Materials for hydrogen storage: current research trends and perspectives

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Storage and transport of hydrogen constitutes a key enabling technology for the advent of a hydrogen-based energy transition. Main research trends on hydrogen storage materials, including metal hydrides, porous adsorbents and hydrogen clathrates, are reviewed with a focus on recent developments and an appraisal of the challenges ahead.

1 Setting the scene

> *Water!* cried Pencroft, *water as a fuel for steamers and engines! Water to heat water*!
>
> *Yes, but water decomposed into its primitive elements*, replied Cyrus Harding, *and decomposed doubtless, by electricity (…) Yes, my friends, I believe that water will one day be employed as a fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light (…) Some day the coalrooms of steamers and the tenders of locomotives will, instead of coal, be stored with these two condensed gases, which will burn in the furnaces with enormous calorific power. There is, therefore, nothing to fear. As long as the earth is inhabited it will supply the wants of its inhabitants (…) I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future.*
>
> *I should like to see that*, observed the sailor.
>
> *You were born too soon, Pencroft*, returned Neb, who only took part in the discussion by these words.
>
> Jules Verne
> *The Mysterious Island*, 1874.

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The above quoted discussion between engineer Harding and sailor Pencroft, sharply settled by servant Nebuchadnezzar –Neb for his friends, shows that as early as 1874 Cyrus Harding was already thinking of water, or more precisely, *water decomposed into its primitive elements* (*i.e.*, hydrogen and oxygen) as the fuel of the future. Jules Verne (in the words of Harding) also reminds us of a well known but sometimes overlooked fact – hydrogen is not available on Earth as a (primary) fuel.

Ever since humankind learned how to control fire, several naturally occurring fuels were used to generate energy: wood, peat, coal, petrol (crude oil) and natural gas compose an approximately chronological list. They all are carbon based fuels generated, in the very end, at the expense of energy coming from our (so far) only efficiently working nuclear-fusion reactor –The Sun. Early use of wood, peat, and also wind (sails and windmills) and animal power (for traction and transportation) as energy sources shifted to coal with the advent, in the 18th century, of the Industrial Revolution; made possible by the invention of the steam engine.[1] By the end of the 19th century, invention of the internal combustion engine, and concomitant introduction of petrol as a fuel, resulted in a gradual transition from coal to oil. This new shift, which progressively gained impulse along the 20th century resulted in petrol being today a main energy source. Taken together, oil and natural gas account for well over 50% of present day primary energy supply, as shown in Fig. 1. However, at the humankind timescale, both of these (carbon based) fossil fuels are not renewable, and currently known reserves would not last for longer than a few decades. This is so much the case when considering that the rate of energy consumption is expected to increase because of both, the rapidly growing world population and the (reasonable) assumption that inhabitants of less developed countries would wish to increase energy demand; a desire which should not be refused. In addition to that, production of energy by burning carbon-based fuels inevitably leads to an increasing level of carbon dioxide in the atmosphere, thus aggravating greenhouse effect and its global adverse consequences.

Both of the above reasons clearly show that, for sustainable development, a new (energy) transition is needed. The

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potential of hydrogen to play an important role in that transition, already suggested long ago by Jules Verne, was coming into serious consideration along the last 30 years, and a name for this paradigm was coined – *The hydrogen energy transition*[2] (*hydrogen economy* being an alternative term). It should be borne in mind, however, that hydrogen (as such) is not freely available on earth and, hence, it cannot be used as a primary energy source. Referring to hydrogen as a fuel in the same sense as we refer to petrol or natural gas is misleading. Energy is needed in the first place to produce hydrogen (*e.g.*, from water) that can then act as an energy vector[3] (or carrier). Note that electricity constitutes an analogous example. The issue of producing hydrogen without generating carbon dioxide or other undesirable by-products, although being very relevant, is out of the scope of this article. It is true however that (once produced) hydrogen could be used as a clean fuel, and also as a means to store energy in a large amount; which is presently impracticable in the case of electricity.

Although stationary applications could also be envisaged, the main current drive to use hydrogen as an energy carrier comes from its potential to replace petrol derived fuels in cars and other vehicles. At present day, 97% of transportation fuel comes from crude oil, and generates about 25% of global greenhouse emissions. Looking ahead, the situation does not become any better since the number of vehicles worldwide, now about 750 million, is expected to triple by 2050; largely due to expanding buying power of people in developing countries. To demonstrate the technical feasibility of using hydrogen to power vehicles, the European Union launched in 2001 the CUTE (Clean Urban Transport for Europe) project.[4] Within this project, an initial number of 27 hydrogen fuel cell buses were produced (the so called *hydrogen fleet* or, in short, HyFLEET) and put in circulation for urban public transport in nine major cities: Amsterdam, Barcelona, Hamburg, London, Luxembourg, Madrid, Porto, Stockholm and Stuttgart (Fig. 2 shows a hydrogen fuelled bus). All of them have been running for several years without any major safety incident, and the scenario for 2015 contemplates expanding the HyFLEET to 170 fuel cell bus fleets throughout Europe, each of them with 73 buses running on hydrogen.[4]

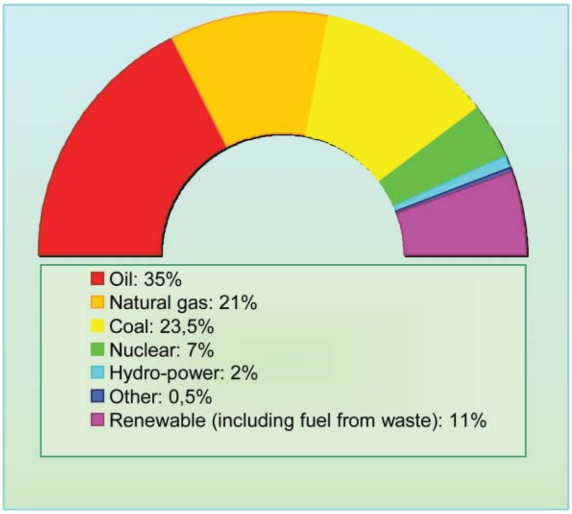

Fig. 1 Distribution, in approximate percentage, of total world primary energy supply.

Gaseous hydrogen, compressed in gas cylinders at an initial (loading) pressure of 350 bar, is used in HyFLEET buses to generate electricity in a stack of fuel cells that powers a central electric engine. However, gas cylinders able to support such a high pressure are too heavy to be used in private cars and, to follow, fuel cells are too expensive for the (non-subsidized) private sector. Although price of fuel cells is expected to come down in the near future, a temporary alternative could be to power cars by burning hydrogen (as done with gasoline) in present-day internal combustion engines. In fact, private cars that can run on either petrol or hydrogen were already put in the market by some commercial firms. Some of these cars use liquid hydrogen stored, at 20.3 K, in a cryogenic tank.[5] This solution, however, does also have some inconveniences; besides technical complexity, the process of hydrogen liquefaction consumes about 20% of the recoverable energy, and daily evaporation (to keep the hydrogen tank cool) takes away another 2%. For these reasons, the search for materials capable of safe and cost effective storage and on-board transport of hydrogen constitutes a major issue in the energy sector; and a large effort is being made worldwide in the attempt to develop functional hydrogen storage materials. Main requirements for such materials and current research trends are summarized below.

2 Materials-based hydrogen storage: research challenges and current trends

Owing to its low molecular weight and high molar combustion heat hydrogen has an outstanding energy value on a unit mass basis. However, low density (in both the gas and liquid state) results in hydrogen having a heating value per volume significantly smaller than that of conventional fuels, as shown in Table 1. A further distinctive feature of hydrogen is its very low boiling point, which results in added cost (and technical complications) for hydrogen storage and handling in the liquid state. Similarly, hydrogen transport as a compressed gas in

Fig. 2 *Wij rijden op water* (we ride on water) is the motto on this fuel-cell hydrogen bus used for public transport in Amsterdam. Actually, the bus is fuelled by hydrogen generated from electrolysis of water.

