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Gas Storage Materials

Gas Storage in Nanoporous Materials

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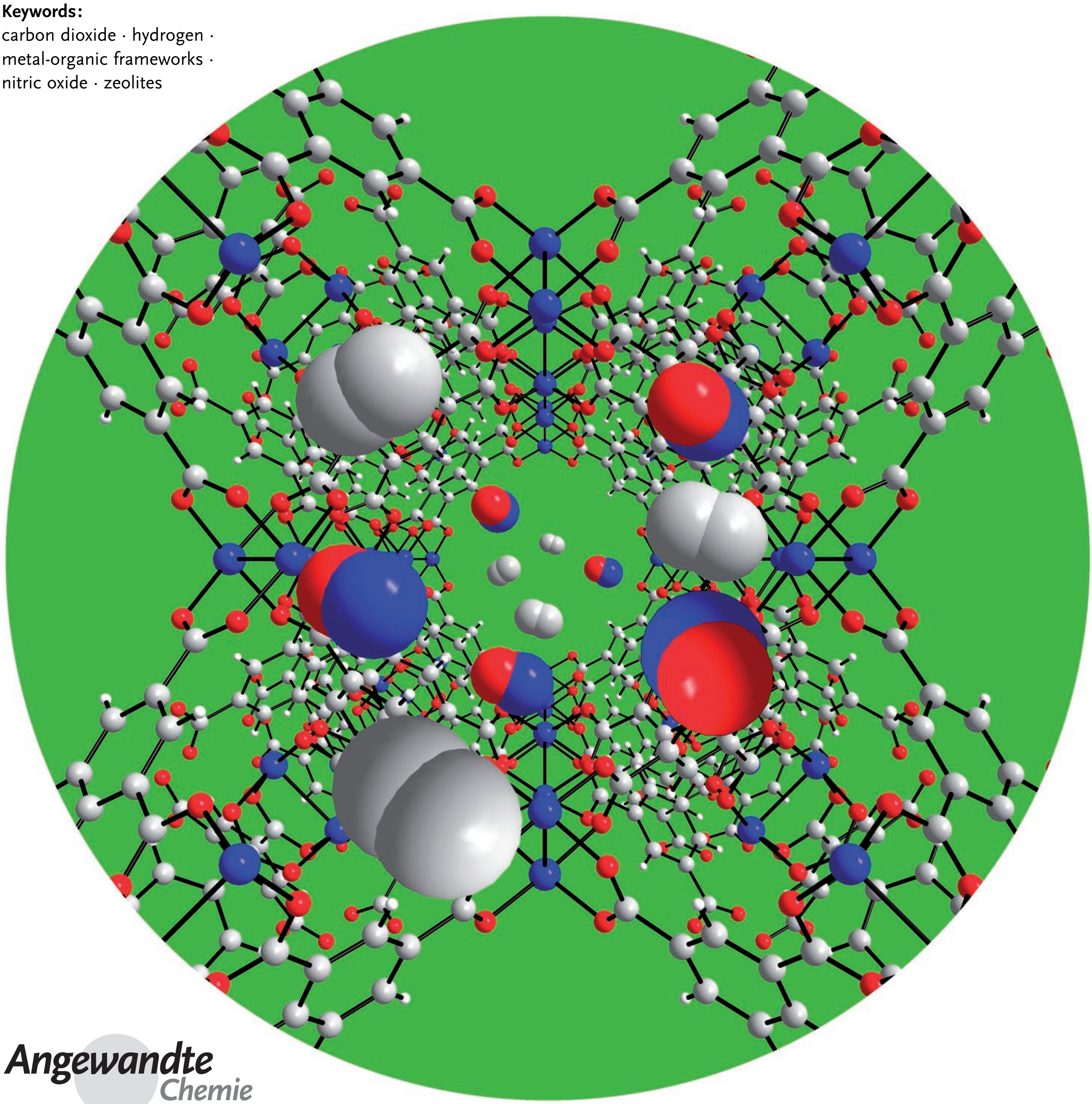

Gas storage in solids is becoming an ever more important technology, with applications and potential applications ranging from energy and the environment all the way to biology and medicine. Very highly porous materials, such as zeolites, carbon materials, polymers, and metal-organic frameworks, offer a wide variety of chemical composition and structural architectures that are suitable for the adsorption and storage of many different gases, including hydrogen, methane, nitric oxide, and carbon dioxide. However, the challenges associated with designing materials to have sufficient adsorption capacity, controllable delivery rates, suitable lifetimes, and recharging characteristics are not trivial in many instances. The different chemistry associated with the various gases of interest makes it necessary to carefully match the properties of the porous material to the required application.

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1. Introduction

The storage of gas in solids is currently a technology that is attracting great attention because of its many important applications. Perhaps the most well-known current area of research centers on the storage of hydrogen for energy applications, with viable energy storage for the hydrogen economy as the ultimate goal. However, there are other gases that are of interest, including several other types of hydrocarbon (e.g. methane), environmentally important gases such as CO_2 and SO_2, and biological gases such as NO. Each gas and its associated applications have criteria that must be met for any gas storage material to be of use in practice.

There are several different reasons why we might want to store a gas inside a material, rather than, for example physically inside a bottle or tank. First, it is relatively common for more gas to be stored in a given volume of solid than one can store in a tank even under relatively high pressures, leading to an increase in storage density of the gas. Second, there may be safety advantages associated with storage inside solids, especially if high pressures can then be avoided. Finally, it is sometimes the case that gases, particularly when needed in quite small amounts, are actually easier to handle when stored in a small amount of solid.

There are several approaches to gas storage that have been employed, depending on the gas of interest. One important strategy involves the reaction of the gas molecule with a bulk solid, for instance an alloy, such that the gas is stored reversibly as a compound where there are bonds formed between the gas and the substrate (one might term this chemical storage). Another strategy involves the adsorption of the gas inside a porous material where the adsorption may or may not involve bonding between the gas and the material (can be either physical or chemical storage). In this review we will concentrate on describing the types of material that make good porous gas storage materials, why different porous solids are good for the storage of different gases, and what criteria need to be met to make a useable gas storage material. The aim is not to be a comprehensive review of all the literature but to highlight the different types of gas storage possibilities that exist. It is clear from reading the literature that there is little crossover between scientists developing, for example, energy gas storage and those interested in medical gas storage. The aim of this review is therefore to bring together the different types of application in a way that has not been done before so that the reader gets an overview of the areas in which gas storage may impact over the coming years.

1.1. Gas Adsorption, Desorption, Storage, and Triggered Delivery

The verb "*to store*" means (according to the Collins English Dictionary) "to keep, set aside, or accumulate for future use."[1] This general meaning implies that the stored gas must be recoverable in some useable form after the gas-loaded material has been left for a certain amount of time. Very often in scientific publications authors use gas adsorption experiments to characterize the maximum adsorption capacity of a material, as well as surface area, and pore volume. These experiments clearly give one the maximum possible storage capacity but do not necessarily equate to the useable capacity. This is particularly true when the gases interact strongly with the storage material or when kinetic effects mean that some of the adsorbed gas is not easily recoverable quickly enough to make it useable. Desorption experiments, essentially the opposite of adsorption, provide some clues as to the nature of the properties of the storage materials.[2] For example, a desorption isotherm (Figure 1 a) that follows exactly the adsorption isotherm probably means that all the gas is easily accessible for use, and most likely only interacts weakly with the material, whereas a large hysteresis between the adsorption and desorption arms of the isotherm (Figure 1 b) indicates that extraction of the gas is less easy

