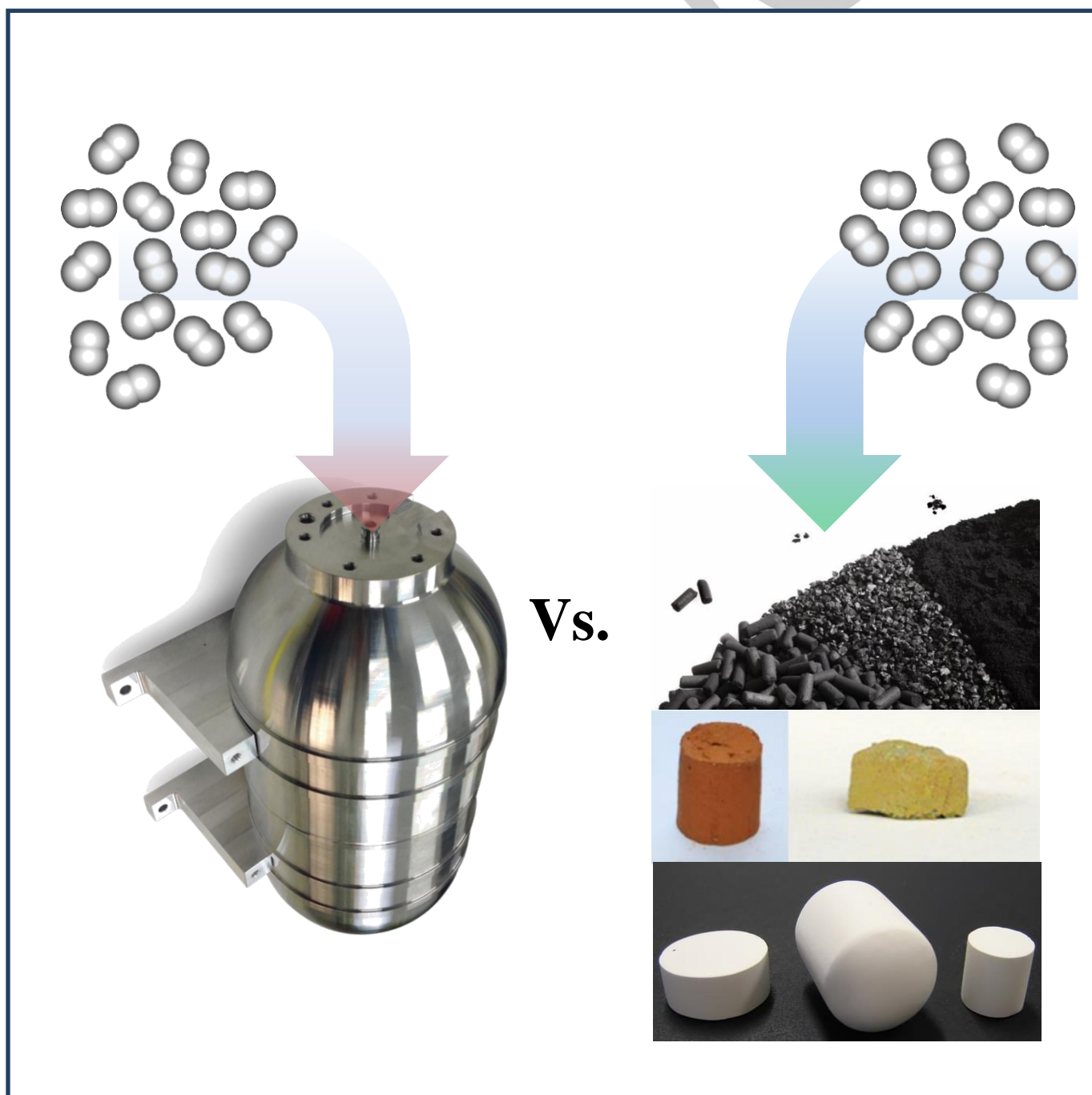


Hydrogen Storage in Porous Materials: Status, Milestones, and Challenges

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Dedication **Dedicated to Prof. Eduardo Ruiz-Hitzky**



