Microporous Materials

Strategies for Hydrogen Storage in Metal–Organic Frameworks

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Increased attention is being focused on metal–organic frameworks as candidates for hydrogen storage materials. This is a result of their many favorable attributes, such as high porosity, reproducible and facile syntheses, amenability to scale-up, and chemical modification for targeting desired properties. A discussion of several strategies aimed at improving hydrogen uptake in these materials is presented. These strategies include the optimization of pore size and adsorption energy by linker modification, impregnation, catenation, and the inclusion of open metal sites and lighter metals.

1. Introduction

The scope of the United States Hydrogen Initiative[1] has captured the attention of industrial and academic researchers around the world.[2] A measure of success has already been achieved by the initiative; specifically, the uncovering of the extent by which current technology must advance to bring about the use of hydrogen as an energy carrier.[3] Among the challenges facing hydrogen production, distribution, storage, and usage, the improvements required for the safe and efficient storage of the volatile fuel have been cited as the most formidable. As a corollary, it has been claimed that if a breakthrough in hydrogen storage were realized, a favorable impetus would be applied to resolving the other issues. Several reviews have appeared on the use of hydrogen as a fuel and its storage in various media, many of which are cited below. Herein, a brief discussion is presented on hydrogen storage requirements and the current state-of-the-art of established systems. This Review is focused on the use of metal–organic frameworks (MOFs) as new hydrogen storage materials.

2. Hydrogen Storage Requirements

The most compelling goals for hydrogen storage involve transportation (on-board) applications. There are two reasons for this: first, the transportation sector represents the largest consumer of oil, thus making it one of the largest sources of airborne pollutants such as carbon and nitrogen oxides. Secondly, the efficiency and economic demands to make hydrogen competitive with fossil-fuel technology are more challenging than for stationary storage. The current targets set by the U.S. Department of Energy (DOE) have been made with the concept that today's vehicles will be powered by tomorrow's higher efficiency fuel-cell power sources. The vehicles should have a similar range (480 km or 300 miles), operate at close to ambient conditions, and be quickly and safely refueled. As hydrogen has approximately three times the gravimetric energy density of petrol, and fuel cells are expected to perform at least twice as efficiently as internal combustion engines, only 5–10 kg of hydrogen must be stored (although 4 kg or less would be required by smaller, more practical passenger cars[4]). The 2010 energy density targets for the hydrogen storage system (including container and necessary components) are 7.2 MJ kg^{-1} and 5.4 MJ L^{-1}, which translates as 6.0 wt% and 45 kg H_2 per m^3.[3] The goals for 2015 are even more demanding: 9.0 wt% and 81 kg H_2 per m^3, which approach the expectations of the automotive industry.[5] This daunting task is easily put into perspective by noting that the mass density of elemental hydrogen is only 70.8 kg m^{-3} in its liquid state at 20 K (1 atm), and that 5 kg of hydrogen gas

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fills a volume of 56 m^3 under ambient conditions. Furthermore, both of these insights ignore the contribution of the mass of the necessary container.

3. Current Storage Technologies

Compressed hydrogen gas and cryogenically stored liquid hydrogen are the most developed technologies, and are currently utilized in the demonstration vehicles of several automotive manufacturers. While a systems analysis shows that they meet the technical aspects of the DOE 2010 targets, they are unlikely to comply with future ones.[6] In all cases, the containment vessel contributes at least 90% of the system mass, but there is still room for improvement with respect to the maximum pressure that can be maintained (operation at 825 bar is now being demonstrated[7]) or the minimization of liquid boil-off in cryogenic systems.[8] A significant drawback of cryogenic storage is the large amount of energy input necessary for condensation, approximately 40–50% of the fuel's lower heating value.

Understandably, the possibility of breakthroughs in storage efficiency has been sought by chemical means.[9] Solid metal hydrides[10] have been studied for many years, particularly for understanding the process of metal embrittlement upon absorption of hydrogen at interstitial sites. After surface adsorption, molecular hydrogen may dissociate into atoms that form a solid solution of a hydride phase in the metal or alloy or generate an intermetallic region. The uptake of hydrogen continues at nearly constant pressure until the pure hydride phase is formed, which may have volumetric densities of 150 kg H_2 per m^3 (Mg_2NiH_4).[4] In favorable cases this process is reversible and cycling can occur at desirable pressures (1–10 bar). For materials with a significant capacity for hydrogen, however, desorption usually occurs at a higher temperature than the targeted conditions. Improving the uptake/release kinetics and retention of cycling capacity are currently the major areas of materials research. The disadvantages of these compounds include high cost, susceptibility to impurities, and low reversible gravimetric capacity (typically less than 3 wt%).

To circumvent some of these issues chemical hydrides (also called complex or covalent hydrides) such as $NaAlH_4$ have been studied and shown to reversibly cycle hydrogen on doping with a catalyst.[11] Indeed, the DOE has deemed this material worthy of extensive study, as a result of its reversible release of 4.5 wt% hydrogen.[3] Other alanates and borohydrides of Groups 1, 2, and 13 elements have large gravimetric capacities (>7 wt%), but the extent to which their hydrogen sorption is reversible requires continued investigation. Hydrolysis of alkali metals and their hydrides is also a convenient route for hydrogen release, but requires off-board recycling of the decomposition products.[3,12] Most of these chemical methods still require demonstration of both physical and economic viability.