Table 1 Properties of hydrogen compared with those of some common fuels

	Hydrogen	Petroleum (gasoline)	Methane	Methanol
Boiling point/K	20.3	350–400	111.7	337
Liquid density[a]/kg m^{-3}	70.8	~700	425	797
Gas density[b]/kg m^{-3}	0.08	~4.7	0.66	—
Vaporization heat/kJ kg^{-1}	444	~300	577	1168
Combustion heat[c]/MJ kg^{-1}	120	44.5	50.0	20.1
Combustion heat[d]/MJ m^{-3}	8960	31170	21250	16020
Ignition temperature[e]/K	858	495	807	658

[a] At boiling point. [b] At STP. [c] Neglecting the energy in the exhaust (combustion) gases. [d] Referred to the liquid fuel. [e] In air.

high pressure cylinders also meets with the limitation of added cost.[6] Means for safe and cost effective storage are needed for widespread usage of hydrogen not only in transportation, but also in stationary and portable (*e.g.* portable electronics) applications; with the transportation sector posing the most demanding challenges.

For light-duty cars, the on-board hydrogen storage system should allow a driving range of about 500 km, and fast refuelling, in order to meet customer requirements. By translating present-day vehicle performance into storage system needs, the U.S. Department of Energy (DOE) has stated the following targets. The on-board hydrogen storage system should have a specific (gravimetric) energy of 2.0 kWh kg^{-1} (6 wt% hydrogen), and an energy density of 1.5 kWh l^{-1}, by the year 2010. For 2015 corresponding targets are 3.0 kWh kg^{-1} (9 wt% hydrogen), and 2.7 kWh l^{-1}. Besides that, refuel time should not be larger than about 3 min, and durability of the system should be higher than 1000 hydrogen uptake and delivery cycles.[7] Note that the quoted gravimetric and volumetric energy density figures refer to the hydrogen storage system as a whole, which includes all of the hardware (*e.g.* tank, valves and regulators, cooling or heating systems if needed, insulation, *etc.*). Hence, the actual capacity of the hydrogen storage material might need to be significantly higher than the system targets.

Despite the above demanding challenges, the realization that hydrogen storage constitutes a key enabling technology for the (potential) advent of a hydrogen economy prompted research on materials-based solutions. In general terms, solid materials most actively investigated can be regarded as belonging to two distinct groups; they either show (mainly) hydrogen chemisorption usually followed by compound formation or they reversibly adsorb molecular hydrogen. The first group is typified by metal hydrides and related compounds, although non-metal hydrogen compounds are also being investigated. The second group, constituted by highly porous solids, comprises mainly active carbons (including carbon nanostructures) and solids formed by open metal–organic frameworks (MOFs), however, other porous solids such as zeolites and (organic) polymers having intrinsic microporosity (PIMs) are also under active research. From the applications point of view, perhaps the most remarkable difference between metal hydrides and microporous adsorbents is their operational temperature, although other relevant differences are also considered below. Because of their relatively high stability, metal hydrides usually have to be heated at a temperature higher than about 500 K for thermal decomposition and consequent hydrogen release. By contrast, a problem with most (physical) adsorbents is that they usually need a low temperature (about 77 K) for storing hydrogen in a reasonable amount. Since operation at (or near) ambient temperature is highly desirable, main strategies aim at either lowering operational temperature for hydrides or increasing it for porous adsorbents.

Altogether, metal hydrides, carbons and MOFs account for the vast majority of research reports being published. A search through the recent literature gave the result shown in Fig. 3, which testifies to the brisk pace at which research is conducted. Added to that, there is also relevant research on potential hydrogen storage materials not strictly belonging to any of the above mentioned groups, such as hydrogen clathrates and nanostructures not based on carbon (*e.g.*, inorganic nanotubes and nanowires).

We aim at reviewing the field of hydrogen storage (solid) materials with a focus on recently published reports. However, in order to keep this article within a reasonable length, no effort was made to be comprehensive; rather than that, we shall try to summarize relevant developments on each kind of material and to point out relative merits and drawbacks. For the same reason of brevity, the fields of hydrogen storage in liquid carriers (*e.g.* carbazoles and imidazoles) or in materials that release hydrogen by reaction with water (*e.g.* CaH_2, $LiBH_4$ and several magnesium and aluminium based powdered materials)[8–10] are not reviewed here. It should be noted, however, that the corresponding hydrolysis reactions of the

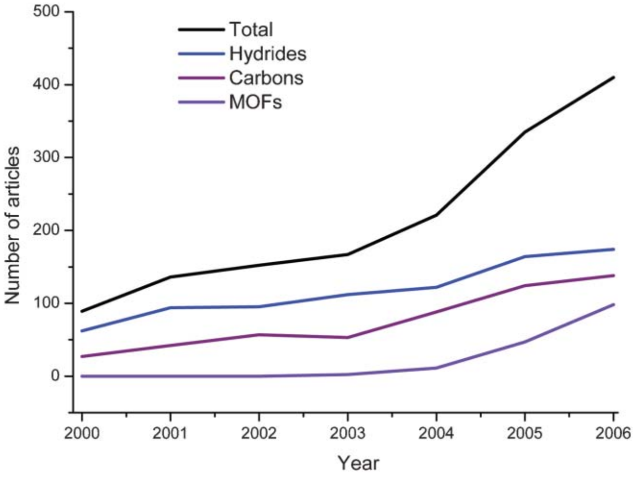

Fig. 3 Number of scientific articles per year dealing with some different types of hydrogen storage materials.

latter materials are irreversible and could not provide the basis for rechargeable hydrogen storage systems.

3 Metal hydrides

Studies on solid-state hydrogen storage in metal hydrides and related materials constitute a major research activity in the field of materials-based hydrogen storage, as testified by data in Fig. 3. Besides binary metal hydrides (*e.g.*, MgH_2),[11] ternary hydrides, complex metal hydrides (*e.g.*, alanates) and hydrides of multinary alloys (such as TiZrV, Mg_2Ni, $LaNi_5$, *etc.*)[12] are under active investigation; each group has its own merits. For instance, although hydrides of multinary alloys (or intermetallic hydrides) tend to be too heavy to meet the criterion of high storage capacity, they usually show good reversibility, which gives them clear advantage in some niche applications (*e.g.*, as electrodes in metal-hydride batteries). Because of its vast extension and variety, reviewing the whole field of metal hydrides and related materials would be impracticable here. We shall focus on main characteristics of metal hydrides (as compared to other hydrogen storage solids) and on latest developments. For a broader scope, the interested reader is referred to more extensive recent reviews by several authors,[13–21] which also quote earlier work in the field. It should also be noted that both, metal hydrides and chemical hydrides constitute an important part of the DOE Hydrogen Program; annual progress reports by several research groups can be found at the relevant website.[22]

Under appropriate (temperature and hydrogen pressure) conditions, most metals react with hydrogen to form metal hydrides. When considered in detail, properties of these compounds are too complex to allow them to be classified into well defined (distinct) groups.[23] However, broadly speaking, transition metals tend to form hydrides having a variable, non-stoichiometric, composition (*e.g.*, $PdH_{0.6}$) and retaining metallic properties (interstitial metal hydrides). On the other hand, metals of groups I and II of the periodic table give stoichiometric hydrides (*e.g.*, CaH_2), most of which have a marked ionic character.[24] Besides that, many complex hydrides are also known; among them aluminohydrides (alanates) and borohydrides (*e.g.*, $NaAlH_4$ and $LiBH_4$, respectively).[25] Regarding gravimetric density of stored hydrogen, hydrides of the light metals clearly stand a better chance of fulfilling the DOE targets; examples are given in Table 2. However, other key issues for metal hydrides are reversibility, favourable thermodynamics and fast kinetics.