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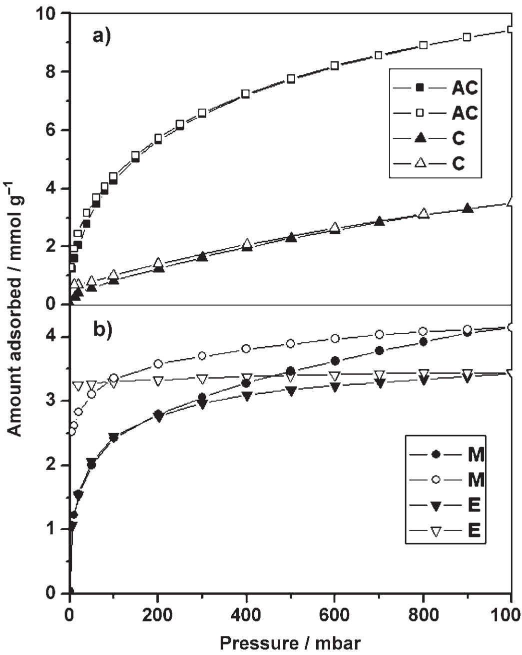

Figure 1. Adsorption (closed symbols)/desoprtion (open symbols) isotherms for hydrogen on various carbon and MOF materials up to 1000 mbar at 77 K. a) Little or no hysteresis occurs for AC and C; b) significant hysteresis occurs for E and M. AC is an activated carbon material, whereas C, E, and M are nickel-based metal-organic frameworks. Reproduced by kind permission of the AAAS from reference [70].

than the adsorption. This may be because of a very strong interaction between the gas and the material or some other kinetic effect, such as those caused by a flexible framework, which means that full desorption is not achieved. Such hysteresis is not always a problem, and in fact can point to an exciting storage material.

The real indicator of whether a material has a high storage capacity (at least for most applications) is not its maximum adsorption capacity but rather how much gas is deliverable under the conditions in which the material is to be used. These two amounts can be quite different for some materials and the difference may well depend on the exact conditions used to trigger the delivery of the gas. For example, in Figure 1, desorption of the gas is triggered by simply reducing the pressure of gas in the vessel in which the gas storage material is contained. There are, however, other methods of triggering gas delivery. Raising the temperature or exposure to UV light may trigger the gas to be desorbed, as can contact with chemical species that can replace the gas triggering its release into the environment. The last method of triggering release has found particular uses in gas storage materials for medical applications (see Section 4). A good gas storage material should not only have a high maximum adsorption capacity, but should also have the correct deliverable capacity for the chosen application. It may also be the case that the material should have a long storage shelf life, and that the delivery of the gas should not change overly after storage of the material for days, months, or even years.

Of course, even materials with excellent properties in all the above might not end up being suitable for practical applications. Scale-up, kinetics of charging and recharging, and engineering considerations play equally important roles in the choice of materials, as of course do the economics of the system. However, from a chemistry point of view, and especially where materials discovery is concerned, studies of adsorption/desorption, deliverable capacity, and storage lifetimes are the first experiments that define the success or likely success of a gas storage material.

The way maximum adsorption capacities are reported can sometimes cause confusion, especially as workers in different fields report them in different ways. An adsorption capacity can be quoted as mass or weight percentage (e.g. 10 wt %), a mass per unit mass (e.g. 0.1 g of gas per g of material), or moles of gas per unit mass (e.g. 0.01 moles of gas per g of material). The capacity can also be quoted on a volume basis, either per unit mass (e.g. 100 cm^3 of gas per unit g of material) or volume (e.g. 100 cm^3 per cm^3 of material). The last measure is also sometimes quoted as a ratio (e.g 100 v/v, the volume of gas adsorbed in a particular volume of storage material). Finally, one should always remember that each of these figures should always be accompanied by a temperature and a maximum pressure of measurement to be at all useful.

2. Nanoporous Materials

Porous materials comprise a wide-ranging family of materials.[3,4] They can be structurally well ordered with very well-defined pore sizes, or they can be structurally disordered with a wide variety of different pore sizes. In this review we define nanoporous solids (also called microporous solids) as having pore sizes of similar magnitude or only

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slightly larger than common gas molecules (i.e. maximum pore diameter of up to about 2 nm). Zeotypes[5,6] (porous aluminosilicates[7,8] and aluminophosphates[9,10]) are perhaps the archetype for crystalline solids in this class (Figure 2). Naturally occurring and synthetic zeolites have been studied extensively for many different types of gas manipulations, and are particularly well-known for separations (e.g. of O_2 from N_2 in air). Porous coordination polymers, generally built from metal ions connected by organic linkers (giving rise to the name metal-organic frameworks or MOFs) are a more recent addition to the ranks of highly crystalline porous materials.[11,12] The large number of possible organic linkers combined with the quasi-infinite ways in which they can be used to connect metal ions and metal ion clusters leads to a huge range of potential materials. The most interesting feature of these materials is that they can be prepared as highly porous materials with internal surface areas exceeding 5000 $m^2 g^{-1}$ in the most porous materials.[13,14] For comparison this is significantly higher than zeolites, which typically have surface areas of several hundred $m^2 g^{-1}$.

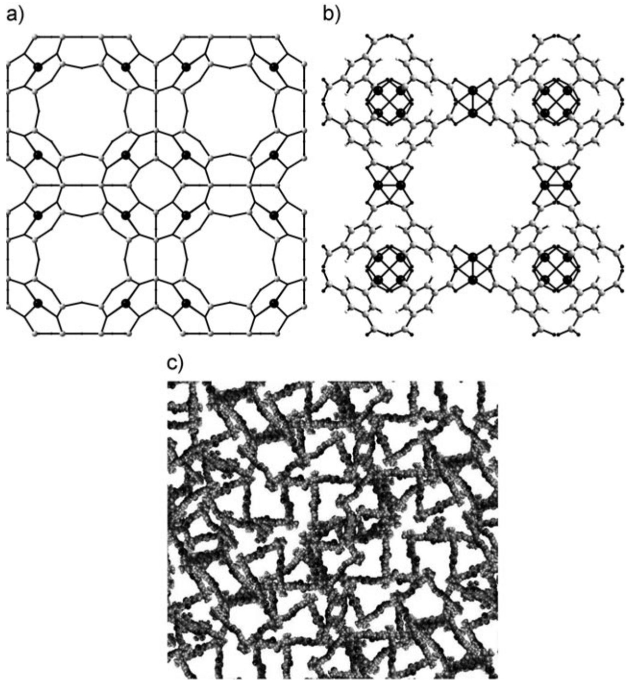


Figure 2. Schematic representations of a zeolite with the dehydrated LTA stucture (a), a metal-organic framework with the dehydrated HKUST-1 structure (b), and a polymer of intrinsic microporosity (c). The large black spheres in (a) and (b) represent accessible metal coordination sites in zeolites and MOFs, respectively.

The great advantage of highly crystalline materials is that they can be characterized extremely well by using diffraction techniques to yield crystal structures—accurate three-dimensional representations of the time and space averaged structure, from which the maximum possible porosity can be calculated. However, the maximum porosity is not always accessible in practice perhaps because of problems removing guest molecules from inside the materials, defects in the crystalline structure, or even the presence of impurities. For MOFs in particular, the rather lower thermal stability of the frameworks compared to inorganic materials such as zeolites means that many potentially very interesting solids cannot be made at all porous because the structures collapse on thermal treatment before the guest molecules are removed. Early literature on MOFs is littered with examples of reported "maximum adsorption capacity" that were lower than expected from the structures, which were caused most likely by incomplete removal of guest molecules.[15] Great care must be taken over this "activation" step to ensure as many of the guest molecules are removed as possible. However, there are now many examples where MOFs can be rendered highly porous and these materials show great possibilities for gas storage applications.[16–18]

Noncrystalline materials also have a great part to play in gas storage applications. The most important of these are probably activated carbons, but nanoporous organic and organometallic network polymers are of increasing interest. They are often not so easy to characterize and perhaps don't have the visual impact of crystalline nanoporous solids, but each of these types of materials has its own particular advantages and disadvantages. Activated carbon[19,20] is probably the original useful adsorbent material and has been known as a gas adsorber for many years. The pyrolysis of any number of carbonaceous starting materials (coal, wood, coconut husks etc) can lead to polymeric materials with large surface areas, often well in excess of 1000 $m^2 g^{-1}$ and even up to $>3000\,m^2 g^{-1}$.[21] Unfortunately, the internal surfaces of activated carbons are often quite poorly defined in chemical terms and the pore sizes can vary widely. However, this has not stopped them being used extensively for filtering and adsorption applications. In recent time other carbon structures, in particular single-walled carbon nanotubes (SWCNTs), have been prepared and their gas adsorption properties studied.[22]

Various types of cross-linked, network polymers can be prepared that possess intrinsic nanoporosity (sometimes called polymers of intrinsic microporosity, PIMs).[23,24] The great advantage of organic polymers is their wide range of chemical functionality (stemming from the great choice of monomers available) and their potential processabililty, which could lead to both tuneable and easily manufactured and formed solids.

