sensing, and drug delivery. However, we will focus on those that depend specifically on the high physical gas adsorption capacities of porous materials, namely gas storage[25,45–48] or gas separation and purification.[1,2,6,49,50]

Gas storage

Gas storage applications exploit the enhancement in the density of an adsorbate in the pores of a material due to overlap of the adsorption potentials. For any given pressure, using nanoporous materials should, in principle, allow the storage of a gas at a higher density as compared to a compressed gas store or at a more practical temperature compared to a liquid. Two of the most prominent applications are the storage of supercritical hydrogen and methane for use as alternative energy carriers or fuels for transportation. In this case, the challenge is to find a material that can adsorb significant amounts of either species

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at ambient temperature and reasonable pressures (e.g., <10 MPa). This tends to rely on adsorption in micropores. Low temperatures are generally required for hydrogen adsorption, although other properties can be exploited to potentially raise the operational temperature, including the enhanced interaction of gases with specific surface sites and structural flexibility, which offers the possibility of trapping the adsorbate molecules within the pore structure.[51]

Many nanoporous materials have been investigated for hydrogen storage.[25,45,46] An increasing number are MOFs, but zeolites, silicas, carbons, and MOPs have all been the subject of recent studies.[45,52] Investigations of methane storage are increasing, and this trend is likely to continue due to the renewed interest in natural gas as an energy source.[53] Previous studies of methane storage tended to focus on carbons[54] and, to a lesser extent, zeolites and silicas.[55] However, the emergence of MOFs as a potential storage material has inevitably led to an increased interest in their use for methane storage.[47,48,56–58] The materials exhibiting the highest hydrogen and methane storage capacities reported to date are listed in **Table I**. In practical applications, the compressed gas stored between the particles in the bed and in larger macropores, in which significant adsorption does not occur, also needs to be considered, together with the weight and volume of the storage system itself.

Related applications include the sequestration of carbon dioxide and the exploitation of shale gas and coal bed methane. In the former, CO_2 is removed from the atmosphere by injecting it into locations such as shale formations and non-economic coal seams.[32,66–68] This is related to the use of coal bed methane[34] and shale gas.[69,70] The latter is classified as an unconventional gas resource. Recent advances in hydraulic fracturing and horizontal drilling[70] have made exploitation economically viable.[69] This has been successfully demonstrated in the United States and has had a dramatic effect on the natural gas market.[71] The small total pore volume of shale causes a problem for gas adsorption studies because of the low uptakes, which are difficult to measure. However, in practice, the low sorption capacities of shale are counterbalanced by the prevalence of shale resources.[69]

For geological applications, it is important to assess the capacity of different formations, which can contain both compressed gas in macropores and an adsorbed phase in nanopores. Different materials have different storage capacities, and accurate assessment of this is an important challenge in adsorption research. However, for the exploitation of coal bed methane and shale gas, it is also important to understand the depletion of the resource, which is dependent on both the thermodynamics and kinetics of adsorption.[34]

Separation and purification

Adsorption by nanoporous materials is used extensively for gas separation[1–6] and is often the technology of choice for the production and purification of industrial gases.[72] Examples include H_2 purification, N_2 and O_2 production from air, and He production from natural gas. The most common mechanism used is the difference in the equilibrium uptakes of different gas or vapor species by the same adsorbent.[5,44] In fixed bed adsorption, a gas mixture is passed through an adsorbent column, in which one component is more strongly adsorbed. The bed is then regenerated by reducing the pressure or by heating. The former is known as pressure swing adsorption (PSA) and is the most commonly used method;[5,6] the latter is known as temperature swing adsorption.

A key factor for any separation process is the selectivity, the definition of which depends on the mechanism. If separation is based on differences in equilibrium uptake, a simple selectivity can be calculated by comparing the isotherm uptakes at specific pressures. In the case of kinetic separations,[1,2,5,44] the ratio of the linear driving force rate constants can be compared. For air separation by PSA using carbon molecular sieves, for example, the equilibrium amounts of adsorbed O_2 and N_2 are very similar, whereas the linear driving force rate constant for O_2 is at least 20 times that of N_2, which results in highly selective adsorption of O_2.[20,73–75] However, for both types of separation, the working capacity of the adsorbent is also important. This may be defined as the difference between the uptake at the adsorption and desorption or purge pressures. Other important considerations include the ease of regeneration, the kinetics of adsorption/desorption, and the thermal stability of the material. The ease of regeneration requires a relatively low enthalpy of adsorption, to ensure the adsorbate is not too strongly bound, and the kinetics must be rapid enough to not inhibit the adsorption and regeneration processes.