In simple terms, formation (hydrogen uptake) and decomposition (hydrogen release) of a metal hydride can be represented by eqn. (1) below:

Table 2 Relevant data for some light-metal hydrides

Material	Max. wt% H_2	T_d/°C	Ref
$LiBH_4/½MgH_2$	11.4	400	34
$NaAlH_4(Ti)$	5.5	35–130	49
$NaAlH_4(TiCl_3)$	4.0	100–125	21
$NaAlH_4(TiO_2)$	5.5	125	15
$MgH_2/2LiNH_2$	5.6	180–200	11,21
Mg_2NiH_4	3.6	Ambient	15

$$M_{(s)} + H_{2(g)} \rightleftarrows MH_{2(s)};\ \Delta H_f^0 \tag{1}$$

where M is a metal and ΔH_f^0 is the standard enthalpy of formation of the metal hydride, MH_2. Thermodynamic stability of a metal hydride means $\Delta H_f^0 < 0$ in eqn. (1), and the larger the absolute value of ΔH_f^0 the higher the stability. Read from right to left, eqn. (1) applies to thermal decomposition of the hydride (and consequent hydrogen release). For a reversible process, the enthalpic term involved (ΔH_d^0), which is now positive, has the same absolute value as ΔH_f^0, *i.e.*, $\Delta H_d^0 = -\Delta H_f^0$. Moreover, following simple thermodynamics, the decomposition temperature, T_d, of a pure metal hydride (at equilibrium pressure) is given by eqn. (2) below:

$$T_d = \Delta H^0/\Delta S^0 \tag{2}$$

where ΔS^0 is the standard entropy change involved in formation of the metal hydride. Ignoring entropy change in the solid phase, ΔS^0 approximately coincides (in absolute value) with the entropy content of gas phase hydrogen, and has opposite sign. Hence, eqn. (2) shows that T_d is expected to be approximately proportional to ΔH^0. Actually, quoted values[26–28] of ΔS^0 range from about 90 to 130 J mol^{-1} K^{-1}. Inserting these ΔS^0 values into eqn. (2) leads to a range of ΔH^0 values going from about 27 to 50 kJ mol^{-1} if the dehydrogenation temperature is to lie between ambient and about 130 °C.

Besides temperature, hydrogen equilibrium pressure is another important parameter for a reversible metal hydride. Correlation between temperature and pressure for prospective metal hydrides is shown in the van't Hoff plot of Fig. 4, where the optimum temperature-pressure operational window for hydrogen fuel cells having a polymer electrolyte membrane (PEM) is depicted as a shaded rectangle.[20,29] Interstitial hydrides formed by a few alloys[30] (and also by some pure metals) fall inside the operational window, but their gravimetric capacity is too low for on-board hydrogen storage; *e.g.*,

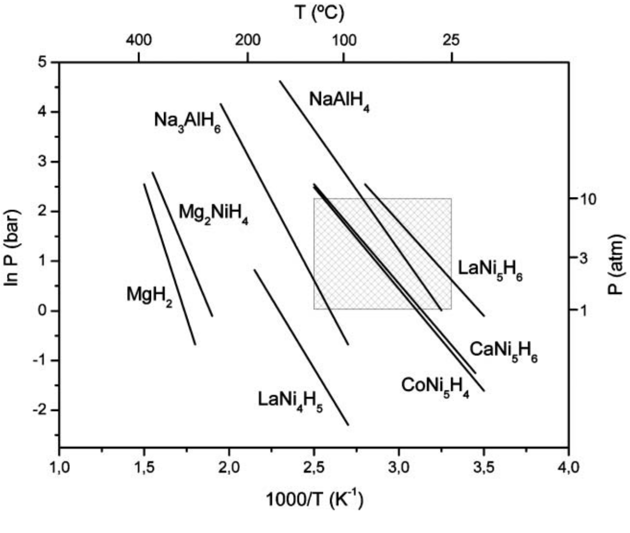

Fig. 4 Logarithm of pressure *vs.* reciprocal temperature (van't Hoff plot) for several metal hydrides. The shaded area shows the *P–T* operational window for PEM fuel cells.

1.1 and 0.9% for $CoNi_5H_4$ and $LaNi_5H_6$, respectively. By contrast, MgH_2 has a large hydrogen content (7.6% by weight) but its decomposition temperature is too high.

Aside from thermodynamics, the kinetics of hydrogen uptake and release is another important factor to consider; a slow kinetics of hydrogen uptake (which is often the case) would make on-board refuelling impracticable. As a general rule both, formation and thermal decomposition of a metal hydride require activation energy and, in practice, a temperature higher than that dictated by thermodynamics is needed for both hydrogen uptake and release.[20,31–33] Kinetics can be improved by adding a catalyst, while better thermodynamics can be achieved by lowering the enthalpic term (which is usually too high) in eqn. (1).

A way to reduce the enthalpy of the hydrogenation–dehydrogenation process is to add a chemical species that either destabilizes the hydrogenated state or stabilizes the dehydrogenated state. In both cases, this strategy is usually referred to as *destabilization* (of the system). This strategy of improving thermodynamics by using additives to form compounds which are energetically favourable was recently exploited by Vajo and collaborators,[34] who showed that addition of MgH_2 (as a destabilizing agent) to $LiBH_4$ results in significant improvement. Pure $LiBH_4$ yields 13.6 wt% hydrogen upon thermal decomposition following eqn. (3) below:

$$LiBH_4 \rightleftarrows LiH + B + H_2 \qquad (3)$$

which involves a standard enthalpy change of about 67 kJ (mol H_2)$^{-1}$. However, dehydrogenation of a 2 : 1 mixture of $LiBH_4$ and MgH_2 proceeds according to eqn. (4):

$$LiBH_4 + \tfrac{1}{2}MgH_2 \rightleftarrows LiH + \tfrac{1}{2}MgB_2 + 2H_2 \qquad (4)$$

Although maximum hydrogen capacity is now reduced to 11.4 wt%, formation of MgB_2 stabilizes the dehydrogenated state, which results in lowering of hydrogenation-dehydrogenation enthalpy by 25 kJ (mol H_2)$^{-1}$.[34] Although more research on this system seems to be needed for detailed understanding, and also with a view to obtain faster hydrogen sorption rates, the reported results are encouraging. Similarly, experimental studies on the possibility of improving thermodynamics of other systems by destabilization were recently reported by several authors; Lu *et al.*[35] ($Li_3AlH_6/LiNH_2$), Aoki *et al.*[36] and Pinkerton *et al.*[37] ($LiBH_4/LiNH_2$) and Zhu *et al.*[38] (magnesium based alloys), among others. On the theoretical side, Alapati *et al.*[27,39] have used density functional theory to predict the reaction enthalpy for more than 300 destabilization reactions of metal hydrides involving elements of periods 2 and 3 (of the Periodic Table). Hydrides of these light elements are promising candidates for hydrogen storage, but most of them have a formation enthalpy that is too high. The aim of the study was to screen potential additives and reaction schemes. In particular, values of ΔH^0 in the range of 25 to 30 kJ mol^{-1} were found for the systems $MgH_2/LiNH_2$, $3Ca(AlH_4)_2/2Si$, $17MgH_2/6Ca(AlH_4)_2$ and $3Ca(AlH_4)_2/4LiH$; which have a maximum hydrogen release capacity of 11.56, 6.69, 6.67 and 7.17 wt%, respectively. While practical viability of these systems has yet to be tested experimentally, particularly regarding hydrogenation and dehydrogenation kinetics (among other factors), theoretical screening does help to orient experimental investigation. The power of a theoretical (and computational) approach was also highlighted by Grochala and Edwards[15,40] who showed that, (i) the thermal decomposition temperature (T_d) of metal hydrides correlates with the standard redox potential of the cation-metal couple, and (ii) T_d can be tuned (till some extent) by judicious choice of stoichiometric ratio and Lewis acid–base character of the chemical elements constituting mixed metal hydride formulations.