Some of the most interesting porous materials show other properties that greatly affect their gas adsorption and storage properties. Flexibility is one such property that promises to be extremely important in this context. Most inorganic frameworks are generally regarded to be fairly rigid, although even zeolites show some flexibility that gives rise to unusual effects such as negative thermal expansion.[25,26] Most MOFs and carbon materials are also regarded as quite rigid. However, some notable MOFs, such as MIL-53[27] and MIL-88,[28,29] and many polymers exhibit considerable flexibility. Such properties clearly affect how much gas can be stored, and can also affect how much, and under what conditions, it can be released.[30,31]

A final structural characteristic that affects gas adsorption and storage capability is accessible interaction sites in the material. In some important solids coordinatively unsaturated metal ions or organic functional groups are available to interact with gas molecules, leading to stronger interactions than are present in materials where there are no such possible interaction sites. Dehydrated aluminosilicate zeolites contain extraframework cations that balance the negative charges present on the framework (Figure 2), and these are very often accessible for interaction with gas molecules.[32,33] MOFs[18,34,35] and polymers[36] can also be prepared that contain such accessible metal functionality. This looks to be a particularly interesting structural feature for gas storage.

Porous materials are very often characterized by their specific surface area, most commonly derived from the Brunauer–Emmett–Teller (BET) equation applied to data from the adsorption of nitrogen into the material. It should be noted however that the BET equation is applicable to materials with large pores (e.g. mesoporous materials) in the absence of capillary condensation but is not strictly applicable to nanoporous materials. The BET surface area reported for nanoporous materials is really an "equivalent surface area" as if the material had only planar surfaces. It is still a useful number, but only as a comparative and not as an absolute value. To complicate matters sometimes the Langmuir-derived surface area is quoted so one should know exactly which equation is being used before making comparisons.

3. Gas Storage for Energy Applications

Given the current worldwide interest in reducing emissions from energy production it is not surprising that the storage of gases that can be used for energy applications is attracting a great deal of attention. In particular, hydrogen storage is currently of great interest but other gases, such as methane and other small hydrocarbons have also been studied to varying degrees.

3.1. Hydrogen Storage

Many governments throughout the world have the "hydrogen economy" as a stated aim for future energy needs. One of the challenges that needs to be overcome before the hydrogen economy becomes a reality is how to store hydrogen safely and economically. The US department of Energy has, famously, set quite stringent targets for hydrogen storage capacity for mobile applications that are yet to be met (6.0 wt % and 45 $\mathrm{g\,L^{-1}}$ by 2010 and 9.0 wt % and 81 $\mathrm{g\,L^{-1}}$ by 2015).[37] It should be noted that these are system requirements, and not just targets for the storage capacity of the material itself.

There are essentially three ways to store hydrogen. Storing the gas in a simple tank is attractively simple, but to store reasonable amounts per volume requires liquefaction at very low temperatures and/or high pressures. Storing the hydrogen as a chemical compound such as a metal or nonmetal hydride is an option, but the large energy change between the stored and the released hydrogen leads to many complications in reversibility, kinetics, and heat management issues.[38] The third alternative is to use physisorption on a nanoporous material. Zeolites,[39] MOFs,[40,41] and carbon materials[42,43] have all been extensively studied for their hydrogen adsorption properties and organic polymers are of increasing interest.[24] The following discussion will compare the various types of materials and describe the challenges that face chemists as we strive to design new hydrogen storage materials.

The interaction between physisorbed hydrogen molecules and a porous material is quite weak with ΔH_{ads} typically being less than 10 $\mathrm{kJ\,mol^{-1}}$. This means that there are no problems with reversibility or large heat release on charging that can be associated with hydride storage. Unfortunately, however, the low interaction energy tends to mean that appreciable adsorption only takes place at low temperatures—typically hydrogen adsorption measurements are conducted at 77 K. Clearly such low temperatures of application are a disadvantage in certain situations, and it is very much a goal of the community to increase adsorption and storage capacity to significant levels at or around room temperature. Similarly, the high adsorption capacities are only found at relatively high pressures, and it would be advantageous to reduce this requirement as much as possible.

It is clear, however, that storage of hydrogen in nanoporous materials can lead to higher capacities than gas storage in a simple tank. Figure 3 shows the results of large laboratory scale experiments completed by Müller et al.[44] who compared the hydrogen uptake on MOFs with the storage capacity of an empty tank at 77 K and up to 40 bar pressure. The three MOFs measured all showed greater H_2 uptake than the empty container, with a variant of the copper-based MOF HKUST-1[18] being particularly good.

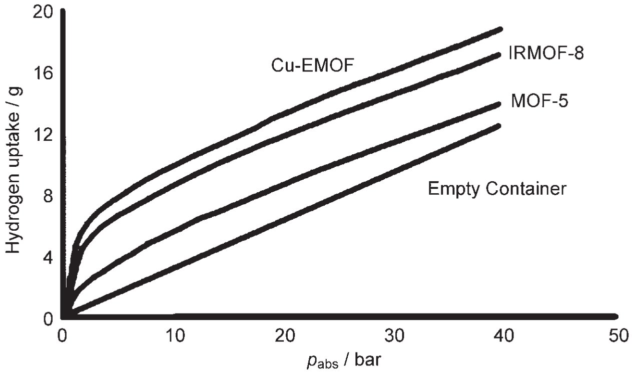


Figure 3. A comparison of the uptake of hydrogen (77 K) in an empty container and three MOF materials, Cu-EMOF (a variant of HKUST-1 shown in Figure 2), IRMOF-8, and MOF-5. Cu-EMOF takes up approximately 44 % more hydrogen than the empty container. Note that at higher pressures than that shown on this graph the curves may cross. Reproduced by kind permission of the RSC from reference [44].

The hydrogen adsorption capacity for different nanoporous materials varies quite widely. The striking feature of all the work is that it is the surface area of the porous material that governs the maximum adsorption capacity. Hirscher et al.[42] showed that for various different types of carbon materials the high pressure (up to 70 bar) adsorption capacity at 77 K correlates well with the specific surface area. Assuming that the upper limit of H_2 adsorbed in a multilayer cannot exceed the density of liquid hydrogen, the maximum hydrogen storage capacity per specific surface area of carbon can be theoretically calculated as 2.28×10^{-3} mass % m^{-2}g. Measurements at 77 K show a direct correlation between surface area and hydrogen uptake, with a slope of 1.91×10^{-3} mass % m^{-2}g, a value similar to that obtained by other researchers.[45] The difference between the measured and theoretical numbers can probably be explained simply by the differences in temperature and the lower density of the monolayer at 77 K.[42] Several research groups have shown that this surface area–hydrogen uptake correlation approximately holds for zeolites, MOFs, and Prussian blue analogues as well as carbon materials (Figure 4).[46–49] It seems that the chemical composition of the material is less important than the surface area of the materials in determining the maximum uptake. However, there are features that do depend on the chemistry of the materials. One of these is the pressure needed to reach maximum uptake and another is the behavior at low pressures. In a comparison between two MOF materials (MOF-5 and HKUST-1) Hirscher and Panella[40] showed that at low pressures (and so low coverage) the adsorption is dominated by differences in heats of adsorption and low pressure uptake correlates most strongly with ΔH_{ads} rather than surface area. Pore size also has a strong influence on how hydrogen molecules bind in porous solids. It is well known that materials containing small pores with walls of high curvature interact with hydrogen molecules more strongly than large-pore materials.