CO_2 is widely used in a range of industries and can be produced from many different sources, the most common being synthesis gas, or syngas, a term that covers a variety of gas mixtures consisting mainly of H_2, CO, and N_2, with lower concentrations of hydrocarbons, CO_2, and Ar.[72] Syngas itself can be produced in a number of ways, including the gasification of fossil fuels and biomass and steam reforming of natural gas.[72] However, an emerging application is carbon capture and storage (CCS) for the reduction of greenhouse gas emissions from power plants.[76–79] This involves CO_2 removal from both pre- and post-combustion gas streams, and adsorption is one of the proposed methods for its capture. It has potential advantages over absorption by liquids, such as amine solutions, and a variety of porous adsorbents are therefore being considered.[80–84]

Pre-combustion capture refers to the separation of CO_2 from syngas that has undergone the water-gas shift reaction, in which H_2O reacts with CO, to convert the CO into CO_2 and produce further H_2. The mixture therefore consists primarily of H_2 and CO_2, so the capture process mainly involves CO_2/H_2 separation. Depending on the gasification or reforming process, the pressure is typically a few MPa.[77,85] Post-combustion capture predominantly involves the removal of CO_2 from N_2-rich flue gases at ambient pressure.[76,86] It therefore requires CO_2/N_2 separation, normally in the presence of water vapor, and so hydrothermal stability is crucial.[80–82,84,86,87] Both hydrothermal and thermal stability are issues for MOFs and MOPs, because they are typically less stable than traditional adsorbents. However,

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Table I. Absolute hydrogen and methane storage capacities of the best performing nanoporous materials, with some activated carbon and zeolite capacities included for comparison.

Material	Hydrogen Storage Capacity			
	Gravimetric (mg g^{-1})	Volumetric (g L^{-1})	*P* (MPa)	*T* (K)
Na-X[46]	25.5	–	4	77
AC[45]	56	–	4	77
PPN-4[59]	158	–	8	77
NU-100[60]	164	–	7	77
MOF-210[61]	176	44	8	77
	Methane Storage Capacity			
	Gravimetric (mg g^{-1})	**Volumetric (cm^3 (STP) cm^{-3})**	***P* (MPa)**	***T* (K)**
Ca-X[55]	82	–	3.45	298
Maxsorb-A[54]	197	152	4	298
ACF[54]	148	166	4	298
PPN-4[59]	389	–	5.5	295
MOF-210[61]	476	–	8	298
UTSA-20[62]	–	195	3.5	300
NOTT-107[63]	–	196	3.5	298
Ni-MOF-74[64]	–	200	3.5	298
PCN-14[65]	–	230	3.5	290

AC, ACF, and Maxsorb-A are porous carbons; Na-X and Ca-X are zeolites; PPN-4 is a porous organic polymer; the others are types of metal-organic frameworks. For comparison, the 2017 US Department of Energy (DOE) storage system targets for hydrogen include a gravimetric capacity of 0.055 kg H_2 kg^{-1} (55 mg g^{-1} or 5.5 wt%) and a volumetric capacity of 0.04 kg H_2 L^{-1} (40 g L^{-1})[25] in the (delivery) temperature range of 233 to 358 K. The US DOE methane target, set in 2000, is 180 cm^3 (STP) cm^{-3} at 298 K and 3.5 MPa (where cm^3 (STP) cm^{-3} is the standard temperature and pressure equivalent volume of methane per unit volume of the adsorbent).[56,57] Note: AC, activated carbon; ACF, activated carbon fiber; MOF, metal-organic framework; NOTT, Nottingham University; NU, Northwestern University; PCN, porous coordination network; PPN, porous polymer network; UTSA, University of Texas at San Antonio.