Regarding kinetics of hydrogen uptake and release, main aspects to be considered are as follows.[21,41,42] The hydrogenation rate is controlled by three (main) factors, (i) the rate at which hydrogen molecules dissociate at the metal surface, (ii) difficulty for hydrogen penetration from the surface into the metal (which can be covered by a metal oxide layer), and (iii) hydrogen diffusion through the hydride layer already formed and into the bulk metal. Dehydrogenation rate, on the other hand, involves (i) elementary stages proceeding in the bulk, including chemical and structural changes, (ii) bulk to surface transfer (*i.e.*, bulk diffusion) and (iii) recombination on the surface. Although the combined effect of these processes involves high complexity, it should be clear that catalysts can be used to enhance kinetics by decreasing activation energy barriers; as usually done for many chemical reactions involving hydrogen transfer.

Nickel and palladium are well known catalysts for molecular hydrogen dissociation, and it should be no surprise that both of these metals are under research as catalysts for hydrogen storage on metal hydrides. In particular, nickel alloys (palladium is far more expensive) usually show a fast kinetics which can be attributed to the catalytic effect of nickel.[43–45] Enhanced kinetics and significant lowering of hydrogenation and dehydrogenation temperature (from 275 to 175 °C and from 350 to 275 °C, respectively) was also obtained by adding 1% nickel to magnesium.[46] Besides nickel, many other transition metals and their oxides (*e.g.*, Ti, Cr, Nb_2O_3 and Cr_2O_3)[21] are under active research as catalysts for improving kinetics of hydrogen storage on metal hydrides. Lanthanide oxides (see below) constitute another research line. It should also be mentioned that recent reports showed that addition of carbon nanotubes (5 wt%) to magnesium[47] and to MgH_2/FeTi nano-composites[48] (obtained by ball milling) resulted in significant improvement of hydrogen uptake kinetics and lowering of sorption temperature. Carbon was suggested to have a minor role on hydrogen dissociation but a remarkable effect on enhancing hydrogen diffusion kinetics.[48]

Considerable attention is currently focused on improving hydrogenation and dehydrogenation rates of sodium alanate ($NaAlH_4$) by means of catalysts. $NaAlH_4$ has a relatively high hydrogen storage capacity (theoretical, 5.6 wt%) and it is readily available at a low cost. However, although thermodynamics is favourable, sodium alanate was not considered to be rechargeable, because of very slow kinetics, until Bogdanovic and Schwickardi[49] showed that titanium-doped $NaAlH_4$ can reversibly be dehydrogenated and rehydrogenated following a two-step process described by eqn. (5) and (6) below:

$$3NaAlH_4 \rightleftarrows Na_3AlH_6 + 2Al + 3H_2 \text{ (3.7 wt\% } H_2) \quad (5)$$

$$Na_3AlH_6 \rightleftarrows 3NaH + Al + 1.5H_2 \text{ (1.8 wt\% } H_2) \quad (6)$$

At atmospheric pressure, the first step proceeds at about 35 °C and the second one at about 130 °C (see Fig. 4). Altogether, these features render titanium-doped sodium alanate one of the most promising candidates (among metal hydrides) for on-board hydrogen storage.[14] However, practicable feasibility of the step described by eqn. (6) depends on the working temperature of the fuel cell, and it also poses technical problems for heat management.[50] Ongoing research aims at improving catalyst performance and, to that purpose, two main lines are under investigation. First, both catalyst precursor (*e.g.*, $TiCl_3$, titanium powder, Ti-colloids, *etc.*) and doping method are known to be factors influencing performance,[14,51–54] and it is hoped that current systems can be improved. Secondly, there are some reports suggesting that other catalysts, *e.g.* lanthanides, can actually perform better than titanium;[55–57] addition of a co-catalyst (*e.g.*, Fe, Sn or Al) might also have a favourable effect.[58–60] There seems to be room for significant improvement, particularly if basic research leads to a better understanding of the mechanisms of catalysis, which at present are poorly understood.

To conclude this section, it is worth mentioning that recent research trends on metal hydrides aim at combining the strategies already highlighted with size reduction of the solid particles to the nanometre scale. By doing so, two main advantages can be exploited. First, nano-sized particles show an enlarged solid/gas interface and, secondly, size reduction shortens hydrogen diffusion paths. For both of these reasons, kinetics should be improved. In addition, as pointed out by Kishore *et al.*,[61] nanoparticles (in presence of hydrogen) often exhibit dilated lattices and hence larger interstitial volume for hydrogen storage (and possibly, lower binding energy). In fact, palladium nanoparticles (in the 4–10 nm range) were found to store 10–20% more hydrogen than micron-sized Pd powders (at 50 °C and 10 bar).[61] And both, reduced particle size and crystallite size were found to improve hydrogen sorption kinetics in magnesium and Al-based hydrides.[19,38] For a detailed account on size effects on the hydrogen storage properties of nanostructured metal hydrides, the interested reader is referred to recent reviews by Bérubé *et al.*[33] and by Fichtner.[62]

4 Hydrogen storage by physisorption

Besides metal hydrides, highly porous solids that can retain hydrogen by physical adsorption (physisorption) are under active research as hydrogen storage materials. Zeolites and related microporous solids, polymers having intrinsic microporosity (PIMs), metal–organic frameworks (MOFs) and active carbons (including carbon nanostructures) are the main kinds of adsorbent currently being investigated. Since physisorption is a non-activated process, fast kinetics and reversibility can be expected (as a general rule) and these are the main favourable characteristics of physical adsorbents. The major drawback is that physisorption is brought about by (weak) van der Waals forces comprising dispersion (London), orientation (Keesom) and induction (Debye) energy. In the absence of relatively strong polarizing centres, interaction between the adsorbent and the non-polar hydrogen molecules relies on dispersion forces, which are weak; typically of the order of 3–6 kJ mol^{-1}. Hence, significant hydrogen adsorption often takes place only at a cryogenic temperature.[63–66]

Thermodynamic constraints for hydrogen storage by physisorption were analysed recently by Bhatia and Myers[67] with a focus on porous carbons. Assuming Langmuir-type adsorption and following standard thermodynamics, they derived eqn. (7) below:

$$\Delta H^0_{opt} = T\Delta S^0 + [(RT/2) \ln(P_1P_2/P_0^2)] \quad (7)$$

which gives the optimum value of adsorption enthalpy (ΔH^0_{opt}) for maximum hydrogen delivery as a function of temperature (T) and adsorption entropy (ΔS^0), P_0 being the standard pressure value to which ΔS^0 is referred (1 bar), P_1 the hydrogen loading pressure and P_2 the exhaust delivery pressure. In other words, eqn. (7) applies to hydrogen storage-delivery cycles between pressure P_1 and P_2 at a temperature T. Alternatively, the optimum operational temperature (as a function of standard adsorption enthalpy and entropy) is given by:

$$T_{opt} = \Delta H^0/[\Delta S^0 + (R/2) \ln(P_1P_2/P_0^2)] \quad (8)$$

Note that consideration of a storage-delivery cycle, instead of storage capacity only, is of the utmost importance. Too high an adsorption enthalpy would impair performance, because a large amount of hydrogen would be retained by the adsorbent at the exhaustion pressure. But, on the other hand, little hydrogen could be stored if ΔH^0 is too low.