The fastest way to charge and discharge a storage vessel with hydrogen is to maintain its molecular identity. To reduce the mechanical requirements of pressurized vessels highly porous materials have been investigated for their ability to physisorb molecular hydrogen. This arrangement could potentially allow the confinement of greater masses of fuel within a smaller volume. Carbon materials have received the most attention in this area, because of their low density, high surface area, good chemical stability, and amenability to a wide range of processing conditions. It is precisely this last aspect that has led to controversy with respect to the maximum volume they can adsorb. Since the first account of hydrogen adsorption by carbon nanotubes,[13] a wide range of uptake values have been reported, from negligible to fantastically large. Recently, more consistent results have been achieved by research groups examining many varieties of sample preparations, morphologies, and activations in a single study. Unfortunately, these have revealed adsorption of approximately 5% at 77 K and <1% at room temperature under high pressure.[14] Theoretical modeling studies of the interaction of hydrogen with carbon in systems of many geometries and scales has been performed to provide a rationale for the larger uptake values. The general conclusion reached is that uptake of only a few wt% is achievable with this class of materials.[15] However, reports of improved uptake on changing the morphology have appeared recently.[16]

Research surrounding hydrogen uptake in carbon materials has highlighted several key points, including the importance of sample and measurement reproducibility by independent investigators, the necessity of establishing standard samples for instrumental calibration (especially for gravimetric methods where adsorbate contamination is a significant

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issue), and the utility of theoretical studies to gain insight into the details of the uptake mechanism. These lessons can (and should) be applied to the future studies of novel adsorbents. The other point that has been gleaned from this period of research is that hydrogen storage is still awaiting its breakthrough material.

4. Crystalline MOFs as New Materials for Hydrogen Storage

Metal–organic frameworks (MOFs) are crystalline solids that are assembled by the connection of metal ions or clusters through molecular bridges.[17] As such, they have the potential to exhibit properties inherent to the building blocks, such as geometric rigidity, chemical functionality, or chirality. Their simple preparations are generally high yielding and scalable, and by careful use of the building blocks a certain degree of design can be wielded to produce targeted products from the vast number of MOFs that are potentially accessible. One simple outcome of the use of molecular, rather than monatomic, bridges is the extension of the length between the metal centers, which can lead to the definition of large void regions (Figure 1). Considerations of the geometric requirements for a target framework and implementation of the design and synthesis of such a framework have been termed reticular synthesis. This process requires both an understanding of the local coordination patterns of the metal and organic units and foreknowledge of what net topologies they will adopt.[18] The accumulation of knowledge that has given rise to such precepts has primarily resulted from their crystalline nature, which allows a high degree of structural characterization to be achieved through X-ray diffraction methods.

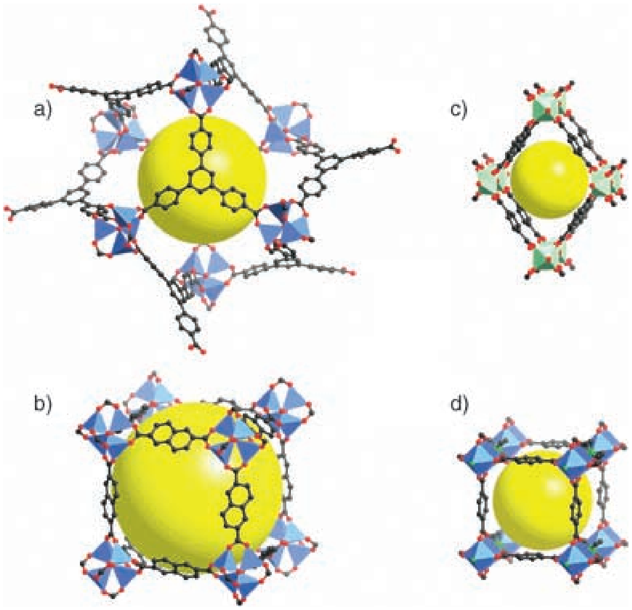

Figure 1. Examples of metal–organic frameworks (MOFs) studied for hydrogen adsorption include a) MOF-177, $Zn_4O(btb)_2$ (btb = benzene-1,3,5-tribenzoate), b) IRMOF-8, $Zn_4O(ndc)_3$ (ndc = naphthalene-2,6-dicarboxylate), c) MIL-53, M(OH)(bdc) (M = Al^{3+} or Cr^{3+}), and d) $Zn_2(bdc)_2(dabco)$ (dabco = 1,4-diazabicyclo[2.2.2]octane). The properties of these compounds are listed in Table 1. Pores in the evacuated crystalline frameworks are illustrated by yellow spheres that contact the van der Waals radii of the framework atoms (C: black, N: green, O: red, Zn: blue polyhedra, M: green octahedra).

Highly crystalline MOFs are also inherently pure in form. The materials are generally prepared in “one-pot” solvothermal syntheses under mild conditions. Powder X-ray diffraction is a simple and effective technique to establish the purity of the crystalline fraction, which often approaches 100 % of the sample. Synthetic reproducibility with high purity is essential for the establishment of structure–property relationships, and this issue has been reiterated many times in the studies of hydrogen storage materials.