Abstract: In this account the most relevant advancements in hydrogen storage in porous materials are presented. These include the current state-of-the-art, the challenges which have been overcome, and the hurdles which still remain. The most important milestones which will be discussed in this work will be the development of new apparatuses capable of delivering reliable results under a broad range of operational conditions, in which analysis temperature and pressure are critical parameters. Other aspects such as the materials storage capacity in gravimetric and volumetric terms will be critically discussed to identify the conditions required from an ideal material. Finally, different upgrade possibilities from modifying the adsorbate-adsorbent interaction to using rigid or flexible materials will be presented and put into perspective with current literature.

1. Introduction

Among the commodities which became essential during the 20th century and will most likely dominate the 21st are information^[1] and energy^[2]. Focusing on the latter and due to stricter environmental regulations, there is an increasingly strong drive towards the implementation and use of clean, efficient fuels. From this perspective, Hydrogen stands out as a promising energy vector because apart from its aforementioned virtues it is abundant, well distributed worldwide, and presents a flexible and efficient energy conversion. As a result, it is a firm candidate as fuel in mobile applications (e.g. cars, buses...) for devices powered by conventional (i.e. internal combustion engines) and/or fuel cells, which results in a much more efficient conversion (60% versus 20% for combustion engines). Furthermore, fuel cells imbue these devices with added benefits like portability which would in turn allow their applications in portable electronics or even to produce heat and electricity for stationary applications in domestic, industrial and energy sectors. Despite these characteristics, Hydrogen is far from an ideal energy source. That is mainly due to its inherent issues in production and storage. On the former, unlike coal or natural gas Hydrogen is not a primary source. In the atmosphere, it is combined to a large degree (forming mostly water leaving less than 2% of hydrogen as molecular hydrogen). As a result, in order to meet current and future demands, Hydrogen has to be produced. The good news is, Hydrogen can be obtained through several different routes, using a wide range of technologies including primary energy sources, such as fossil fuels, nuclear

power and renewable energy^[3]. From this perspective, Hydrogen is close to being an ideal fuel and energy carrier since (i) it can be generated from several different feedstocks and (ii) it can be converted into energy without releasing harmful emissions at the point of use, thus reducing the emissions of greenhouse gases and other pollutants thus decreasing the dependence on fossil fuels^[4].

The other (major) drawback comes with storage. This is especially relevant considering the case of mobile and portable applications where storage is one of the main problems for use in such applications as fuel^[2-6]. Hydrogen has a chemical energy per mass (on a gravimetric basis) of 120 MJ/kg (33.3 kWh/kg), which is approximately three times greater than that of gasoline (44.4 MJ/kg or 12.4 kWh/kg). However, the energy density of hydrogen (on a volumetric basis) is very low compared to gasoline or other hydrocarbons. Thus, two examples are: i) at room temperature and at atmospheric pressure, 1 kg of hydrogen occupies 11250 L and ii) gasoline has a volumetric energy of 31.7 MJ/L (8.8 kWh/L) which is approximately six times more energy than hydrogen compressed at 70 MPa (4.7 MJ/L, 1.3 kWh/L). Therefore, great efforts have been carried out in order to increase the volumetric energy of hydrogen.