Assuming P_1 = 30 bar and P_2 = 1.5 bar as being reasonable pressure values for the hydrogen storage-delivery cycle, and taking $\Delta S^0 = -66.5$ J mol^{-1} K^{-1} as being a representative value of entropy change,[67] eqn. (7) yields $\Delta H^0_{opt} = -15.1$ kJ mol^{-1} at 298 K. (Note, however, that smaller values of ΔS^0 were also quoted in the literature).[68] On the other hand, for an enthalpy change of $\Delta H^0 = -5.8$ kJ mol^{-1}, typical of hydrogen adsorption on carbons, eqn. (8) yields T_{opt} = 114.4 K. These results led Bhatia and Myers[67] to conclude that pure carbons are not prospective materials for hydrogen storage at ambient temperature; a conclusion that is also supported by other authors.[69–71]

The above analysis, focused on carbons, should also be valid for other adsorbents showing mainly dispersion-type interaction with adsorbed hydrogen, which gives rise to unspecific (*i.e.* non-localized) adsorption. However, conclusions should not be uncritically extended to all hydrogen adsorbents. Recent studies on several cation-exchanged zeolites (used as model systems to investigate localized adsorption) by means of variable-temperature infrared spectroscopy,[72–74] have shown that ΔH^0 values of about −15 kJ mol^{-1} (or even larger) can be obtained for hydrogen adsorption.[75–78] However, referring to absolute values, increasing ΔH^0 was found to correlate (in general terms) with increasing ΔS^0, meaning that entropy change can no longer be taken as a constant. As an example, for hydrogen adsorption on the MFI-type zeolite Na-ZSM-5 the values of $\Delta H^0 = -10.3$ kJ mol^{-1} and $\Delta S^0 = -66$ J mol^{-1} K^{-1} (referred to a standard pressure of 1 bar) were experimentally found,[76,77] whereas for the faujasite-type zeolite (Mg,Na)-Y corresponding values were found to be -18 kJ mol^{-1} and -81 J mol^{-1} K^{-1}, respectively.[78] Note that if the latter values are inserted into eqn. (8), T_{opt} results to be 279 K (*i.e.* still below 298 K), despite ΔH^0 being larger than -15.1 kJ mol^{-1}.

A similar (positive) enthalpy-entropy correlation, also termed compensation effect,[79,80] was also reported for a wide range of chemical processes, including formation of weakly associated (van der Waals) molecular complexes,[79] hydrogen bonding,[81] and Langmuir-type adsorption from solution.[82] Briefly, for the case of hydrogen adsorption, enthalpy-entropy correlation can be explained by considering that interaction of hydrogen molecules with cationic adsorbing centres, which is driven mainly by polarization,[83–85] determines the enthalpic term; and a stronger (enthalpy related) interaction results in a larger decrease of motion freedom, and hence in (entropy related) increased order of the system. In more precise terms, localized adsorption results in loss of translational motion and in a reduction of rotational degrees of freedom of the adsorbed hydrogen molecule.[86,87] Simultaneously, intermolecular (IM) vibrational modes arise; note that the term *intermolecular* is used here to refer to vibration of the adsorbed molecule against the binding site. The stronger the interaction (and consequently larger enthalpy change) the higher will be the frequency of IM modes, and the smaller the entropy associated with them (*i.e.*, the larger will be the entropy change). This reasoning finds support in recent experimental work by Ramirez-Cuesta *et al.*[85] who investigated hydrogen adsorption on Na^+, Ca^{2+} and Zn^{2+} exchanged zeolite X (faujasite) by means of inelastic neutron scattering (INS). In the low energy region of the INS spectra (below 200 cm^{-1}) they observed the fundamental IM vibrational mode and the corresponding frequency was found to be directly proportional to the polarizing power of the cation ($Na^+ < Ca^{2+} < Zn^{2+}$) which is also the main factor determining the cation-hydrogen interaction energy. It should also be noted that while (in principle) no defined limit exists for the enthalpy change, ΔS^0 does have an intrinsic limit because the adsorbed hydrogen molecule cannot lose more than all of its degrees of freedom. Assuming a maximum entropy change of about -85 J mol^{-1} K^{-1} (-81 is the maximum value so far reported), eqn (7) would lead to a value of ΔH^0_{opt} of about -25 kJ mol^{-1} for optimum hydrogen storage-delivery cycles between a loading pressure of 30 bar and an exhaust pressure of 1.5 bar, at ambient temperature. Because of the price to be paid for the entropic term, ΔH^0_{opt} should (in any case) be expected to take a significantly larger value than for carbons (-15.1 kJ mol^{-1}).

4.1 Active carbons and carbon nanostructures

Both, natural and synthetic (amorphous) carbons can be activated following several different procedures to obtain microporous adsorbents showing very large specific surface area (typically in the 1000–3000 m^2 g^{-1} range) and considerable microporous volume. Reversible hydrogen uptake on these carbons was consistently reported to be approximately proportional to surface area and to micropore volume,[88–91] although the best linear correlation is usually obtained when relating hydrogen adsorption capacity to micropore volume,[89,92,93] reflecting the fact that physisorption (and consequent hydrogen storage) is dominated by pores having a diameter in the subnanometer range.[94,95] In fact, interaction energy between hydrogen molecules and carbon adsorbents should be enhanced in narrow pores, because of overlap of the potential fields from both sides of the pore. Note that the hydrogen molecule has a kinetic diameter of 2.9 Å.

Based on extrapolation of some available data relating hydrogen uptake to surface area, Ströbel *et al.*[96] suggested that a gravimetric density of 6 wt% would be attained at a specific surface greater than 4000 m^2 g^{-1}; which does not seem to be yet available. Jordá-Beneyto *et al.*[92] have recently reported on a carbon sample, obtained by chemical activation of anthracite with KOH, which had a surface area of 3183 m^2 g^{-1} and showed a hydrogen uptake of 3.2 wt% at ambient temperature and 200 bar. However, at a pressure of the order of 30 bar or smaller, a gravimetric capacity (for activated carbons) of about of 3–4 wt% seems to be attainable (so far) only at liquid nitrogen temperature.[93,97,98]

Hydrogen storage in carbon nanotubes has also been intensively investigated. However, despite initial expectations, recent reports do not confirm any substantial advantage of carbon nanotubes over activated carbons. Maximum hydrogen uptake appears to be of the order of 4 wt% at 77 K, and less than 1 wt% at ambient temperature.[63,97–100] Similarly, no significant improvement over activated microporous carbons has yet been reported for carbon nanofibres.[101–103] For a comprehensive account on hydrogen storage by carbon materials, including activated carbon, graphene and carbon nanostructures, the interested reader is referred to the recent review article by Ströbel *et al.*;[96] also of interest is the article by Kowalczyk *et al.*,[69] who explored the potential of novel carbon nanostructures by means of grand canonical Monte Carlo simulation.

Finally, it should be noted that ordered porous carbons (carbon replicas) can be obtained by using a zeolite, or other suitable porous solid as a template.[104–112] On account of their large surface area and regular pore size these templated porous carbons might show advantages that, till a large extent, are yet to be explored. It is encouraging that a recent report by Yang *et al.*[113] describes an ordered porous carbon, prepared by using zeolite beta as template, which showed a surface area of 3200 m^2 g^{-1} and a reversible hydrogen storage capacity of 6.9 wt% at liquid nitrogen temperature and 20 bar; the corresponding isosteric heat of adsorption was found to be 8.2 kJ mol^{-1}; rather high for a carbon. No data seem to be available, however, regarding hydrogen uptake at ambient temperature.