The cavities within MOFs are filled with solvent molecules in their as-synthesized forms. Successful establishment of permanent porosity has been accomplished in many cases, with the material stable upon removal of the guest species. This is most conveniently demonstrated by the measurement of gas adsorption isotherms, typically using dinitrogen at its normal boiling point. All porous MOFs to date are microporous by IUPAC definition, having cavities less than 2 nm in size and displaying type I isotherms.[19] Two values are typically calculated from these measurements to allow the porosity to be compared: surface area and pore volume. Type I isotherms can often be described by the Langmuir model, which assumes that a homogenous monolayer of the adsorbate is formed on the walls of the adsorbent. An extension to this model to describe multilayer adsorption has given rise to the commonly used Brunauer, Emmett, and Teller (BET) equation, which is primarily used to determine the point at which monolayer coverage is obtained. In either case, the apparent surface area is calculated as the product of the estimated value of monolayer uptake and an accepted value for the area occupied by an adsorbate molecule. While these models do allow simple comparisons of microporous materials, their assumptions are not always appropriate, especially since pore-filling is the predominant mode of uptake. When multilayer adsorption is possible (such as when the width of the pore is greater than three times the adsorbate diameter) or the assumed molecular area is too large (as can occur if the N_2 molecules are oriented as a consequence of strong quadrupolar interactions with surface sites), then an overestimation of the “true” surface area is possible. Sensibly, all equations and parameters used to calculate surface areas should be reported to facilitate adequate comparisons. The micropore volume, usually calculated by the Dubinin–Radushkevich method, is a complementary and perhaps better descriptor of the porosity of a material.[20]

An outstanding property of MOFs that has prompted their study as hydrogen storage candidates is their large apparent surface areas. Many MOFs are now reported in the literature with surface areas greater than 1000 $m^2 g^{-1}$, which is higher than that demonstrated for zeolites. In particular, the dinitrogen isotherm measured for MOF-177 (Figure 1 a) at 77 K exhibits the highest uptake of N_2 for any material to date, and gives rise to a monolayer-equivalent surface area of 4500 $m^2 g^{-1}$.[21] The micropore volume is calculated to be 0.69 $cm^3 cm^{-3}$, and single-crystal X-ray diffraction studies reveal the framework has cavities of 10.9–11.8 Å diameter connected in all directions by channels. The initial study of the hydrogen uptake by this material at 77 K revealed that while it did not reach saturation at 1 atm, it adsorbed comparatively less than other related materials displaying smaller surface areas.[22] Supercritical hydrogen, as expected, adsorbs more weakly than dinitrogen at 77 K, and pore-filling is not possible at reasonable pressures. Thus, both pore geometry and surface structure must be optimized to increase the uptake in these materials. This study was particularly instructive in demonstrating the diversity in MOFs over nanostructured carbon materials, which show a positive trend in hydrogen uptake with surface area.[14c,15a] As MOFs are composed of a great assortment of chemical moieties that are characterized to a higher degree (by crystallography), they hold more promise for establishing which structural factors are most effective in adsorbing hydrogen.

5. Strategies for Hydrogen Adsorption in MOFs

In the initial report of hydrogen uptake by MOFs alteration of the linking moiety in isoreticular frameworks was shown to improve the uptake to a level of 2.0 wt% in IRMOF-8 (Figure 1b) at 293 K and 10 bar.[23] Saturation uptake is not reached under these conditions and increased pressure results in greater adsorption. For experimental convenience, most reports since then have studied the uptake at 77 K up to 1 atm. The gravimetric uptakes measured under these conditions on a larger subset of Zn_4O-based MOFs also did not exhibit saturation.[22] Calculation of the fraction of the void volume occupied by hydrogen in each material revealed it to be quite low, that is, only a small amount of the surface—let alone the pore volume—is occupied by the guests. This study and others[15a,24] have highlighted the need to optimize pore size to reduce the fraction of under-utilized void space, thereby increasing the volumetric capacity and attractive adsorbate–adsorbent interactions.

5.1. High Porosity with Appropriate Pore Size

The ideal pore size for maximal attraction of an adsorbate is the same as its diameter. This situation results in optimal interaction with all the surrounding adsorbent walls, regardless of geometry, thus maximizing the total van der Waals force on the adsorbate. For adsorbents with thick or dense walls, however, this situation leads to impractically low hydrogen uptake values, as demonstrated for slit and cylindrical pores in nanostructured carbon materials.[15a] Instead, a simple geometric structure resembling a scaffold is preferable. In terms of general considerations, the walls of an adsorbent should be composed of light elements, be as thin as possible (that is, one atomic layer thick, as in graphite), and be highly segmented. A simple calculation demonstrating the advantage of segmenting graphene sheets has recently been reported.[21] The incision process that isolates groups of aromatic rings from each other results in an increased surface area as more edges become exposed. The challenge is to separate these isolated units, and this has already been addressed in MOFs by reticular synthesis. Organic units that represent isolated graphene segments include phenylene, terphenylene, and benzene-1,3,5-triphenylene. These moieties can be reticulated into frameworks where they are isolated from each other by functionalizing their termini with coordinating groups and linking them with metal ions or clusters, as illustrated in Figure 1. This is an alternative perspective of the approach first used to engender porosity in these solids, as described above.

Many MOFs reported, however, have spacings between their walls (or links) that are too large for the effective adsorption of hydrogen. For example, the distance between phenylene faces in MOF-5 describe an approximately spherical pore that is 15 Å in diameter, which is much larger than the 2.89 Å kinetic diameter of H_2 (Figure 2).[25] There would be an unused void volume at the center of these pores that would detract from the volumetric packing density, even at monolayer coverage. To approach the targeted guidelines for H_2 storage it is ultimately required that the density of the adsorbed hydrogen surpasses that of its liquid state. To improve this situation in MOFs, smaller pores are necessary. This arrangement can be afforded by the use of shorter links and the investigation of new topologies. A rigid linear dicarboxylate such as acetylenedicarboxylate is required to stabilize a smaller pore analogue of MOF-5. This is an attractive target for future syntheses, but it is not necessary to only consider simple cubic topologies of this type. By simply distorting the primitive cubic net—for example, by shearing along the face or body diagonals—the pores become elliptical and their shortest dimension is reduced. There are a vast number of smaller pore structures with various topologies that have been published, and their H_2 adsorption requires investigation. While MOFs with constricted pores may exhibit smaller gravimetric capacities, gains may be made in volu-