some types, such as zeolitic imidazolate frameworks (e.g., ZIF-8), are reported to be relatively stable.[49,84] Materials must also be resistant to other contaminants in flue gas.[81,84,86,88]

New materials for CCS should therefore satisfy the stringent performance and long-term stability criteria for large-scale industrial use, involving real gas mixtures under cyclic conditions, as well as exhibiting high selectivities and working capacities, as determined under laboratory conditions. It is important to note that, due to its large quadrupole moment in comparison with other permanent gases, such as H_2, CH_4, and N_2,[75] CO_2 will generally adsorb more strongly, so most nanoporous materials could, in principle, be used for its separation.[81] Demonstrable CO_2 selectivity alone is therefore not enough to qualify a material as a strong candidate for CCS applications. Economic and production scale-up considerations are also critical, which is particularly relevant, for example, when expensive MOFs are considered.[84]

Adsorption measurement

Accurate determination of the adsorption behavior of a material is clearly important, regardless of the application. Data are required by chemical engineers for process design,[7] but such characterization is also critical for new materials discovery and development. Understanding the most important physical or chemical properties of a material and their effect on the thermodynamics and kinetics of adsorption will clearly help guide the materials development process.

Single component adsorption measurement techniques

Single component measurements most commonly involve the determination of adsorption isotherms, which are plots of the uptake of a particular gas versus pressure at constant temperature. In addition to providing the capacity of a material, isotherms measured at a range of temperatures also allow the determination of the enthalpy of adsorption at zero surface coverage,[89] which provides a fundamental measure of the adsorbate-adsorbent interaction. At higher loadings, adsorbate-adsorbate interactions can modify the enthalpy of adsorption.

The traditional methods are the volumetric and gravimetric techniques.[90–94] The most common form of the volumetric technique is the manometric method, in which the sorbed quantity is determined by measuring the change in pressure in a system of fixed volume. This is an indirect measurement in which gas is dosed from a calibrated volume into the sample cell. The pressure drop in the absence of adsorption can be calculated from the ratio of the dosing volume to the total dead volume of the system. Any further reduction in pressure is attributed

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to adsorption, the magnitude of which is calculated from a molar balance expression. This approach is commonly applied to the measurement of adsorption at sub-ambient pressure by commercial surface area and pore size distribution analyzers[95] used as standard characterization tools for new nanoporous materials. The gravimetric method, on the other hand, is a direct measurement that uses a microbalance. A measurement begins at vacuum, and any weight gain at higher pressure is then attributed to adsorption.

In both techniques, isotherms are determined by sequentially dosing gas at increasing pressure. The calculated adsorption data must allow for the presence of the sample in the measurement chamber. The gravimetric method therefore requires corrections for the buoyancy effect, whereas the manometric method requires so-called dead volume or dead space corrections to account for the difference between the volume of the empty and loaded sample cell.

In principle, both techniques also allow for the determination of adsorption kinetics,[96] but the gravimetric approach has the significant advantage that kinetic measurements can be performed under isobaric (constant chemical potential) conditions. The data are then amenable to the application of kinetic models, such as the linear driving force,[20,97] stretched exponential[98–100] and double exponential models,[101] and solutions to the diffusion equation.[20,96,102]

Other methods have also been reported for the measurement of single component gas adsorption, although these are not as widely applied because they are either less convenient to implement or have lower accuracy. For example, there are a number of variations on the volumetric technique, which include differential volumetric measurement[103,104] and flowing methods.[92,105] Frequency response techniques have also been used to study kinetics.[7,96]

Multicomponent (competitive) adsorption measurement techniques

Multicomponent adsorption can be determined from variations of the volumetric and gravimetric techniques, but both require an additional method of determining the amount of each species adsorbed. Flowing gravimetric systems can be used, with the gas phase composition beyond the sample determined using a mass spectrometer.[106] Different volumetric approaches are also available, including both open and closed systems.[3,107] Closed system methods typically involve the circulation of a mixture through an adsorbent bed and the analysis of the gas phase composition after equilibration. Open system approaches involve equilibrating an adsorbent bed with a mixture and either using a molar balance expression to calculate the amount of each component adsorbed, or desorbing the entire contents of the bed and subsequently analyzing its composition.[7]