4.2. Metal–organic frameworks

Metal–organic (open) frameworks (MOFs) are crystalline solids consisting of multidentate organic ligands connecting metal ions or small metal-containing clusters. Similar to zeolites, most MOFs have a three-dimensional framework that encloses uniform pores which are inter-connected forming an ordered network of channels. They are synthesized by a self-assembly process in which different combinations of organic linkers and metal nodules lead to materials having a wide range of varying topologies and pore size.[114] After removal of retained (solvent) molecules, MOFs can show a very large surface area; values in the range of 1500–3000 $m^2 g^{-1}$ are quite common, but even values higher than 5000 $m^2 g^{-1}$ were reported for some MOFs.[115–117] It is relevant to point out that such very large, experimentally determined, BET surface areas were recently confirmed by Walton and Snurr by means of Grand canonical Monte Carlo simulations.[118] Pore volume usually ranges from 0.2 to 0.8 $cm^3 g^{-1}$, but values well over 1.1 $cm^3 g^{-1}$ were also reported for some MOFs.[116,117,119,120]

Outstanding surface area and pore volume confers considerable potential to MOFs as prospective materials for hydrogen storage. And, in contrast to activated carbons, metal-organic frameworks have well-defined crystal structures; which results in a system of pores of uniform size (about 0.5 to 2 nm in diameter) for each particular material. Moreover, the wide range of possible topologies and chemical composition holds the potential for rational design of chemical synthesis aimed at optimizing adsorption properties; strategies include interweaving of isoreticular networks and pillaring (*i.e.*, connecting two-dimensional layers with appropriate pillars).[120–125] For these reasons, it should be no surprise that research on MOFs is developing faster than for any other type of hydrogen storage material (Fig. 3).

As also found for carbons, maximum hydrogen uptake (at 77 K) in MOFs is approximately proportional to surface area and microporous volume,[65,117,119,126] and that explains why initial experimental work was aimed (mainly) at increasing these parameters. Indeed, several metal organic frameworks, including MOF-5,[117,127] MOF-177,[115,117] IRMOF-20,[117,128] MIL-101,[116,129] and $[Cu_2(L^2)(H_2O)_2]$[119] (L^2 = terphenyl-3,3″,5,5′-tetracarboxylate) were reported to show (reversible) hydrogen uptake in the range of 5.2 (MOF-5) to 7.5 (MOF-177) wt% at 77 K and moderate pressure; however, at 298 K maximum hydrogen uptake falls below 1.5 wt%; details are given in Table 3. For a compilation of data on more than 50 MOFs and reference to previous work, the interested reader is referred to the recent review by Collins and Zhou.[130] A very detailed update on MOF-177 was also recently published.[131]

Summarizing, although some MOFs do show encouraging hydrogen uptake values at 77 K, maximum uptake at ambient temperature is not yet good enough. In order to increase uptake at (or near) ambient temperature, two main points are worth considering. First, narrow pores (best in the subnanometre range) are likely to be more efficient than wide cavities; secondly, interaction energy between the porous solid and adsorbed hydrogen molecules should be increased. These two points are actually inter-connected, since the amount of hydrogen adsorbed is expected to correlate with interaction energy only for the first adsorbed monolayer(s). Reported values for adsorption enthalpy (or for isosteric heat of adsorption) of hydrogen on many MOFs are mostly in the range of 3.5 to 6.5 kJ mol^{-1} (*i.e.*, very similar to those found for carbons)[132–135] and, as expected, they tend to decrease with increasing hydrogen uptake. As already discussed, a value of ΔH^0 significantly larger than -15 kJ mol^{-1} is likely to be needed for operation near ambient temperature. Ways to increase interaction energy can, in principle, be focused on, (i) interaction of hydrogen with the organic ligands in MOFs, and (ii) interaction with metal centres. In order to increase rigidity of the framework, organic linkers usually contain aromatic backbones and it could be thought that substituents could enhance interaction energy. However, *ab initio* (MP2) calculations showed that interaction energy with the hydrogen molecule is only marginally enhanced by electron-donating substituents.[136] A more viable approach seems to be to focus on metal centres, particularly for MOFs having short linkers. Increasing the polarizing power of metal centres should significantly enhance interaction energy, as found for zeolites. This can be achieved by using more polarizing cations and also by increasing the degree of coordinative unsaturation.[137–140] Actually, by using this strategy Long and co-workers[138–140] have increased hydrogen adsorption heat up to 9.5–10.1 kJ mol^{-1} in some MOFs containing exposed Mg^{2+} or Mn^{2+} metal centres; which constitutes a significant step in the desired direction.

To conclude this section, it seems highly relevant to point out that (irreversible) hysteresis has been reported for hydrogen adsorption–desorption isotherms on some MOFs having flexible organic linkers. As described by Thomas and co-workers[141,142] this phenomenon could appear because of *kinetic trapping* of adsorbed hydrogen in cavities having pore openings slightly smaller than the kinetic diameter of the

Table 3 Relevant data for some selected MOFs

			H_2 uptake capacity (wt%)			
Material	Surface area/$m^2 g^{-1}$	Pore volume/$cm^3 g^{-1}$	77 K	298 K	ΔH^0/kJ mol^{-1}	Ref.
$Cu_2(L^2)(H_2O)_2$	2247	1.08	6.1 (20 bar)	—	—	119
HKUST-1	2175	0.75	3.6 (10 bar)	0.35 (65 bar)	6.8	130
IRMOF-11	2180	—	3.5 (34 bar)	—	—	117
IRMOF-20	4580	—	6.7 (70 bar)	—	—	117
MIL-100	2800	1.0	3.28 (26 bar)	0.15 (73 bar)	6.3	130
MIL-101	5500	1.9	6.1 (60 bar)	—	9.5	116
Mn(btt)	2100	0.80	6.9 (90 bar)	1.4 (90 bar)	10.1	130
MOF-5	4170	—	5.2 (48 bar)	0.45 (60 bar)	4.8	130
MOF-74	1132	0.39	2.3 (26 bar)	—	8.3	130
MOF-177	5640	—	7.5 (70 bar)	—	—	117
$Ni_3(bct)$	—	0.63	2.5 (15 bar)	0.15 (15 bar)	—	130
ZIF-8	1810	0.66	3.1 (55 bar)	—	—	130

hydrogen molecule. In such a case other factors, rather than thermodynamics alone, would control hydrogen uptake and release; and the situation would resemble that of clathrates (see section 5). Similar behaviour was also reported by Chen *et al.*[143] for a MOF having an interpenetrated dynamic framework. Because of kinetic control, hydrogen adsorption at a relatively high pressure and release at a lower pressure (and higher temperature) becomes possible, and this opens up new potential for hydrogen storage.[142,144]

4.3 Polymers with intrinsic microporosity

Organic polymers usually have enough conformational and rotational freedom to allow them to form densely packed (amorphous) solids. However, as shown by Budd *et al.*,[145,146] when at least one of the monomers contains a site of contortion (*e.g.*, a spiro-centre) or a rigid non-planar unit connected to a rigid backbone (*e.g.*, a ladder polymer) close packing is precluded, and polymers having intrinsic microporosity (PIMs) are obtained. These polymers can enclose interconnected cavities which provide large internal surface area; values in the range of 500 to 1000 $m^2\ g^{-1}$ were reported.[147] Another way to create porosity in an organic polymer is by cross-linking polymer gels. For this purpose, Svec and co-workers[148] described a two-step procedure that includes first the preparation of poly(vinylbenzyl chloride) precursor beads, followed by a second step in which these beads are swollen in dichloroethane and cross-linked by a Lewis-acid mediated Friedel–Crafts process. The final polymer is a cross-linked polystyrene that was termed a hyper-cross-linked polymer (HPC); porosity persists after solvent removal, and optimized polymers were reported to show a surface area of 829 $m^2\ g^{-1}$, as calculated from hydrogen adsorption.[148]