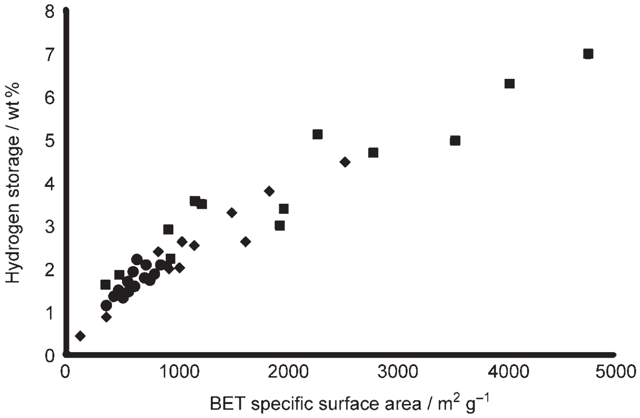


Figure 4. Maximum hydrogen adsorption capacity for zeolites (●), MOFs (■), and carbon materials (◆). Data taken from reference [40] and reference [48].

At 77 K, the temperature at which most measurements are taken, zeolites show maximum adsorption capacities in the 1–2 wt % region at pressures of 1 bar.[48] Zeolites are not particularly light materials in themselves, which is a disadvantage when attempting to reach the Department of Energy targets. Very high surface area carbon materials and MOFs do much better with maximum adsorption capacities of about 7 wt % being reported for MOF-177 at 77 K and 70 bar.[50,51] Polymers still lag someway behind MOFs and carbon materials in terms of demonstrated capacity, but certainly offer some potential for the preparation of high surface area hydrogen storage materials.[52–56]

To be used as true hydrogen storage materials (at least in mobile applications) it seems likely that the adsorption capacity needs to be increased significantly at ambient temperature. At the present time it seems that MOFs or carbon materials may have, or are close to having, high enough capacity for applications to be at least considered if the low temperature of operation is not an issue. Unfortunately, of course low temperature cooling equipment will add to the complexity, weight, and cost of any gas storage system. The question is therefore how one might improve the gas storage capacity of nanoporous solids at or near room temperature. At room temperature even the highest surface area MOFs and carbon materials only adsorb 1–2 wt %. At this temperature the heat of adsorption of hydrogen, which is typically around 5–10 kJ mol^{-1}, is of roughly the same magnitude as thermal vibrations. Significantly increasing the surface area of the material is one strategy for trying to increase the capacity. If one could couple very high surface areas with small pores, this could produce significantly enhanced adsorption. However, given the already high pore volumes of some of the largest MOFs it would seem unlikely that enough improvement could be made using this approach. Another strategy is to increase the adsorption energy. Myers and co-workers[57,58] suggest that increasing the heat of adsorption to as little as 15 kJ mol^{-1} will be sufficient to give improved adsorption at room temperature, and given that Long and co-workers have recently reported materials for which ΔH_{ads} is around 10 kJ mol^{-1} this is perhaps a more promising strategy.[59,60] Several other researchers have also shown that accessible metal sites in MOFs show good hydrogen adsorption.[61]

To design materials it is vital we know in greater detail how hydrogen interacts with the solids, and recent neutron diffraction, inelastic scattering, and IR studies are giving much more information on this aspect (Figure 5).[62–64] Neu-

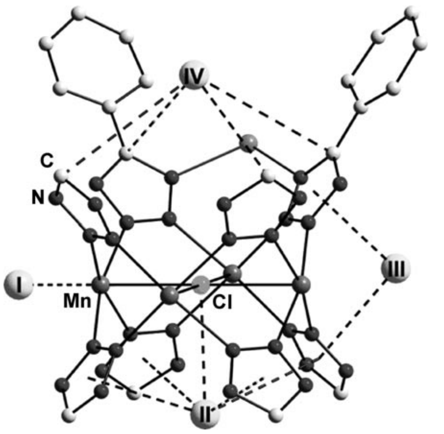


Figure 5. Initial D_2 adsorption sites (I, II, III, and IV) in a manganese 1,3,5-benzenetristetrazolate MOF according to neutron diffraction studies. Site I is only 2.27 Å from the coordinatively unsaturated Mn^{2+} ion in the framework, indicating a strong interaction, which is reflected in the relatively high heat of adsorption. Reproduced by kind permission of the American Chemical Society from reference [59].

tron powder diffraction experiments by Long et al.[59] indicate that the strongest interaction sites are between hydrogen molecules and coordinatively unsaturated Mn^{2+} sites present in the framework of the MOF. There is also evidence from inelastic scattering[35] that there is strong interaction between available metal sites.

The major problem with trying to increase capacity by increasing ΔH_{ads} is engineering enough sites with higher interaction energies into the material to make a significant difference to the overall adsorption capacity. Simulation work on current MOFs indicates that increasing interaction energy does have a significant effect, but only at low pressure because there are not enough sites of high energy in the materials, and these are filled very quickly.[65] The density of high energy sites is therefore something that needs to be increased to improve the capacity at high temperature.

Similar strategies for increasing heats of adsorption have been attempted in polymers, and one particularly intriguing piece of work involves the incorporation of tungsten-based organometallic complexes within a polymer support.[66] The complex is known to form relatively strong bonds to H_2 molecules. A particularly important aspect of this work is that the storage and release of the hydrogen could be UV activated in such a material, leading to new triggering mechanisms.

All the strategies for enhancing hydrogen uptake described above in porous materials essentially involve increasing the interaction between the H_2 molecule and the solid. However, adsorbing hydrogen atoms rather than molecules will also increase the interaction energy between the gas and the solid, and may also increase the effective surface area of the solid by enabling adsorption at sites that H_2 molecules cannot access. Spillover is a technique that has been used to enhance hydrogen adsorption in MOF-5 and IRMOF-8.[67–69] This process involves the use of a metallic catalyst to dissociate the hydrogen molecule into atoms which are then adsorbed into the material. Initial results using spillover have been very impressive, but have yet to be shown to be general. Further development is needed to see whether it can fulfil its promise.

Utilizing the flexibility of MOFs may also be used to improve storage properties. Thomas and Rosseinsky et al.[70] showed that the adsorption/desorption isotherms for hydrogen can show distinct hysteresis (Figure 1b). The flexible linkers used in building the structure lead to the possibility of dynamical opening of the pores in the structure that means that hydrogen adsorbed at high pressure is not released even at much lower pressures. The two nickel bipyridine-based MOF materials, named M and E in Figure 1, contain cavities that are connected by molecule-sized windows. Compound E has windows that are smaller than the kinetic diameter of hydrogen molecules and this leads to the most pronounced hysteresis.

3.2. Methane Storage

Methane, the major component of natural gas fuels, is another obvious target for energy storage materials, and unlike hydrogen it is adsorbed to an appreciable extent at room temperature. To be effective in energy applications the methane adsorbed in nanoporous materials (adsorbed natural gas, ANG) needs to compete with compressed natural gas (CNG), which will require a storage target for methane of approximately 35 wt %[71] or 180 v/v.[72] In the late 1990s Menon and Komarneni[73] reviewed the results and prospects of several different types of porous material, such as carbon materials, zeolites, silica gels, and mesoporous solids. The heats of adsorption for the physisorption of methane generally range from 10–20 $kJ\,mol^{-1}$, and as with hydrogen, the startling feature of the results was the direct correlation of surface area with adsorption capacity irrespective of the chemistry of the adsorbent material. At the end of the 1990s carbon materials had established themselves as the materials with the highest capacity for methane storage, although because of the low packing densities of carbon there was no real advantage of these materials over CNG storage.[73] In more recent times however there have been several more studies on carbonaceous materials that point to improved methane storage capabilities, including comparative reviews of the effect on adsorption capacity of changing the form of carbonaceous materials (e.g. powdered or fibrous, wet or dry).[74–80]

A particularly interesting piece of work involves the combination of adsorption in porous carbon materials with different potential gas storage materials—natural gas hydrates (NGH).[81] NGH materials consist of methane stored inside water cages as a clathrate. Adsorption of methane into wet carbon materials leads to formation of clathrates inside the pores of the material, which overcomes some of the disadvantages of NGH themselves.