The volumetric and gravimetric techniques can also be combined such that the total adsorption is determined both volumetrically and gravimetrically. Providing that the adsorbates under investigation differ sufficiently in molecular weight, the amount of each component adsorbed can be calculated. The isotope exchange technique, which is a closed loop cycle approach involving isotopic tracers, can also be used.[7,108]

The measurement of breakthrough curves for packed beds, which show the time required for the components of the challenge (inlet) mixture to reach a preset fraction of the input concentration (C_0) at the outlet (see **Figure 2**), can also be used to study multicomponent adsorption.[81] Breakthrough curves can provide both a qualitative and quantitative comparison between materials, but the data can also be fitted to expressions, such as the Wheeler–Jonas[109,110] and constant pattern linear driving force[111] models, and others based on assumptions applicable to the adsorbate-adsorbent system under investigation. These expressions allow the quantification of kinetic parameters, as well as the breakthrough time (see Figure 2). The assumptions can include models for the variation in flow velocity across the reactor, isothermal or non-isothermal conditions, and linear or nonlinear isotherm behavior.[1,2] Model breakthrough curves for single component and binary mixtures are shown in Figure 2.

Experimental challenges

Despite its conceptual simplicity, adsorption is surprisingly difficult to measure from a practical standpoint. Although low pressure single component gas adsorption measurements are relatively straightforward, care is still required to avoid common pitfalls and hence perform accurate measurements. However, some of the potential error sources increase significantly at higher pressures, which are often required in order to analyze the performance of materials for practical applications. The measurement of multicomponent adsorption, on the other hand, is challenging regardless of pressure.

Challenges in single component adsorption measurement

Single component gas adsorption measurements are common, partly due to the popularity of BET (Brunauer–Emmett–Teller) analysis of N_2 adsorption data at 77 K to provide a comparative measure of the surface area of powders and porous materials, in particular, in catalysis, separation, and purification applications.[92,95] This approach, and the use of N_2, Ar, and CO_2 adsorption for the determination of pore volumes and pore size distributions, typically involves the measurement of adsorption at sub-ambient pressure using a manometric apparatus.[95] These measurements can still be subject to significant experimental error,[19,112,113] but at elevated pressures, the errors increase notably due to a number of factors, including those related to the calculation of the adsorbed quantity, such as error propagation, and experimental problems, such as leaks in the apparatus and the presence of impurities in the gas phase at higher partial pressures.

Apart from the practical difficulties of working at higher pressures, there are two main issues: the definition or determination of the volume of the solid and the description of the behavior of real gases. Both issues affect the dead volume

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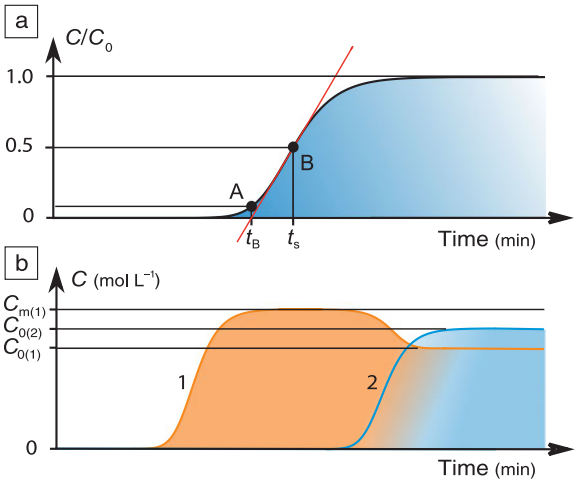


Figure 2. Model breakthrough curves for (a) a single component in a carrier gas and (b) a two component mixture in a carrier gas.[109] C/C_0 is the breakthrough fraction, or the relative concentration of the adsorbate in the effluent gas stream, where C is the concentration at any given time, and C_0 is the inlet (challenge) concentration. A curve can be characterized by the breakthrough time, t_B, which is the time taken for C/C_0 to reach a particular threshold (A), and the stoichiometric time, t_s, which is the time taken to reach $C/C_0 = 0.5$ (B). The gradient of the red line is dependent on interparticle diffusion and intraparticle sorption kinetics, axial flow dispersion, and heat transfer effects.[1] For the binary mixture, $C_{m(1)}$ is the maximum concentration in the bed reached by component 1, which is greater than its concentration at the inlet, $C_{0(1)}$. $C_{0(2)}$ is the inlet concentration of component 2, for which the adsorbent has a higher adsorption capacity.