On account of their relatively large surface area and low density, PIMs were investigated as potential hydrogen storage materials; and the experimental work done in this field was recently reviewed in detail by Budd *et al.*[149] Regarding maximum capacity, the largest values so far reported correspond to a network-PIM (incorporating a triptycene subunit) that showed a maximum hydrogen uptake of 2.71 wt% at 77 K and 10 bar,[150] and to an HPC polymer capable of adsorbing 3.04 wt% hydrogen at 77 K and 15 bar[151] (2.75 wt% at 77 K and 10 bar). Presumably, by optimizing synthesis procedures (aiming at developing subnanometre porosity) a higher hydrogen uptake at 77 K can be reached, thus rendering PIMs and HPCs good candidates for reversible hydrogen storage under cryogenic conditions. However, since interaction between the polymer and adsorbed hydrogen involves only weak dispersion forces, adsorption enthalpy is bound to be low (in fact, values ranging from −4 to −6.6 kJ mol^{-1} were reported for some cross-linked polymers)[148,152] and hence maximum hydrogen uptake near ambient temperature is probably much lower than at 77 K; no actual values seem to have been reported. In this sense, PIMs stand on a similar ground as activated carbons; although the former might be more amenable to tailored design of pore size aimed at optimizing performance.

4.4 Zeolites and other hydrogen adsorbents

Because of the high density of the aluminosilicate framework, zeolites themselves are not likely candidates for on-board hydrogen storage. However, well known crystal structure and easy ion exchange make zeolites ideal materials for systematic studies of hydrogen binding to a large variety of metal cation centres, and those studies should give insight useful for work on other hydrogen adsorbents as well. From a large number of both theoretical[73,83,153] and experimental reports[75–78,154] on zeolites and related materials, the following main points emerge. (i) When dealing with alkali or alkaline-earth metal cations, interaction energy with hydrogen tends to increase when the polarizing power of the cation (*i.e.*, charge/radius ratio) increases. However, the actual structure of the cationic adsorbing centre has also to be considered; for instance, the zeolites Li-ZSM-5 and Li-FER showed smaller values of interaction energy than Na-ZSM-5 and Na-FER, respectively[73,76] (despite Li^+ being more polarizing than Na^+) because Li^+ is more tightly surrounded by oxygen atoms of the zeolite framework than Na^+. (ii) When the configuration of the adsorption site is adequate, each cation can adsorb two hydrogen molecules with (approximately) the same energy; an example is depicted in Fig. 5. (iii) For zeolites containing only alkali or alkaline-earth cations, the maximum hydrogen adsorption enthalpy so far reported was found for magnesium-exchanged faujasite Y:[78,155] $\Delta H^0 = -18$ kJ mol^{-1}. Despite this large value of ΔH^0, hydrogen adsorption was found to be fully reversible. (iv) Cu^+ exchanged zeolites show very high interaction energy with adsorbed hydrogen, as determined by both experimental and theoretical calculations; values in the range of −50 to −60 kJ mol^{-1} were reported.[83,156] However, such high values of interaction energy (which point to formation of chemically bonded dihydrogen complexes) are likely to be detrimental for reversible hydrogen uptake and release cycles at ambient temperature.

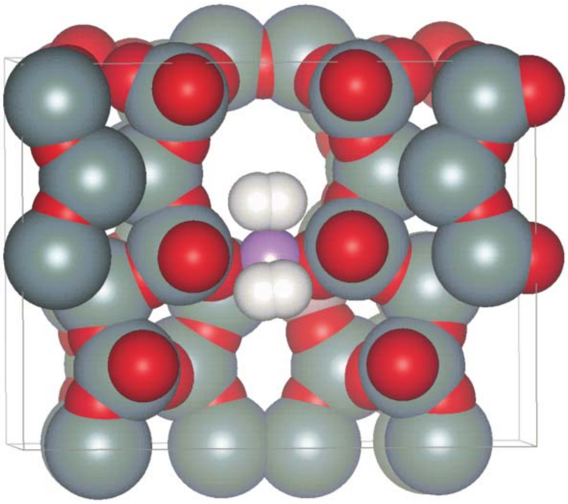

Fig. 5 Two hydrogen molecules (white) can be adsorbed on a single Li^+ ion (violet) in the zeolite Li-FER; silicon and oxygen atoms of the zeolite framework are depicted in grey and red, respectively. (Adapted from ref. 84).

Maximum hydrogen storage capacity of zeolites was calculated to be in the range of 2.6 to 2.9 wt%.[157] However, it should be noted that values of adsorption enthalpy quoted above correspond to monolayer coverage, *i.e.*, to the situation in which hydrogen molecules can interact directly with adsorbing centres, giving rise to localized adsorption. For higher loadings, the interaction energy is bound to fall down to a value of about -5 to -6 kJ mol^{-1}, corresponding to a weak (London-type) interaction. For these reasons, zeolites (while being useful models) are unlikely to be a material of choice for hydrogen storage in the transportation sector.

To conclude this section, it is worth pointing out that several other types of porous solids were investigated as potential candidates for hydrogen storage. Among them, materials having a sodalite-type framework and varying chemical composition,[158–160] and nickel-containing nanoporous frameworks.[161,162] While none of them meets yet the DOE targets, it is notable that a gravimetric hydrogen storage capacity of 4.15 wt%, at 77 K and 10 bar, was found for a 12-connected metal–organic framework having Ni^{2+} centres and pyridine-3,5-bis(phenyl-4-carboxylic acid) ligands;[161] and also that a nanoporous hybrid (inorganic–organic) material having the composition $NaNi_3(OH)(SIP)_2$ [SIP = 5-sulfoisophthalate] showed,[162] when dehydrated at a high temperature, coordinatively unsaturated Ni^{2+} centres adsorbing molecular hydrogen with a ΔH^0 in the range of -9.4 to -10.4 kJ mol^{-1}. As already discussed above, this relatively large adsorption enthalpy goes in the right direction towards increasing the temperature for useful hydrogen storage. The wide variety of porous solids being tested for hydrogen storage was recently further enriched by reports on nanotubes made of inorganic compounds having a varied chemical composition[163] (*e.g.*, BN, NiO and TiO_2). Some theoretical calculations[164] suggest that boron nitride nanotubes might perform better than carbon nanotubes. However, more experimental measurements seem to be needed in order to assess the potential of these nanostructured materials.

5 Clathrates: encapsulation

Besides chemical reaction and physisorption, a third way of storing hydrogen is also receiving current attention – namely, encapsulation of the gas inside a guest (solid) structure to form a clathrate; from which hydrogen can be released by a pressure and temperature swing. Since long ago, several natural gases (*e.g.* methane and carbon dioxide) are known to form water clathrates, also termed clathrate hydrates,[165] but it was only in 1999 when the first reports on hydrogen clathrate hydrates appeared,[166,167] prompting research on these and other hydrogen clathrates as potential materials for hydrogen storage.[168–170]