When it comes down to its use as an energy source, Hydrogen must be competitive with already available fuels (namely gasoline), and thus storage techniques must meet the appropriate standards. These were initially set by the U.S. Department of Energy (DOE, USA)^[7,8] and while they were revised recently^[9], the target figures for implementation remained unchanged. While more detailed information on the requirements might be found in Refs. [2, 7-9] and references therein, there are two figures that demand mention: (i) For a Hydrogen-powered vehicle to be competitive, it must possess a range of 500 miles (804.7 km) and (ii) in order to reach that figure, the "Ultimate Full Fleet" (i.e. meant to capture virtually all light-duty vehicle platforms) target is set at 7.5 wt%. H₂ in terms of gravimetric capacity (target was 5.5 wt% H₂ for 2015) and 0.07 kg H₂/L (2015 target = 0.04 kg H₂/L). While we have already reported H₂ storage values on gravimetric basis that meet this criterion^[2], it must be noted that the figures values refer to the complete storage system, including material, tank, and auxiliary systems (pipes, valves, gauges, flanges, etc.). Therefore, our figures, which were calculated purely on a materials basis (as all reports found in the literature) should be significantly higher. In addition, other requirements to be met by storage system have been established: loading/unloading should be reversible below 85°C, consume <10% in the process of unloading and the loading must be rapid (<3.3 min according to the 2017 target).

In a nutshell, while all the Hydrogen storage technologies revolve around increasing the fuel energy density they follow four different avenues to reach their goal, namely (i) H₂ compression, (ii) H₂ liquefaction, (iii) chemical storage (i.e. formation of metal hydrides or other hydrogen containing compounds), and (iv) physical adsorption (i.e. adsorption on different types of porous materials). The first one involves the use of very high pressures (up to 70 MPa) which delivers a hydrogen density just under the 2015 DOE target (0.039 kg/L),

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but falls short of the mark if the “Ultimate Full Fleet” target is sought. Furthermore, the design on materials that can withstand such pressures further adds to the challenge. Storing Hydrogen as a liquid requires reaching very low temperatures (under 20 K) and thus is an extremely energy-demanding process. Formation of metal hydrides is an interesting means towards achieving high Hydrogen capacities by chemical storage, but since the process is based on an exothermal formation process, heat exchange issues arise. Besides, release of Hydrogen for its use as fuel requires heating of the storage tank. Under this perspective, adsorption on porous materials is an alternative to solve these problems. Research on hydrogen storage in porous materials has grown significantly over the last two decades. Thus, in this Personal Account, we will review the state of the art in the field of hydrogen storage by adsorption in porous solids, focusing in the use of different porous solids concerning their chemical composition, porous texture, pore network. Special attention will be paid to recent developments on new materials which have shown promise in this application of great current environmental relevance.

2. Gas Adsorption at High Pressures: Fundamentals and Experimental Considerations

While not as demanding in terms of pressure or energy, adsorption of Hydrogen on a porous matrix still requires the application of pressures (around 4 MPa) and the use of cryogenic temperatures (77 K) to reach acceptable levels of energy density. Given the critical point of Hydrogen (33.1 K and 1.28 MPa), the aforementioned working conditions lie in the supercritical regime. Thus special attention must be paid in this regard.

It is well-known that the isotherm obtained experimentally in conventional gravimetric or volumetric systems is the Gibbs isotherm or excess adsorption isotherm. In other words, the amount of adsorbed gas determined is that whose density is higher than the density of the gas at the same pressure and temperature. Figure 1 shows a schematic representation of the Gibbs adsorption where the relation between excess adsorption and absolute adsorbed amounts are shown.

The relationship between the excess, n_e (region I in Fig. 1), and the absolute adsorbed amount, n_a (sum of region I + II), is given by the following equation:

$$n_e = n_a - \rho_{gas} \cdot V_{ad} \quad (1)$$

where ρ_{gas} is the gas density and V_{ad} is the volume of the adsorbed phase. Both n_e and ρ_{gas} are experimentally measurable parameters, but the other parameters must be obtained indirectly.