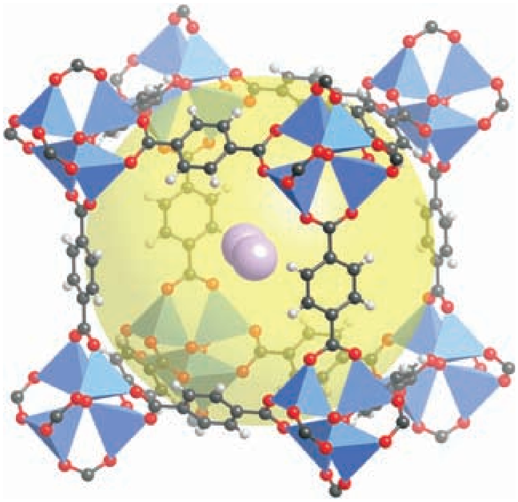

Figure 2. The large pore (yellow sphere) in MOF-5 is 15.2 Å in diameter, much larger than the size of a hydrogen molecule (lilac, shown with atomic van der Waals radii of 1.2 Å) which has a kinetic diameter of 2.89 Å. Framework atoms C: black, H: white, O: red, Zn: blue tetrahedra.

metric capacity.[24] In addition, MOFs with very short linkers that may at first not appear to be porous from dinitrogen adsorption studies, may be composed of apertures that are too small to admit N_2, but are large enough to allow the passage of H_2.[26] From a design perspective, however, it must always be borne in mind that as the framework density increases, the gravimetric H_2 capacity decreases and therefore a compromise must be found.

5.2. Impregnation

Another approach for pore-size and hydrogen volumetric density optimization is to insert another adsorbate surface within large-pore MOFs. This can be achieved by either impregnation with a nonvolatile guest or catenation by another identical framework. It has been shown that large molecules such as C_{60} and Reichardt's dye can be included into MOF-177 from the solution phase.[21] In addition to reducing the free diameter of the pores, such guests may provide additional adsorptive sites (Figure 3). Impregnation with reactive species could provide the more attractive sites that are ultimately necessary to improve hydrogen uptake at room temperature. As expected, there is a doping level that is reached where the additional mass added by the guest is not compensated by additional hydrogen uptake. The guest should also not block the existing adsorptive sites on the framework, instead straddling the pore with minimal framework contacts. Conversely, the guest must be well-anchored or have very low vapor pressure to prevent its desorption along with the hydrogen. These considerations imply that lightweight and reactive, but large and spindly molecules or complexes are required. Structure–property relationships of impregnated MOFs are essentially unexamined to date.

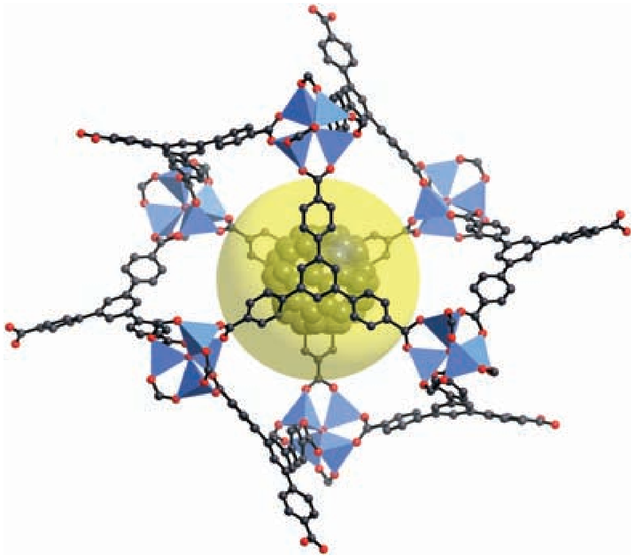

Figure 3. The large pore (yellow sphere) in MOF-177 is 11.8 Å in diameter, large enough to include C_{60} molecules that may provide additional surface sites for the physisorption of H_2.

5.3. Catenation

Framework catenation has long been a topic of interest in MOF research. The intergrowth of two or more frameworks is allowed for many high-symmetry, default topologies and is often observed when long linkers are used. Catenation can take the form of interpenetration, where the frameworks are maximally displaced from each other, or interweaving, where they are minimally displaced and exhibit many close contacts.[27] The most immediate consequence of catenation is a reduction of the free diameter of the pores (shown schematically in Figure 4a–c), therefore, it is a viable strategy for improving hydrogen uptake. There is already some evidence supporting this: in a series of Zn_4O carboxylates studied, the interwoven IRMOF-11 material showed the greatest hydrogen uptake at 77 K.[22] Fourfold catenated IRMOFs have been reported recently to adsorb approximately 1 wt% hydrogen at room temperature and 48 bar.[28]

Interpenetration rather than interweaving is desirable to maximize the exposed surfaces of catenated frameworks. Although interweaving can lead to reinforcement of the individual frameworks, by improving the rigidity and favoring stability in the absence of guests, this is a result of an effective