The requirement of high surface areas for high adsorption capacity that is clear from the work on carbon materials points directly to the high porosity MOFs that have made such an impact in hydrogen storage. As long ago as the late 1990s Mori and Kitagawa demonstrated that MOFs adsorb large amounts of methane,[82] and there have been some remarkable demonstrations of high methane adsorption by various groups,[83] but in particular those of Yaghi, who, for one material, IRMOF-6, demonstrated exceptionally high uptake of methane.[84]

Düren et al.[72] have used computational methods to calculate the adsorption capacity, heats of adsorption, and surface areas of various different MOFs, zeolites, and carbon materials. Their conclusions indicate not surprisingly that the important features of materials that control methane adsorption are primarily the surface area, followed by free volume, framework density, and heats of adsorption. Other computational approaches have also been completed in recent years, with contributions to understanding the mechanism and density of methane on carbon materials[85,86] and MOFs.[87–89]

Another intriguing development is the use of mixed hydrogen/methane ("hythane") storage, particularly aimed at on-board vehicle storage of fuel for storage of the mixture and separation of the two gases. Kowalczyk and co-workers used Monte Carlo simulations to predict the properties of different carbon materials, and concluded that bundles of single-walled nanotubes in the 1–2 nm diameter range will be the best for this type of storage.[90]

The challenges for the synthetic chemist designing methane storage materials are similar to those posed for hydrogen storage materials, in particular the need for higher surface area. The main difference is that the interaction energy between methane and the surface of the materials is already enough to give reasonable adsorption at room temperature, and the volumetric targets for methane adsorption are well within sight for both carbon materials and MOF-type solids. However, the engineering (and economic) challenges facing these materials before application have yet to be overcome, and this is particularly true in the case of MOFs, for which such studies are only now beginning.

3.3. Other Hydrocarbons

Other small gaseous hydrocarbons, such as acetylene, ethylene, and light alkanes, have been studied to a very small degree, although these tend to concentrate mainly on adsorption or separation rather than true storage applications. However, some experiments have shown interesting features, and in particular the work of Kitagawa et al. on acetylene adsorption shows how interaction of the gas with a nanoporous solid (a MOF) can lead to unprecedented chemistry, which in this case is stronger than expected hydrogen bonding between the acetylene and the framework.[91,92] Müller et al.[44] have shown that MOF-5 tablets in a lecture bottle adsorb three times as much propane as the empty lecture bottle alone at 10 bar. Further specific application requirements may lead to more detailed investigations of these gases in the future.

4. Gas Storage for Medical Applications

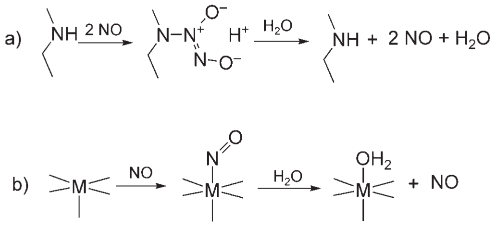
While energy applications of gas storage materials have recently taken the spotlight in this area, gas storage materials for medical applications are arguably much closer to commercialization. The field is dominated by the potential applications of nitric oxide, but there is scope for the development of other gases also. Prime amongst these is probably carbon monoxide as our understanding of the important biological relevance of this molecule is developing very quickly.

Unlike energy applications there is much less emphasis on gas storage capacity when designing materials for medical applications. Often much more important is matching the release of a gas to that required biologically. This control over release kinetics is vital as the gases of interest are often toxic in large amounts (e.g. NO and CO), while they may be ineffective if delivered in too small amounts.

4.1. Nitric Oxide

Nitric oxide (NO) is extremely important in mammalian biology. It is implicated in many processes in the body including vasodilatation, the prevention of platelet aggregation and thrombus formation, neurotransmission, and wound repair. There are tremendous possibilities for the use of exogenous NO (i.e. NO delivered from outside the body) in prophylactic and therapeutic processes, including potential applications in anti-thrombogenic medical devices, improved dressings for wounds and ulcers and the treatment of fungal and bacterial infections (amongst many many others).[93] Homogeneous donors that deliver NO directly from solution (e.g. delivery of NO from glyceryl trinitrate to treat the symptoms of angina) are well advanced in some areas, but this approach is limited by the systemic nature of delivery, which can cause unwanted side effects. Inhaled NO gas has been used with some success to treat some lung disorders[94] but, in general, delivery of NO gas from a cylinder is not practical for most therapeutic applications. A significant proportion of the NO therapy market will therefore necessarily involve targeted delivery of NO to specific areas of the body, which will avoid systemic effects.[95] In practice this means a material that is placed at a specific location in the body and that delivers NO from its surface. The short biological lifetime of NO means that any effect will be restricted to the immediate locality of the material's surface. The lack of suitable materials is a significant barrier to the use of NO as a therapeutic agent, and it is vital that we discover new materials and develop technologies to store and deliver NO in biologically important amounts.

Most work on such NO storage materials has concentrated on the use of polymers. In most cases the porosity of the polymers has not been well established but it is clear from the adsorption capacity of the gases that there is often significant nanoporosity in some, if not most, cases. The strategy for NO storage and delivery is dominated by triggered release mechanisms, and in particular release on contact with water contained in biological solutions. A number of materials have been proposed as delivery agents for exogenous NO. Perhaps the chemically most advanced are those based on polymers functionalized with secondary amines, which on reaction with NO form ionic diazeniumdiolates (Scheme 1).[96–100] Two molecules of NO react with each amine (giving rise to the trivial name NONOate) and are released on contact with moisture at an appropriate pH. The different types of chemistry associated with varying the organic monomers used to prepare the polymers means that there is a wide range of control over the kinetics of NO release in these materials, making them very promising candidates for therapeutic applications.



Scheme 1. The two methods of storing NO on a material: a) by diazenium diolate formation and b) by coordination to a metal ion. Both release NO on contact with water.

Applications of the NO-releasing materials that have been tested include thrombosis-resistant coatings,[101–105] antibacterial materials,[106–112] topical delivery agents for dermatology,[113] and organ preservation.[114] Thrombosis-resistant coatings are of great interest and several research groups have demonstrated excellent thrombus resistance[101–105] in both indwelling and extracorporeal medical devices. Decreasing the pro-thrombotic tendencies of polymer coatings also improves the biocompatibility of diagnostic medical devices, such as oxygen sensors.[103,115] Other applications that have been considered for NO-releasing polymers include antibacterial coatings, where the NO is an effective antibacterial agent that reduces the formation of microbial films.[106–112] Topical applications to the skin are probably the nearest to commercialization, and NO-storage polymers, incorporated into bandages, are in early clinical trials for the treatment of the parasitic disease leishmaniasis.[113,116] Other methods of triggering release from polymers have also been explored, such as the light-activated release of nitric oxide from metal-containing polymers.[117,118]

More recently porous materials such as zeolites and MOFs have also been investigated for their properties. Zeolites, with their well-known toxicology, are particularly interesting materials and a deliverable capacity (about 1 mmol NO per g of zeolite) similar to the best diazeniumdiolate polymers. A great deal is known about the interaction of NO with zeolites from the large volume of literature on deNOx catalysis applications of zeolites. The large hysteresis in the adsorption/desorption isotherms (Figure 6) of NO on zeolites is indicative of the strong interaction of the gas with the extraframework cations that are present in zeolites. This is easily proven by IR spectroscopy to be coordination of the NO to the metal site. This chemisorption is the general method of NO storage in zeolites, and the high adsorption energy (in the region of 90 kJ mol^{-1} for copper-exchanged zeolites[15]), means that the gas is strongly held. The key to delivery of the gas is the triggering mechanism, which in zeolites, just as in diazeniumdiolate polymers, is exposure to water in physiological solutions.

The different structures of zeolites also give some measure of control over the kinetics of release. The requirements for the flux of NO delivery varies for the type of application, but for anti-thrombosis applications this flux can be as low as 1×10^{-10} mol cm^{-2} min^{-1}.[95] Controlling the release rate of the materials is therefore the key to producing a potentially applicable material. For zeolites there is evidence that choice of structure type or material composition, and blending with polymers can affect the rate of diffusion of water in and NO out of the materials and help to control the rate of NO delivery. As with energy gas storage the storage capacity is important as in some cases the duration of delivery, even at very low fluxes, may be important. This is particularly true where it may not be easy to replace the materials easily when the NO stored is exhausted (e.g. for devices that are inserted into the blood stream).