As shown in Fig. 6, hydrogen-bonded H_2O molecules can generate polyhedral cages around guest molecules to form solid clathrate hydrates having three (common) structure types:[165,171] sI, sII and sH. The structure-type sII (shown by hydrogen clathrate hydrates) consists of an ordered stacking of pentagonal dodecahedral (5^{12}) and larger hexakaidecahedral ($5^{12}6^4$) cages. When empty, these cages are unstable (collapsing into the conventional ice crystal structure) but they can be stabilised by the inclusion of gas molecules. Mao *et al.*[168] reported the preparation of a binary hydrogen-water clathrate, containing 5.3 wt% hydrogen, at 2 kbar and 250 K. Soon afterwards, Florusse *et al.*[172] proved that the hydrogen sII-type clathrate hydrate can be formed at 50 bar and 279 K when tetrahydrofuran (THF) is added as a second guest component to promote clathrate formation. However, most of the large ($5^{12}6^4$) cages of the binary clathrate hydrate are filled with THF, leaving only the small (5^{12}) cages available for hydrogen storage. There is some dispute about the maximum hydrogen uptake in the THF/H_2 binary hydrate at moderate pressure. While values ranging from 2 to 4 wt% H_2 (depending on THF concentration) were reported by some authors,[173,174] Strobel *et al.*[175] found the maximum hydrogen storage capacity of binary THF/H_2 hydrates to be approximately 1.0 wt%, at 13.8 kbar, independently of THF concentration (within the range of 0.5 to 5.56 mol%). It is relevant to add that: (i) other additives (such as 2,5-dihydrofuran and tetrahydropyran) were found to have a similar effect as THF on the formation of hydrogen hydrates, but none of them gave better results that THF;[176] and (ii) synthesis of the pure hydrogen clathrate hydrate was found to proceed much faster when using for that purpose crystalline ice instead of water,[177] presumably because of a larger surface area favouring hydrogen diffusion.

Recently, the possibility of using exclusively organic molecules (*e.g.*, hydroquinone,[178] crown ethers[179] and several calixarenes)[180] for hydrogen encapsulation is coming into active research. Interestingly, Thallapally *et al.*,[180] reported that crystals formed by *p*-*tert*-butylcalix[4]arene and

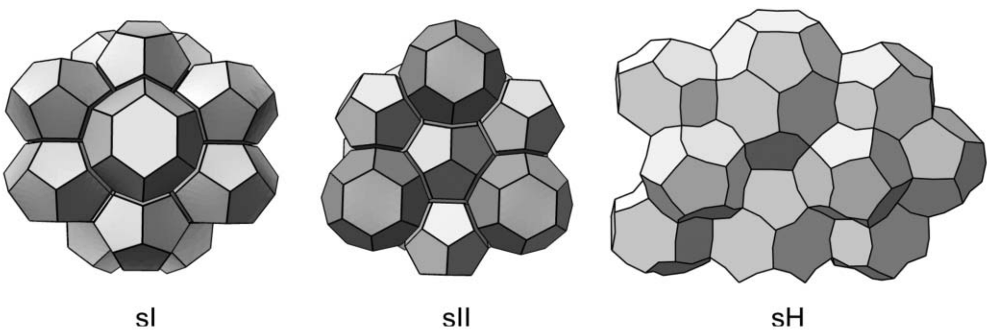

Fig. 6 Schematic representation of the sI, sII and sH water clathrates, in which the shape of the cages and the connectivity between them are visible. The three- and four-connected vertices are the O-atoms of the water molecules and the H-atoms lie in the middle between two such vertices.

by *p-tert*-pentylcalix[4]arene possess lattice voids of about 270 and 110 $Å^3$, respectively. The entrance to these cavities consists of small pores of about the same size as the kinetic diameter of the H_2 molecule. Although reported hydrogen uptake is smaller than that of many MOFs, the possibility of kinetic control (through narrow pores) opens up a field worth of further research.

Hydrogen encapsulation in zeolites containing sodalite-type cages was studied by means of both, experimental measurements[181–184] and theoretical calculations involving (mainly) molecular dynamics and grand canonical Monte Carlo simulations.[184–187] The sodalite cage is a polyhedron formed by six 4-member rings and eight 6-member rings (*i.e.*, 4 and 6 corner-sharing SiO_4 tetrahedra, respectively).[188] The opening to the cage (through a non-deformed 6-member ring) is about 2.6 Å in diameter; *i.e.*, slightly smaller than the kinetic diameter (2.9 Å) of H_2. The hydrogen molecule can be forced into the cage at a high temperature and pressure; it becomes trapped upon cooling to room temperature, and can then be released by raising the temperature.[189] Detailed calculations showed that the activation energy involved in hydrogen diffusion critically depends on flexibility of the zeolite framework,[186] which also affects (till some extent) maximum hydrogen uptake. The insight gained from these studies (and the methodology developed) should help to advance rational design of other materials for hydrogen storage by encapsulation. In particular, it should be acknowledged that porous solids lighter than zeolites and having framework flexibility hold a potential that merits closer examination.

6 Summary and outlook

This concise review on the state of the art in the field of hydrogen storage materials (including metal hydrides, porous adsorbents and hydrogen clathrates) necessarily leads to two main conclusions. First, it should be recognized that, despite the vast effort being put in the endeavour worldwide, we are still short of making Jules Verne's visionary dream come true. No material so far tested meets yet the ideal requirements for on-board hydrogen storage; although some of them could be useful for less demanding (stationary) usage. Secondly, the foregoing statement notwithstanding, it should also be acknowledged that there seems to be ample room for improvement, building up on already gained basic knowledge and practical experience. While this applies in general terms to the three kinds of materials quoted above, each class shows its own perspective for improving performance.

For hydrogen clathrates, main objectives are to increase hydrogen uptake and to stabilize the clathrate at near ambient temperature and pressure. To this end, the quest should be aimed at, (i) finding more efficient promoters for stabilizing already known (*e.g.* water) clathrates, and (ii) searching for new hydrogen-clathrate forming molecules. Computer simulation aided by appropriate calculation tools (*e.g.*, molecular dynamics and Monte Carlo methods) should help to screen prospective compounds.

Regarding porous adsorbents, attention should be focused on improving thermodynamics (*i.e.*, increasing the absolute value of adsorption enthalpy) rather than on merely increasing pore volume. Larger pores would certainly increase hydrogen uptake, but what really counts is *excess capacity*, meaning how much hydrogen can be stored in that pore volume that would not be stored, at the same temperature and pressure, in the same volume of a standard container (a gas cylinder). Excess capacity means tighter packing of hydrogen molecules and that implies increased interaction energy. For that purpose, what would work best is a large void volume made up of narrow pores. Ideally, all adsorbed hydrogen molecules should interact directly with adsorbing centres located in the pore walls (*i.e.*, monolayer adsorption) and that implies an optimum pore diameter of just slightly over twice the kinetic diameter of the hydrogen molecule (*i.e.*, a pore diameter of about 6–7 Å). Further improvement should come from a large concentration of relatively strong hydrogen adsorbing centres; unsaturated metal binding sites, preferably formed by light metals (*e.g.*, lithium or magnesium) could constitute such adsorbing centres. MOFs and other porous coordination polymers having light frameworks can hopefully be engineered to meet such requirements.[142,190,191] New developments in this field can also be expected from exploitation of framework flexibility arising from either rotation around single bonds or from slipping motion of interpenetrated framework layers. Note that both, increased interaction energy and kinetic trapping of hydrogen molecules could help to bring useful hydrogen adsorption and desorption closer to ambient temperature.

Concerning metal hydrides, there seems to be room for performance improvement by acting on both, thermodynamics and kinetics. Purposeful screening of more (prospective) destabilizing reactions, as already done for many systems,[39] would be a very valuable help to the experimentalist in the quest for less stable metal hydrides. On the side of kinetics, we still need improved knowledge about the basic mechanisms of catalyst action; understanding heterogeneous catalysis in complex systems is not an easy task, but it could yield ground-breaking advancement. On the other hand, size reduction to the nanometre scale (in order to shorten hydrogen diffusion paths) constitutes a relatively new development which should lead to finding metal hydrides having substantially improved kinetics of hydrogen uptake and release.

Valuable as the above considerations can be, we acknowledge that several other approaches to improve performance of hydrogen storage materials could well be already nestling in the minds of many colleagues working in this field. We are eager to see fruitful developments coming out soon.

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