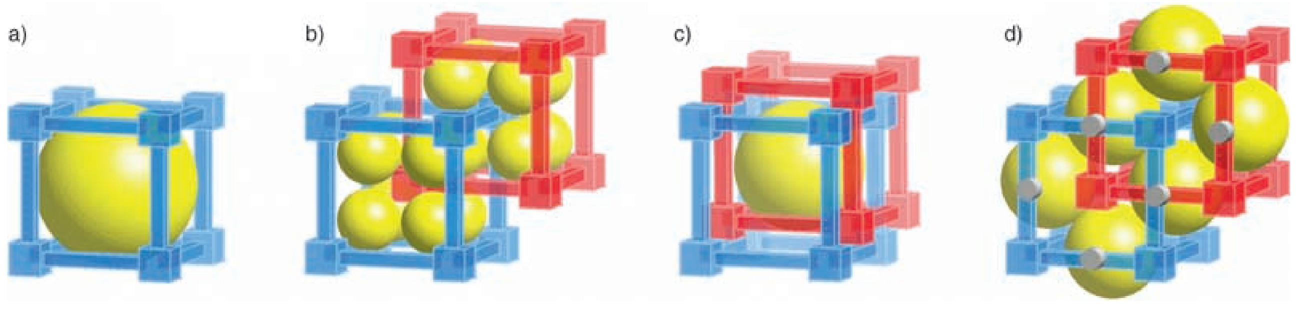

Figure 4. a) Schematic representation of the repeat unit of a crystalline, single-framework MOF with secondary building units (SBUs) shown as cubes and linkers depicted as rods. The yellow sphere represents the large pore defined within the framework. Catenation of two identical frameworks can be used to restrict the dimensions of the pore considerably by interpenetration (b) or to a lesser extent by interweaving (c). Interweaving can improve the material's rigidity by mutual reinforcement; however, this is a result of thicker walls and results in the blockage of potential adsorptive sites. An alternative catenation mode (d) can be achieved by reducing the close contacts between the frameworks to only the midpoints of a proportion of the linkers, as represented by gray discs. The pore dimensions are considerably reduced while a large proportion of the framework atoms, including the SBUs, are still exposed.

thickening of the walls. Thus, the number of framework atoms and their associated adsorptive sites that are exposed to the pore volume is reduced. Conversely, interpenetration decreases the pore size without blocking any adsorptive sites and in most cases also leads to a more convoluted void region. This is not expected to have an appreciable impact on the diffusion rate of supercritical hydrogen through the solid unless the apertures constrict to the size of the H_2 kinetic diameter.

Although conceptually it seems that interpenetrated frameworks should be targeted over interwoven ones, this mode of catenation is unlikely to be sustained in the evacuated state. Most catenated frameworks to date in fact exhibit interweaving, while those that are truly interpenetrated have free solvent molecules separating the individual frameworks where void regions do exist. Examples of the latter include MOF-9[29] and IRMOF-15.[30] It is inevitable that during the evacuation process attractive interactions between catenated frameworks will result in their interweaving. The extent to which this occurs, that is, the proportion of framework atoms that are involved in close contacts, could be minimized by incorporating specified chemical features that would locally attract each other. For example, the inclusion of a hydrogen bond donor–acceptor group at the midpoint of a linker could lead to localized interframework contacts only at the linker midpoints, thus leaving ample distance between the secondary building units (SBUs, Figure 4d). This arrangement would be optimal in the situation where the primary adsorptive sites are on the SBUs and blocking of them results from full interweaving.

5.4. Open Metal Sites

Perhaps the most attractive structural element of secondary building units in some MOFs is coordinative unsaturation, which can be achieved for metal clusters that have additional terminal ligands bound to them. Quite often these are solvent molecules coordinated to the metal by a Lewis acid/base interaction, and may be liberated with heating as neutral guest species. In the most favorable cases, the terminal ligand is removed without detriment to the framework and an open metal site is exposed to the void region. This has typically been achieved for axial ligands bound to metals displaying a Jahn–Teller distortion, most prominently Cu^{2+} ions.[31] Ligand field effects result in the binding of the axial ligand being sufficiently weak to allow its release. In addition, the resulting geometry (square planar for the example of the dimeric Cu^{2+} "paddlewheel", Figure 5a) is stable and consistent with the symmetry requirements of topologies such as those adopted by MOF-11 and HKUST-1 (Figure 5b and c, respectively). MOFs composed of metal clusters with lesser rigidity or constructed of metal ions that lack the electronic requirements to sustain an open metal site commonly collapse after loss of the terminal ligands, but may rearrange to a new form displaying permanent porosity.[32] Another strategy for constructing MOFs with open metal sites is to embed these within the linker. This has been achieved using the equatorially chelating ligand *N*,*N'*-phenylenebis(salicylideneimine)dicarboxylate, that can be used to construct a framework isoreticular with MOF-69[33] after binding a metal ion at its center.[34] The solvent molecules axially coordinated to the linker-bound metal should be removable after framework construction, since the metal is not a key component of the framework. The prospects of exposing open metal sites in a porous material are exciting indeed. To date, these have been divalent cations that are too electron deficient to be expected to form metal hydrides or hydrogen σ complexes. Their coordinative unsaturation, however, may lead to stronger physisorption and is concurrent with a decrease in the density of the framework as a result of the loss of the terminal ligands. Evidence for stronger binding of H_2 to open Ni^{2+} sites has been presented recently for an open-framework phosphate.[35] The possibility of incorporating other metals with coordinative unsaturation that will reversibly chemisorb hydrogen is plausible and this is an admirable target for future syntheses.