NO-releasing zeolites show the expected biological activity. Wheatley et al.[119] demonstrated anti-thrombosis activity on human platelet-rich plasma (Figure 7) and Mowbray and co-workers have completed studies on human skin that show no significant inflammation of the skin on application of NO-releasing zeolites, in contrast to chemically produced NO (from acidified nitrite creams), which is a competitor to gas storage materials for topical delivery.[124]

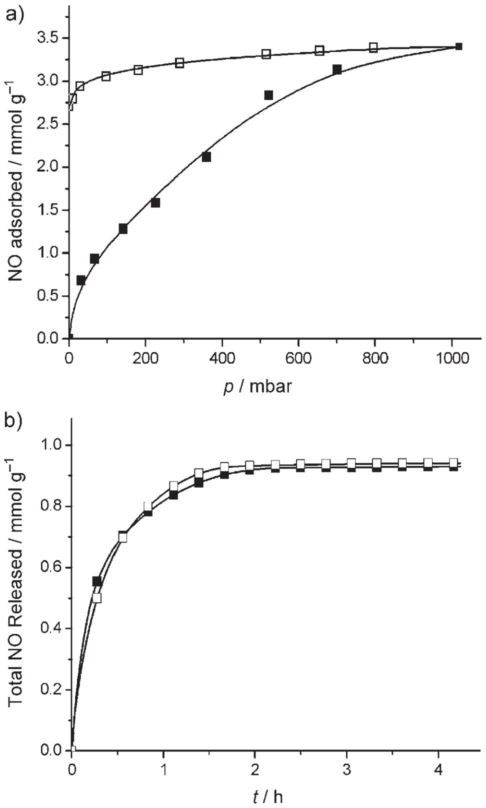


Figure 6. a) Adsorption (■)/desorption (□) isotherms ($T=298$ K) for NO on Zn-exchanged zeolite-A showing the large hysteresis. b) NO release profiles on contact with water after storage of the samples for three weeks and one year showing that there is little or no loss of NO on storage.[119]

Long-term experiments with zeolites indicate that the gas is stored without loss of deliverable capacity for more than one year (Figure 6), making these easily good enough storage materials for most applications.[119] This stability, combined with their benign nature and well-known toxicology from detergent applications, makes them particularly well suited for such topical applications (as for example, wound healing promoters), and it is clear that further trials on human skin will be completed in the future.

MOFs with accessible metal sites offer a similar environment to zeolites in that the NO can bind to the metal sites. The extremely high porosity of MOFs once again offers the prospect of high storage capacity, and there are now materials known that have adsorption[15] and deliverable capacities[125] of NO almost five times greater than zeolites. As with zeolites, IR experiments show that the NO is adsorbed strongly onto the exposed metal sites in these types of MOFs, and once again substitution of NO by water is one method of triggering the gas release. However, MOFs are often somewhat less hydrolytically stable than polymers and zeolites, and their toxicology is only beginning to be studied and so their

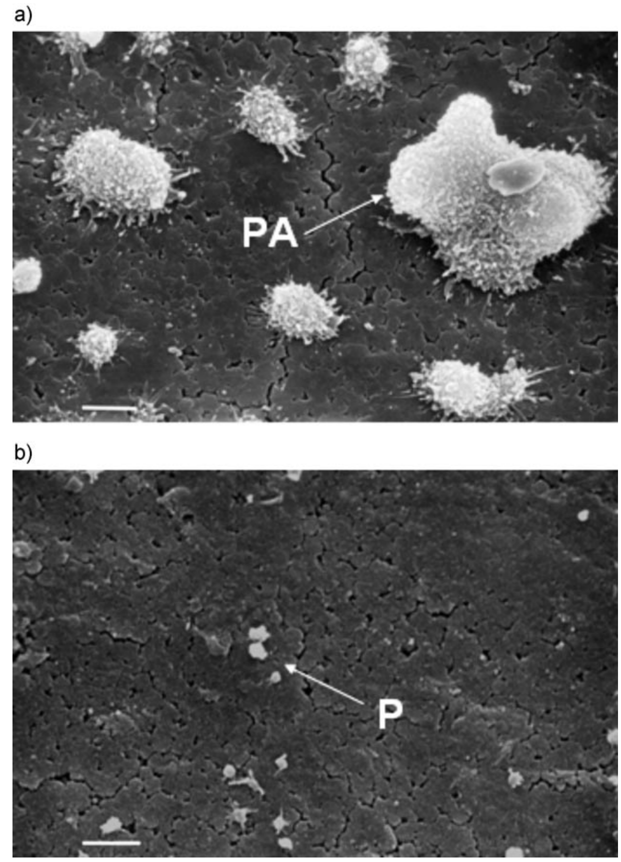


Figure 7. Scanning electron micrographs of the surface of a) untreated disks of Co-zeolite-A and of b) NO-loaded Co-zeolite-A disks after exposure to human platelet rich plasma (human blood that has had the red and white blood cells removed). Panel (a) shows large platelet aggregants (PA) on the surface of the untreated zeolite disk, panel (b) shows only a few, isolated platelets (P) on the NO-releasing zeolite disk, indicating significant reduction of platelet adhesion to the surface. The scale bar is 10 μm. See reference [119] for further details.

applicability in biological situations is yet to be proved. Nevertheless, the wide range of structure and composition of MOFs, coupled with the obvious advantages they possess in terms of their chemistry and porosity warrant further studies of these materials in the future.

4.2. Carbon Monoxide

Like NO, carbon monoxide (CO) is a molecule that is often associated with its toxicity, and adsorption and sequestration of CO (and NO) may be of interest in environmental remediation. Many people are therefore surprised to learn that there are many potential applications for CO in biology and medicine. There is now considerable literature on carbon monoxide releasing molecules (CORMs), soluble CO storage molecules that release the gas in biological situations.[126,127] Surprisingly, however, there is little or no information on CO storage in porous materials, especially as the advantages of solid gas-delivery mechanisms will be the same as those for NO. Some metal-containing porous polymers have been shown to reversibly bind CO but they do not seem to have been applied to biology as yet.[128]

A great deal is known about how CO interacts with many different porous materials as it is one of the most used probe molecules in IR spectroscopy.[64,129,130] There are even several crystal structures that show exactly how CO binds in zeolites.[131] Given such a broad base of knowledge we should consider this as a great opportunity for chemists to design potentially important gas storage materials in an emerging field.

4.3. Oxygen

In most cases oxygen storage materials tend to be ceramic oxides, but recently there has been some discussion of porous carbon materials as oxygen stores and their potential uses to improve the effectiveness of radiotherapy in the treatment of cancerous tumors.[132] There are also examples of porous polymers, similar to those that reversibly bind CO (see Section 4.2). Initially, these materials were designed as models for proteins but do have potential for gas storage in their own right. A relatively large amount of O_2 is stored in these polymers (0.9 mol O_2 per mole of metal in the polymer, considerably more than on similar complexes encapsulated in zeolites) and the release of the gas is triggered by using nitrogen gas.[133] These materials are well set up for the controlled release of small amounts of the gas, and biological applications again seem likely, although the toxicology of the metals used (currently cobalt) would need to be addressed.

5. Gas Storage for Environmental Applications

In the context of environmental remediation the word storage quite often implies removal of the gas from the environment for a very long time (indefinitely) to prevent the environmental effects of the gas becoming a problem. The emphasis here is then mostly on developing materials with high adsorption capacities and usually high interaction energies or "irreversible" chemistry. Greenhouse gases like carbon dioxide are clearly of most interest, but other toxic gases such as sulfur dioxide and ammonia also have an important impact on the environment, although the reasons why we might want to store the gases differ considerably. An alternative approach is based on separation of gases like carbon dioxide from other exhaust or flue gases, which are then released for some other use. Porous materials are also well known in these applications.