and buoyancy effect corrections, which are equivalent.[114] The magnitudes of both corrections depend on the density of the displaced gas and therefore increase with pressure. They also depend on the sample density and, for a given sample mass, increase with decreasing material skeletal density.

The measured quantity in an adsorption experiment is the excess adsorption.[115,116] In the volumetric case, this is defined as the difference between the amount of gas present in the dead (unoccupied) volume of the apparatus in the event of adsorption and the amount of gas that would otherwise be present in its absence. The latter is typically determined using helium, under the assumptions that helium adsorption is negligible and the volume accessible to the helium is equal to the volume accessible to the adsorbate. Neither assumption is likely to be completely satisfied, and any associated error will contribute to the error in the calculated excess adsorption. Application of the buoyancy effect correction in the gravimetric case, without accounting for the adsorbed phase, also yields the excess adsorption.

At higher pressures, it is necessary to account for real gas behavior.[117] The molar balance expressions used to calculate adsorption in the manometric method include the compressibility factor, Z, of the gas. Similarly, the gas density is also required for the buoyancy effect corrections. The determination of Z requires the use of an accurate equation of state, but also high accuracy measurement of both pressure, P, and temperature, T. The effect of errors in P, T, and Z depends on the gas species because of differences in their behavior. The problems are particularly acute for CO_2[34,118] because of the strong dependence of Z on temperature and pressure near its critical point (7.38 MPa, 304 K), which is a region of practical interest. Any error in Z will again contribute to the error in the calculated excess adsorption.

A further consideration is the conversion of the excess adsorption, n_{ex}, to the absolute adsorption, n_{abs}, which is defined as the total amount of adsorbate in the adsorbed phase. This can be calculated using the following equation,

$$n_{abs} = n_{ex} + V_a \rho_g, \quad (1)$$

where V_a is the volume of the adsorbed phase, and ρ_g is the bulk gas phase density. At low pressures, $V_a\rho_g$ will be small and can be insignificant when there is a significant amount of adsorption. However, this is not the case at elevated pressures and supercritical temperatures, so careful attention must be paid to the conversion under these conditions. The difference between n_{ex} and n_{abs} is illustrated schematically in **Figure 3**. It can be seen that n_{ex} reaches a peak at elevated pressures and then decreases as the $V_a\rho_g$ term becomes more significant.[66–68,115,119] The difficulty is that V_a is unknown.[115,116]

The crystallographic structures of zeolites and MOFs can be determined using x-ray or neutron diffraction. Both techniques give a good indication of the pore volume, V_{pore}, which consists mainly of micropores. In this case, it seems reasonable to assume that $V_a = V_{pore}$, and this approach is used in the recent literature on hydrogen storage by MOFs.[120,121] However, this is only an assumption, and it is possible that this approach may overestimate the absolute adsorption at lower pressures, in particular, and for larger pore materials, in general.

On the other hand, the structure of amorphous materials, such as activated carbons, polymers of intrinsic microporosity, and hyper-cross-linked polymers, as well as natural adsorbents, including coals and shales, cannot be determined crystallographically. These materials also possess a distribution of pore sizes, which cannot be determined precisely. The only methods currently available for pore volume and pore size distribution determination are based on gas adsorption, and these have their own limitations.[32,122–124] Therefore, the use of the assumption $V_a = V_{pore}$ is more problematic for these materials, and the use of other approaches[125] may be more appropriate. The main alternative is to assume that the adsorbed phase has a constant density, but its exact nature, particularly at supercritical temperatures, is unknown.[66–68,115,116]

This issue is likely to remain an active area of research, particularly as the absolute adsorption isotherm is also required for the comparison of experimental data with simulation results,[126] which is an area of significant current interest.[127–129] It is also crucial for the exploitation of shale gas and coal bed methane because, at higher pressures, although n_{abs} may decrease as