5.5. MOFs of Light Metals

One consideration that should not be overlooked while exploring MOFs composed of other metals is the need to reduce the framework density to enhance gravimetric hydro-

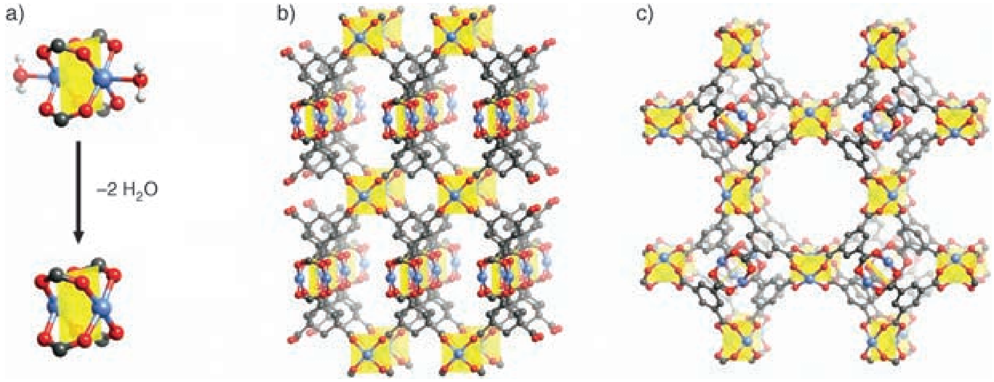

Figure 5. a) The Cu^{II} carboxylate "paddlewheel" cluster is an important square SBU used in some reticulated MOFs. Axial ligands, such as water (shown), may be removed without rearrangement of the cluster and consequent collapse of frameworks such as in MOF-11 (b) and HKUST-1 (c) to yield materials with permanent porosity and a periodic array of open metal sites. Atoms shown as spheres, C: black, H: white, O: red, Cu: blue.

gen capacity. This approach requires investigating the MOFs formed by light main group metal cations such as Li^+, Na^+, Mg^{2+}, and Al^{3+}. While the monovalent cations will most likely produce frameworks that are susceptible to hydrolysis, the large polarizing power of Mg^{2+} and Al^{3+} should give rise to relatively strong coordination bonds. Oxophilicity and predominantly octahedral coordination are well-known characteristics of the two cations, and novel solvent systems will probably need to be employed to avoid formation of dense oxide/hydroxide phases. The only aluminum MOF to date was prepared hydrothermally by using fluoride ions as a mineralizer. The aluminum hydroxide terephthalate MIL-53 (Figure 1c) displays an uptake of 3.8 wt% at 77 K and 16 bar, but an unusual amount of hysteresis upon desorption.[36] Magnesium MOFs are also very rare, in fact few systematic studies of Group 2 MOFs have been reported, as has been recently discussed.[37] None have displayed permanent porosity.

5.6. Functionalized Linkers, SBU Adsorptive Sites, and the Energetics of Physisorption

The impetus for constructing MOFs with constricted pores stems from the need to increase the heat of adsorption of hydrogen in host materials. Ideally, the adsorbent should have both large gravimetric and volumetric capacities at ambient temperature, with the additional criterion of facilitating quick uptake and release of the gas. Since the van der Waals forces that underlie physisorption are weak, the hydrogen capacity of even materials with a very high surface area becomes small at room temperature. An energy of interaction of about 20 $kJ\,mol^{-1}$ has been suggested for porous materials to maintain high capacity at ambient temperatures. A great deal of work, both theoretical and experimental, has gone into estimating the interaction energy of hydrogen with nanostructured carbon materials. There is now reasonable agreement that this value is approximately 5 $kJ\,mol^{-1}$, both from high-level calculations of the gas-phase interaction of H_2 with substituted and expanded aromatic compounds[38] as well as variable-temperature adsorption studies on various carbon materials.[14a,d] Most experimental evidence regarding desorption of hydrogen from activated carbon materials at elevated temperatures have attributed this to chemisorbed hydrogen at dangling bonds.[39] Importantly, it appears that the influence of chemical substitution or nanostructuring of carbon materials on the physisorptive interaction energy is rather small.

Organic linkers with aromatic backbones such as phenylene, naphthalene, bipyridine, and biphenylene have been employed in MOF structures to increase the rigidity of the frameworks. These molecular units mimic the nanostructure of activated carbon materials and nanotubes which are primarily composed of sp^2-hybridized carbon atoms, and hence it is believed that adsorption energetics should be similar for both classes of materials. This situation would be especially true for MOFs where only a small proportion of the framework is composed of metal, such as those with small nuclearity secondary building units. Ab initio calculations indicate that the energy of interaction of hydrogen with substituted benzene is marginally enhanced by the addition of electron-donating groups.[38] The effects of these modifications remain untested in MOFs. Chemical modification with the retention of topology has been demonstrated for a large series of Zn_4O-based MOFs,[30] and initial studies reveal that the linker length and width appear to have an influence on the hydrogen uptake at 77 K[22] and room temperature.[23] As the metrics of the linker have a profound impact on the framework pore size, it is not clear at present whether gains in uptake are more easily achieved by the surface energetics of the linker or the resulting geometric changes in the pore. Further alteration of the linker energetics, such as inclusion of heteroatoms in the aromatic backbone also requires investigation.