5.1. Carbon Dioxide

The abatement of carbon dioxide (CO_2) is applicable to both environmental and energy applications. CO_2 is a significant contributor to global warming, and new technologies are required to reduce CO_2 emissions to ease the effect of climate change. This can be achieved by CO_2 sequestration or generating energy from sources that do not add CO_2 (e.g. renewable, nuclear) or simply by consuming less energy. Several approaches have been proposed such as injection of the gas into deep saline aquifers or old oil/gas fields, solvent extraction (e.g. amine solutions), chemical fixation (carbonates), or sorption. Additional uses for CO_2 reduction include the purification of gases such as natural gas as it reduces energy content and corrodes pipelines.

Numerous studies have explored methods of physisorption using nanoporous solids for the abatement of CO_2. This has been mainly restricted to zeolites and MOFs; however, investigations have also been carried out on activated carbon materials, polymers, and mesoporous materials. A review article published in 2002 dealt with the adsorption of carbon dioxide at high temperatures.[134] It discussed the use of materials such as carbon matierals, metal oxides, zeolites, and hydrotalcite-like compounds to adsorb CO_2. Zeolites have been well characterized for this purpose and many framework topologies and compositions have been analyzed; from pure siliceous silicalite (MFI) to aluminosilicates containing different ion-exchanged cations. Various gas adsorption studies have centered on silicalite. At first glance it would not be expected to adsorb much CO_2 as it does not possess any obvious adsorption sites. However, it has been shown to adsorb an adequate quantity with typical heats of adsorption in the range of about 27 $kJ\,mol^{-1}$.[135] This implies that CO_2 must have some degree of interaction with the purely siliceous framework, which has been attributed to defect sites. Similar results for silicalite were obtained independently by other researchers who also investigated other siliceous zeolites (BEA and FAU) and uncovered an interesting trend.[136,137] Zeolite beta was chosen as a direct comparison to silicalite and both samples were considered approximately neutral frameworks so any difference is attributed solely to changing the framework topology. Beta adsorbs more CO_2 than silicalite (explained by the more open system); however, silicalite has higher initial heats of adsorption due to a more confined pore system. Compared with siliceous faujasite (zeolite-Y), which has an even more open framework, the adsorption is higher again and the initial heats are lower. These three examples follow the pattern with the more open pore system adsorbing more and the more confined having higher heats of adsorption. Similar behavior has also been suggested for hydrogen storage (see Section 3.1).

Several activated carbon materials[138] have been studied for the adsorption of CO_2 (enthalpies all consistent with physisorbed species ca. 16–26 $kJ\,mol^{-1}$) with Maxsorb (BET surface area of 3250 $m^2\,g^{-1}$ and pore volume 1.79 $cm^{-3}\,g^{-1}$) absorbing the greatest amount (ca. 13 $mmol\,g^{-1}$ at 10 bar or ca. 24 $mmol\,g^{-1}$ at 50 bar). Polymers have also been investigated as CO_2 sorbents, with the interesting observation that the crystalline δ-phase of syndiotactic polystyrene adsorbs more CO_2 than a semicrystalline phase.[139]

However, it is the MOFs that are making the most current impact on CO_2 adsorption, and it is here that the most interesting and unusual results have been obtained. CO_2 has a significant quadrupole moment (-1.4×10^{-35} Cm) that induces interaction with any available binding sites. This is in contrast to hydrogen and methane for which interactions are necessarily quite weak, but not as strongly interacting as, for example, NO.

The first MOF studied for CO_2 adsorption was MOF-2,[140] with a "paddlewheel" structure based on Zn and benzenedicarboxylate. It had an uptake of more than 2 $mmol\,g^{-1}$ at 1 atm and 195 K. Desorption was studied and revealed that all CO_2 was desorbed easily without hysteresis. Yaghi and coworkers have subsequently reported that many MOFs show remarkable CO_2 adsorption capacities (e.g. MOF-177 exhibits a CO_2 capacity of 33.5 $mmol\,g^{-1}$),[141] which exceed the capacities of zeolites and activated carbons.

Lanthanide-containing MOFs were investigated as an alternative to d-block metal ions. It was suggested that the lack of accessible metal sites using d-block metal ions (which are regularly saturated by ligands) might be overcome using lanthanide ions, as they generally possess higher coordination numbers than d-block metal ions. This would lead to the incorporation of coordinated solvent molecules that could be removed without collapse of the structure giving unsaturated lanthanide metal ions.[142–144] Two such MOFs that are isostructural are based on lanthanum or erbium and 1,4-phenylendiacetic acid.[143] Is this case, both the guest and coordinated water molecules can be reversibly removed. CO_2 adsorption was studied on the dehydrated Er analogue. The authors conclude that, although there are unsaturated Er ions and a hysteresis loop present, adsorption occurs by means of physisorption ($\Delta H_{ads} = 30.1$ $kJ\,mol^{-1}$) and the hysteresis is due to the kinetic diameter of CO_2 being similar to the pore dimension.

However, perhaps the most interesting (although by no means highest capacity) CO_2 adsorbing materials studied are the "breathing" MIL-*n* MOFs prepared in Férey's group. Several of the materials, particularly MIL-53[145] and MIL-88[28,29] show extreme changes of shape when guest molecules are inserted or removed (Figure 8). MIL-53 shows a very pronounced breathing effect, and this has great influence on its adsorption/desorption isotherms. In the dehydrated (closed) material there is only small uptake of CO_2 (up to 3 $mmol\,g^{-1}$ at 5 bar) but at higher pressures there is a step in the adsorption isotherm as the structure opens up to admit more CO_2 (ca. 8 $mmol\,g^{-1}$ of CO_2 at 10 bar).[146] Perhaps even more striking is the effect of hydration on the uptake. The selectivity for methane (which does not induce any breathing of the framework) increases significantly when the material is hydrated.[147,148]

MIL-96[149] adsorbs 4.4 $mmol\,g^{-1}$ of CO_2 at 10 bar with initial adsorption enthalpies of about 32 $kJ\,mol^{-1}$ (similar to that seen for MIL-53) before falling off to similar values as associated with silicalite. This suggests that there are a small number of reasonably strong adsorption sites, probably through interaction with μ_2-hydroxo groups within the pores, but the interaction between CO_2 and the rest of the framework is weaker. MIL-102,[150] a chromium-based MOF, absorbs about 3.1 $mmol\,g^{-1}$ of CO_2 at 10 bar, which makes it comparable with silicalite, but lower than several types of activated carbon material and well below the best MOFs.

One other interesting, and as yet, rather poorly understood, ramification of flexibility in framework structures is gated adsorption, where below a certain threshold pressure

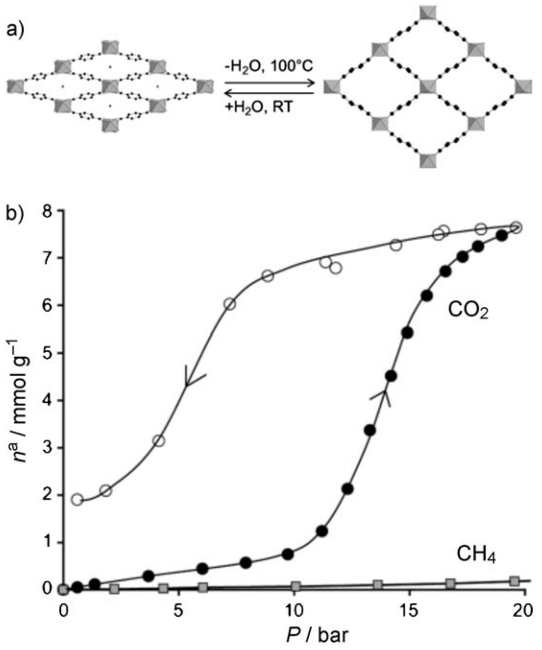


Figure 8. a) The flexible structure of MIL-53 and b) the adsorption (●)/desoprtion (○) isotherm of CO_2 on wet MIL-53. The adsorption isotherm for methane on the same material is also shown for comparison. Reproduced with permission from reference [148].