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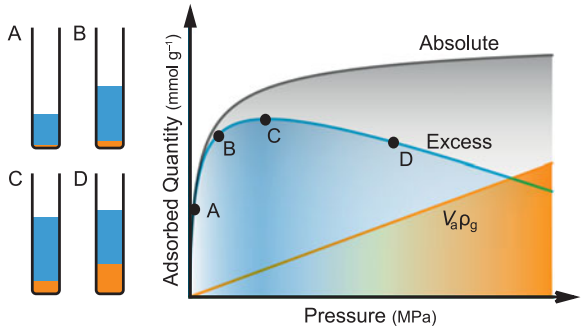


Figure 3. A schematic representation of the difference between the excess and absolute adsorption as a function of pressure at constant temperature. The pores on the left-hand side are shown filling up as a function of the total pressure. The blue and orange regions represent the magnitude of the excess adsorption and the $V_a\rho_g$ term, respectively. At low total pressure (A), the majority of the absolute adsorption is due to the excess, but at high pressures (D), the $V_a\rho_g$ term contributes significantly to the absolute value. The excess begins to decrease once the $V_a\rho_g$ term reaches a sufficient magnitude. The pressure at which this occurs is usually above ambient, but its actual value is dependent on the measurement temperature and the adsorbate-adsorbent system. Note: V_a, volume of the adsorbed gas; ρ_g, bulk gas phase density.

the resource is depleted, n_{ex} may increase. Understanding the relationship between these two quantities is therefore important.

Challenges in multicomponent (competitive) adsorption measurement

The difficulty with multicomponent adsorption measurement is the determination of the concentration of each species in the adsorbed phase. Total uptakes from gas mixtures may be measured gravimetrically, but the composition of the adsorbed phase can only be inferred indirectly by assessing the amount of each species removed from the gas phase. This approach is limited by the sample size and the amount of adsorption exhibited by the material. Desorption of the adsorbed phase is then required to establish the amounts of each component present.[106] Similarly, volumetric techniques rely on the determination of the composition of a gas mixture in equilibrium with the solid, rather than the direct determination of the amount of each adsorbed component.

At elevated pressures, both volumetric and gravimetric measurements of multicomponent adsorption are affected by the same issues as single component adsorption, namely the definition and determination of the volume of the solid and the description of real gas behavior. For process design, the excess quantities may be used,[3,6,7,115,116] so for some applications the excess to absolute conversion is not necessarily required. However, multicomponent volumetric measurements have additional issues. According to Talu,[3,107] closed systems have significant advantages in terms of accuracy. The open system methods require accurate measurement of both the flow and gas composition at the outlet, which is difficult to achieve. Closed system measurements provide higher accuracy because they rely on the measurement of equilibrium pressures rather than flow, but it is important to ensure that the gas composition throughout the system is under equilibrium. Accuracy considerations require the use of relatively large sample sizes, which are not always available for newly synthesized materials, and there is also no way of controlling the equilibrium pressure of each component.[7,108]

In addition, multicomponent measurements are laborious. The time required can be appreciated by considering that one measurement yields a single data point, in terms of pressure, temperature, and composition (of either the bulk gas or adsorbed phases), yet equilibrium may take several hours or days, depending on the species, the adsorbent and, to a certain extent, the measurement method, because closed systems equilibrate more slowly than open systems.[3]

The above points constitute serious practical challenges to the efficient and accurate measurement of multicomponent gas adsorption and have undoubtedly contributed to the shortage of comprehensive multicomponent adsorption data in the literature.[6] The number of materials being considered for adsorption applications and the laborious nature of multicomponent measurements means that the amount of multicomponent data available is likely to remain small compared with the number of possible adsorbate-adsorbent combinations. Models for the prediction of the adsorption of binary or higher mixtures from single component data, such as the ideal adsorbed solution theory,[1,2] offer an alternative for the determination of multicomponent adsorption equilibria, but these models still require experimental datasets for their validation. The measurement of breakthrough data offers an attractive alternative, as this technique is more rapid than the equilibrium methods. However, more work is required in order to correlate multicomponent breakthrough data with detailed single component equilibrium and kinetic measurements.[130]