With respect to adsorption energetics, MOFs have the additional advantage of a heterogeneous surface structure with local dipoles that may enhance the attraction of hydrogen. These are mainly associated with the SBUs where ionic and dative bonding occur. MOFs composed of $Zn_4O(CO_2)_6$ SBUs such as MOF-5 and MOF-177 can be considered as an assembly of six-membered rings (Figure 6). Here one notes that each benzene ring is attached to two six-membered Zn-O-Zn-O-C-O rings which we believe alter the polarizability of

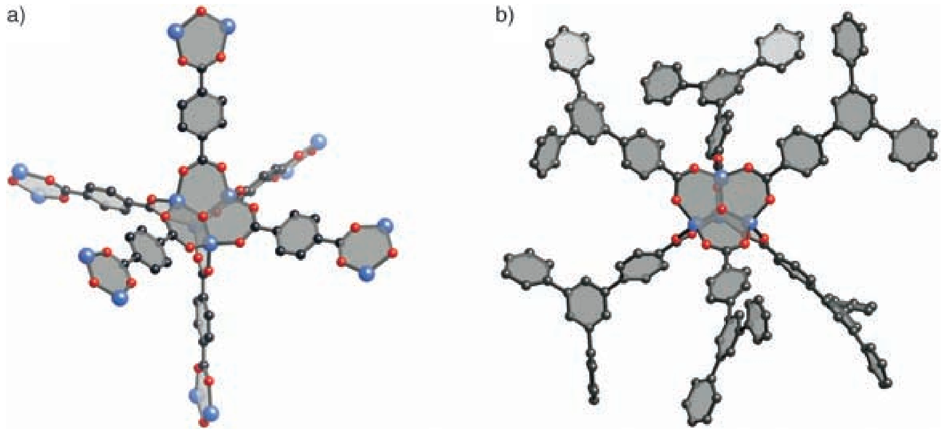

Figure 6. Six-membered rings exist throughout the organic and inorganic backbones of Zn_4O MOFs such as MOF-5 (a) and MOF-177 (b). Atoms shown as spheres, C: black, O: red, Zn: blue.

the π electrons of the link and lead to a higher binding energy for H_2 relative to that of the six-membered rings in graphite and carbon nanotubes. Evidence for stronger binding of H_2 in MOFs was obtained by inelastic neutron scattering experiments.[23] Thus, the composition of such metal-containing ring systems which are incorporated in the SBUs is critical to hydrogen binding. Understanding the details of the hydrogen interaction at the SBUs is particularly important for larger clusters as they begin to resemble an array of metal oxide nanoparticles in a porous organic matrix. As it is clear that the use of alternative metals generates new SBUs and possibly new framework topologies, the search for new MOFs with enhanced uptake is limitless.

6. Characterization of Hydrogen Uptake in MOFs

Metal–organic frameworks have only recently been proposed as candidates for hydrogen storage, but already several reports of uptake in these materials have entered the literature. The uptake is typically characterized by adsorption isotherms measured at 77 K up to 1 atm (the operating range of a typical commercial adsorption apparatus), but data collected at room temperature and high pressure have also been reported. These data have been summarized in Table 1. The high-pressure conditions are more relevant for practical applications, especially as the pressure limits in commercial hydrogen tanks increase. As the low-temperature hydrogen isotherms can be measured using essentially the same apparatus as that used to determine the MOF surface area, these data are also very useful at this early stage of exploration. As always, care must be taken to ensure the accuracy of the results, especially when gravimetric methods are used. As H_2 gas has the lowest molecular weight and physisorbs weakly, ultrahigh-purity gas must be used and the adsorption apparatus adequately tested for leaks. Ideally, the results should be confirmed by a complementary method, such as volumetric adsorption.[22] More extensive measurements are required to quantify the heat of adsorption in the most promising compounds.

Spectroscopic investigation of the hydrogen–framework interaction has been performed using inelastic neutron scattering studies. This technique provides a sensitive probe of the adsorptive sites for molecular hydrogen as it monitors the hindered rotational transitions of bound molecules. Promising observations were made for MOF-5 loaded with varying amounts of hydrogen.[23] These spectra revealed that at least two distinct adsorptive sites exist on the framework,

Table 1: Summary of hydrogen adsorption in MOFs.

Material[a]	Free/fixed diameters[b,c] [Å]	Accessible volume fraction[b,d]	Apparent surface area[e] [$m^2\,g^{-1}$]	Pore volume[i] [$cm^3\,g^{-1}$]	H_2 uptake [wt %]	Conditions	Reference
$Zn_4O(bdc)_3$, IRMOF-1	7.8/15.2	0.59	3362	1.19	1.32	77 K, 1 atm	[22]
					1.0	RT, 20 bar	[23]
					1.65	RT, 48 atm	[24]
$Zn_4O(R^6\text{-bdc})_3$, IRMOF-6	5.9/15.2	0.50	2630	0.93	1.0	RT, 10 bar	[23, 30]
$Zn_4O(ndc)_3$, IRMOF-8	8.4/18.0	0.66	1466	0.52	1.50	77 K, 1 atm	[22]
					2.0	RT, 10 atm	[23]
$Zn_4O(hpdc)_3$, IRMOF-11	6/12.4	0.40	1911	0.68	1.62	77 K, 1 atm	[22]
$Zn_4O(tmbdc)_3$, IRMOF-18	5.4/13.8	0.42	1501	0.53	0.89	77 K, 1 atm	[22]
$Zn_4O(btb)_2$, MOF-177	9.6/11.8	0.63	4526	1.61	1.25	77 K, 1 atm	[22]
Al(OH)(bdc), MIL-53(Al)	6.4/6.4	0.29	1590, 1020[f]	–	3.8	77 K, 16 bar	[36, 45]
Cr(OH)(bdc), MIL-53(Cr)	6.6/6.6	0.29	1500, 1026[f]	–	3.1	77 K, 16 bar	[36, 46]
$Mn(HCO_2)_2$	3/4.7	0.10	297[g]	–	0.9	77 K, 1 atm	[26]
$Cu_2(hfipbb)_2(H_2hfipbb)$	3/4.7	0.03	–	–	1.0	RT, 48 atm	[24]
Ni(cyclam)(bpydc)	6.1/7.6	0.18	817	0.37	1.1	77 K, 1 atm	[47]
$Zn_2(bdc)_2(dabco)$	7.8/9.5	0.45	1450[f]	–	2.0	77 K, 1 atm	[48]
$Ni_2(bpy)_3(NO_3)_4$ (M)	2.4/4.0	0.05	–	0.181[j]	0.8	77 K, 1 atm	[49]
$Ni_2(bpy)_3(NO_3)_4$ (E)	2.1/4.2	0.05	–	0.149[j]	0.7	77 K, 1 atm	[49]
$Ni_3(btc)_2(3\text{-pic})_6(pd)_3$	8.5/10.7	0.30	–	0.63	2.1	77 K, 14 bar	[49]
$Zn_4O(L^1)_3$	3.8/7.8	0.21	502[h]	0.20	1.12	RT, 48 atm	[28]
$Zn_4O(L^2)_3$	3.8/5.4	0.17	396[h]	0.13	0.98	RT, 48 bar	[28]
$Cu_2(pzdc)_2(pyz)$, CPL-1	3.4/5.0	0.04	–	–	0.2	89 K, 1 atm	[40]
$Cu_2(bptc)$, MOF-505	6.7/10.1	0.37	1646	0.63	2.48	77 K, 1 atm	[50]