(the gate pressure) there is almost no adsorption, whereas above the gate pressure there is significant adsorption. Li and Kaneko[151] demonstrated this property for CO_2 adsorption on a copper-bipyridine MOF, and Kitagawa and co-workers have discussed this type of adsorption in other situations.[152,153]

5.2. Sulfur Dioxide

The toxicity of sulfur dioxide (SO_2) causes great environmental concerns as emissions from combustion sources continue to pollute the atmosphere. The combustion of fossil fuels, which contain sulfur compounds, predominantly results in SO_2 formation which is further oxidized in the atmosphere to produce sulfuric acid (acid rain). Much effort has focused on removing SO_2 from emissions of combustion sources (e.g. flue gas desulfurization) and sulfur compounds from fuel sources. However, SO_2 is also a useful compound commonly used to inhibit enzymatic and non-enzymatic browning, food preservation, as an antimicrobial agent, and in the manufacture of sulfuric acid by the contact process.

There are no references in the literature that specifically state that porous materials store SO_2 but there has been a great deal of research conducted on the adsorption and removal of SO_2 from gas streams, particularly for protecting $DeNO_x$ catalysts from sulfur poisoning in vehicle emissions under lean-burn conditions. This research primarily centers around the concept of converting the SO_2 into sulfates that can be stored chemically within the material. Several materials have been suggested for this including zeolites and MOFs. Barium-impregnated HKUST-1 was studied in an oxidative atmosphere during which the SO_2 uptake was measured.[154] The results indicated that SO_2 is irreversibly adsorbed as sulfates (both $BaSO_4$ and $CuSO_4$) and the parent structure of the MOF is completely destroyed during the adsorption process. The SO_2 uptake increased with temperature as the MOF structure was increasingly destroyed, resulting in highly dispersed Cu species becoming available for binding at higher temperatures.

Zeolites have also been investigated for SO_2 adsorption. Silicalite has been investigated for SO_2 adsorption in combustion gases. This is reported to perform better than ZSM-5 and activated carbon, as it can store more gas and retains more in a desorption process in a helium gas stream.[155] Additionally, zeolites synthesized from fly ash (zeolites X, Y, Na-P1, analcime, and sodalite) were also studied, which showed sodalite/analcime to be the most efficient SO_2 adsorber.[156] Further work on zeolite Y was undertaken using powder X-ray diffraction and temperature-programmed desorption, which revealed the presence of both chemisorbed and physisorbed SO_2 species.[157] SO_2 chemisorbs to sodium ions (via oxygen atom) and requires temperatures of 390 K for removal, whereas the physisorbed species require much lower temperatures of 286–300 K for removal.

Manganese oxide octahedral molecular sieves (OMS) have been investigated as high-capacity SO_2 absorbents for controlling diesel emissions.[158] These store SO_2 by oxidation to SO_3 followed by reaction with Mn^{2+} to give $MnSO_4$. Again, the SO_2 is chemically stored and not easily recoverable as gaseous SO_2.

5.3. Ammonia

The storage of ammonia is important for the selective catalytic reduction (SCR) of NOx species in exhaust emissions. Storage in liquid form raises several safety concerns and as a result there is some interest in using other technologies to store ammonia. One potentially safer alternative is to store the ammonia within a nanoporous solid. There is recent interest in chemically storing ammonia in alkali earth halides as well as on ion-exchanged zeolites. It was shown that ion exchange with transition metals increases the total adsorption capacity of ammonia and the amount of irreversible ammonia capacity when compared to Na-, H-, or alkali metal exchanged zeolite-Y (Cu-Y having the highest capacity—5 mmol g⁻¹).[159]

The effect of surface oxidation of active carbon materials was also investigated for ammonia adsorption.[160] The adsorption capacity increased on increasing the number of surface organic oxygen species as adsorption sites for ammonia (2.58 mmol g⁻¹). Ammonia adsorption studies have also resulted from SCR of NO using zeolites with Fe-ZSM-5 able to adsorb significant amounts of ammonia.[161] These materials do not have as high adsorption capacities as the alkaline-earth halides (e.g. MgClOH 26 mmol g⁻¹); however, desorption at ambient temperatures from these halides is difficult.[162]

6. Summary and Outlook

Gas storage in nanoporous materials is a thriving area of research, and it is clear that it is by no means a mature field. It is a very exciting time for chemists as in almost all the applications we have listed above there is a great need for new and improved materials that will outperform those we currently have. The great prize in the field is a hydrogen storage material that meets the US DoE targets at or near room temperature and at reasonable pressures. At the moment the adsorption capacity in some carbon materials and MOFs at 77 K approaches 7 wt %, but the constraints that low operating temperature place on the overall system requirements means that it is unlikely that this will be good enough, especially for mobile applications. The challenge of meeting the goals at room temperature is a great one. On the face of it the task does not seem impossible. The suggested heat of adsorption required for ambient temperature adsorption is only 15 $\mathrm{kJ\,mol^{-1}}$, and in certain MOFs we are already at 10 $\mathrm{kJ\,mol^{-1}}$—surely 5 $\mathrm{kJ\,mol^{-1}}$ isn't that much. In reality this is a very challenging target with a gas like hydrogen and it will take an exceptional material to be successful.

So how can one synthesize a material that reaches the required heat of adsorption? Changing the chemical composition of the solid to include sites that interact strongly with hydrogen molecules has been partially successful, as Long and co-workers have shown.[59] The challenge now is to synthesize materials with enough of these sites to impact adsorption capacity at moderate pressures. In a perfect world one could even imagine incorporating accessible metal sites that act as "spillover" catalysts and induce breakage of the H–H bond so that the adsorbed species will be hydrogen atoms rather than the molecule itself. Such speculation is a long way from where we are now and to crack this problem will certainly require a step change in the type of material available. Han and Goddard have calculated that doping lithium into some MOFS can also increase the interaction energy to give significant adsorption at room temperature. Clearly the onus is now on the synthetic chemists to see how they can make these materials and if they meet the predicted performance.[163]

Clever use of the flexibility of polymers and MOFs may also lead to materials with enhanced hydrogen adsorption and storage properties. Simply targeting materials with higher and higher surface areas would seem a strategy that will bring lower and lower returns in the long run. However, increasing the accessible surface area without increasing the overall pore volume, for example by using interpenetration of frameworks that is sometimes seen in MOFs is one possible approach, which has shown some recent promise.[164] Of course the best chance of success relies on combining all the advantageous properties of the materials that have been shown to be good in the current work.

The challenges in medical gas storage are quite different. Here the interaction energies between the gases of interest and the materials are already high and triggered release of the gas has been developed to such an extent that human trials are already underway. The chemist's goal in this area is to achieve ever more subtle control over the kinetics of the gas release, allowing the materials to match the desired biological flux of the gas precisely. This is still a challenge, but one that is much more tractable than the one facing hydrogen storage. One extra concern in this area is the toxicity of the materials, which must of course be low enough to allow any potential products to succeed in clinical trials. The design of gas storage materials for medical use of carbon monoxide and dioxygen seems surprisingly understudied. There is a great opportunity for materials design and discovery in this area that has not yet been tackled.

For environmental gas storage the focus tends to be on high adsorption capacity materials. The challenge here is to synthesise solids with large numbers of high energy interaction sites. The nature of carbon dioxide in particular means that there has already been demonstration of some interesting adsorption effects, particularly associated with the flexibility of the adsorbent materials, and we expect that as we understand these effects further we will be able to produce better materials.

For most of these applications, but particularly hydrogen storage, we are still in the materials discovery phase of research. Once materials with suitable properties have been made and characterized the research focus will change more towards making the applications work, bringing in engineering. This is already happening to some degree in certain areas but will undoubtedly increase in the others also. There are also some interesting gases (e.g. ozone) that have not yet been studied in this context, and there are opportunities for the innovative chemist here also.

There is no doubt in our minds that gas storage in porous materials is an area of great excitement and potential importance in all the areas covered in this review. It would be a great achievement for such materials to be applied in practice, but the rewards for attaining the targets that have been set in the various areas makes the intense effort that will certainly be required very much worth it.

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