Future outlook

The dramatic increase in the development of new classes of porous materials, such as MOFs and MOPs, will provide the impetus for the development of new gas storage, separation, and purification processes. These new materials possess unique properties based on a wide range of possible pore structures, and their tunable surface chemistry and structural flexibility. Framework flexibility in the new materials[13,36,45,51,131] should provide improved functionality for solving separation problems.[49,50]

The potential applications of porous materials in high pressure supercritical hydrogen[25,38,45,46,51,52,59–61,120,121] and methane[47,48,54–59,61–65] storage for transport applications will continue to be a major driving force. However, the use of these materials for gas separation and purification, liquid phase separations,[49,132] and catalysis[13,27,30,133] is also likely to develop alongside gas storage. Carbon capture and storage[80–84] is likely to feature prominently, but other potential gas and vapor phase applications include the energy efficient separation of H_2/D_2,[89,99,134] xylenes/ethylbenzene,[49] xylene[131] and alkane

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(e.g., hexane) isomers,[49,58] acetylene/ethene,[58,135,136] benzene/cyclohexane,[133] and alkane/alkene mixtures, such as ethane/ethene,[136] propane/propene,[136] and isobutane/isobutene.[49,58] If the emerging materials prove to be practical for industrial use, significant performance improvements can be expected in a range of existing processes, including natural gas and biogas upgrading, H_2 and C_2H_2 purification,[49] air separation,[20,49,73–75] He production from natural gas, and the purification and recovery of Xe and other noble gases.[49,50,72]

Although many new nanoporous materials have been discovered, their use in industrial separation processes remains largely unexplored. Providing the economics and scale-up are feasible, this promises to be a fertile area for future collaborative research between materials scientists, chemists, and chemical engineers. Thorough adsorption characterization, as discussed in this article, will be crucial in this respect.

Geological storage of CO_2 and the exploitation of natural gas adsorbed in geological formations[32,66–68] are also of critical importance in energy research. The primary challenge for adsorption studies in this area is the accurate determination of the adsorption characteristics of these materials, under practical conditions of temperature and pressure, in order to help assess reservoir capacity and available gas reserves. As the interest in unconventional gas resources continues,[71] an increased focus on understanding the gas adsorption behavior of materials found in geological formations is likely.

Conclusions

The discovery of new material classes in recent years has intensified the focus on adsorption applications, among which energy storage technologies for transport applications have been particularly prominent. The development of new nanoporous materials for gas storage requires accurate characterization of their adsorption properties under elevated pressure conditions. Storage in naturally occurring nanoporous materials such as shales and coals requires assessment of the suitability of geological formations for CO_2 sequestration and the exploitation of coal bed methane and shale gas, which involves adsorption characterization under high pressure and temperature conditions. However, the measurement of gas adsorption is technically demanding at elevated pressures where the accuracy of the equation of state, propagation of errors, and adsorption of impurities become significant factors. The conversion of the experimentally determined excess to the absolute adsorbed quantity is also an issue.

Studies of adsorption of pure gases are suitable for storage applications, but gas separation and purification of mixtures requires multicomponent adsorption measurements, since competitive adsorption is an important factor. Improved methodology for routine multicomponent adsorption measurement is needed because current methods are laborious. Detailed comparisons between adsorption bed breakthrough measurements and isotherm adsorption and kinetic measurements are an alternative and should help improve our understanding of gas separation and purification processes. Further work in this area will undoubtedly aid the discovery and development of new nanoporous materials for targeted applications, as well as contributing to the investigation of the use of these materials in industrial processes.

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Preregister by July 12th and Save!

The International Symposium on Integrated Functionalities (ISIF 2013), held every year since its inception in 1987, is the premier forum on fundamental and applied science of ferroelectric and high-dielectric constant thin films, materials integration, and design and fabrication of advanced devices. ISIF 2013 will feature plenary sessions, parallel topical sessions, four tutorials, poster sessions and an industrial exhibition. Mark your calendars today and plan to attend!

For the most up-to-date information on ISIF 2013, visit **www.mrs.org/isif-2013**

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