[a] Acronyms: bdc = benzene-1,4-dicarboxylate, R^6-bdc = 1,2-dihydrocyclobutylbenzene-3,6-dicarboxylate, ndc = naphthalene-2,6-dicarboxylate, hpdc = 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate, tmbdc = 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate, btb = benzene-1,3,5-tribenzoate, hfipbb = 4,4′-(hexafluoroisopropylidene)bisbenzoate, cyclam = 1,4,8,11-tetraazacyclotetradecane, bpydc = 2,2′-bipyridyl-5,5′-dicarboxylate, dabco = 1,4-diazabicyclo[2.2.2]octane, bpy = 4,4′-bipyridine, btc = benzene-1,3,5-tricarboxylate, 3-pic = 3-picoline, pd = 1,2-propanediol, L^1 = 6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4-4′-dibenzoate, L^2 = 6,6′-dichloro-2,2′-dibenzyloxy-1,1′-binaphthyl-4,4′-dibenzoate, bptc = biphenyl-3,3′,5,5′-tetracarboxylate. [b] Calculations were performed using the Cerius^2 software package. Crystallographic data for the evacuated frameworks was used where available. [c] Free and fixed diameters correspond to the largest spheres that can pass through the apertures and fit in the largest pores of the frameworks, respectively. [d] Calculated using a probe radius of 1.45 Å, which corresponds to the kinetic diameter of H_2. [e] Calculated from N_2 adsorption data collected at 77 K using the Langmuir model except where indicated. [f] BET surface area from N_2 at 77 K. [g] BET surface area from CO_2 at 195 K. [h] BET surface area from CO_2 at 273 K. [i] Calculated from N_2 adsorption data collected at 77 K using the Dubinin–Radushkevich method except where indicated. [j] Methanol used as adsorbate.

which were assigned to the inorganic and organic components. MOFs have a further advantage over nanostructured carbon materials and amorphous adsorbents in that they have a high degree of long-range order. If such adsorptive sites are indeed localized, they are additionally periodically arranged. It therefore may be possible to detect the adsorbed hydrogen molecules at very low temperatures by a diffraction experiment. A report has recently appeared describing the modeling of electron density, measured by synchrotron powder X-ray diffraction, of adsorbed H_2 in the small channels of CPL-1.[40] Neutrons are again the ideal scattering probes for such experiments as X-rays are insensitive to the low electron density of hydrogen atoms.

Computational modeling studies of the hydrogen interaction with metal–organic frameworks and their chemical components will also be important for our understanding of physisorption in these materials. The simplicity and high symmetry of some of the structures should make them ideal candidates for study, to the level that has been achieved for zeolites such as Na-A.[41] Grand Canonical Monte Carlo simulations of argon and methane in MOFs have been reported, and these display good agreement with measured isotherms.[42] The physisorption of hydrogen in MOF-5 has also been examined recently, in addition to more detailed calculations for H_2 with models of its inorganic and organic moieties, by using second-order Møller–Plesset perturbation theory.[38,43,44] The Monte Carlo study indicates that binding at the $Zn_4O(CO_2)_6$ clusters is perhaps 1.5 $kJ\,mol^{-1}$ higher in energy than at the phenylene groups, but a broad range of interaction energies was determined for their system at 300 K corresponding to occupation of a broad distribution of sites.[44] Further computations of the hydrogen dynamics in MOFs will be indispensable in providing future directions for materials optimization.

7. Concluding Remarks

The series of considerations proposed above are multifaceted and we expect that significant exploration will be required to satisfy many of them simultaneously. A material with high gravimetric and volumetric hydrogen capacity at practical conditions should have a high surface area with pores of appropriate dimension for hydrogen and a large heat of adsorption. The strategies of impregnation, catenation, and the inclusion of open metal sites are just a few possibilities to be tested. To date, nearly 5000 2D and 3D MOF structures have been reported in the literature, but only a fraction of these have been examined for their porosity and far fewer of them have been tested for their hydrogen storage capacity. This fact, combined with the advantages of MOFs such as ease of synthesis and functionalization of their organic linkers and inorganic SBUs are favorable circumstances for achieving the DOE target for on-board hydrogen storage.

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