Under subcritical conditions (which are the standard for most routine adsorption experiments such as for example N_2 at 77 K or CO_2 at 273 K), it is generally accepted that the density of the adsorbed phase, ρ_{ad} is equal to the density (solid or liquid) of the adsorbate^[10]. Under these conditions, the absolute adsorbed amount can be obtained using the following equation:

$$n_a = \frac{n_e}{1 - \frac{M \cdot P}{Z \cdot R \cdot T \cdot \rho_{ad}}} \quad (2)$$

where M is the molecular weight, Z is the compressibility factor, R is the gas constant, P is the pressure and T is the temperature. Now, under supercritical conditions (vide supra), the problem lies in establishing ρ_{ad} since it is not equal to the liquid or solid adsorbate density because it cannot condense under these conditions. There are essentially two different theoretical approaches to obtain the absolute adsorption isotherm^[11]: those which assume that the density of the adsorbed phase is constant and, therefore, use the previous equation and those which consider that the volume of the adsorbed phase is constant and thus use equation (1).

In any case, to obtain the total amount of gas stored in a tank filled with an adsorbent, it is not mandatory to calculate the absolute isotherm. A simple method to obtain the total storage capacities using only measurable parameters will be discussed in a forthcoming section. For the moment, we shall focus on the direct measurement of excess isotherms by different methodologies, being gravimetric and volumetric methods those most widely used.

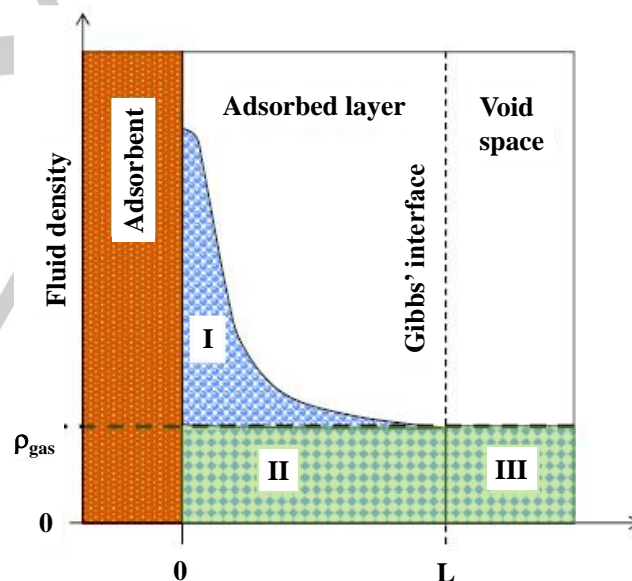


Figure 1. Schematic representation correlating excess adsorption (Region I) and absolute adsorbed amount. Regions II and III represent the fluid with a density given by the conditions (P and T) inside and outside of the adsorption volume, respectively. Absolute adsorption is given by the sum of regions I and II. L is the thickness of the adsorbed phase.

In the gravimetric method, a previously outgassed sample is introduced into a suitable sample holder (i.e. it must not react in any way with the adsorbent under the adsorption conditions). The holder is situated inside an isolated chamber, in which temperature remains constant and which can be submitted to

the pressures at which the analysis will be carried out. The chamber is pressurized with the gas (i.e. hydrogen) and the amount adsorbed is measured by reading the change of weight of the sample when thermodynamic equilibrium of adsorption is reached (the weight of the sample does not change anymore). The advantage of this method is that the weight change can be directly related to the amount of hydrogen that is adsorbed. The main error source is the buoyancy (which can be determined in different ways^[12]) that the gas has on the volume occupied by all mechanical parts connected to the balance, including the sample itself as well as the adsorbed phase. Once the correction is made due to the balance components, sample volume and sample holder, the excess or Gibbs isotherm is obtained. In the gravimetric method, taking into account that Hydrogen is the lightest of all gases, using high purity gases is critical to avoid severe experimental errors.

The volumetric (or Sieverts) method is the most widespread methodology to obtain adsorption isotherms. In this case, the adsorbed gas is quantified indirectly by measuring the pressure variation inside a given (cell) volume and using an appropriate gas equation of state (EOS). A typical device consists of two parts: the sample cell and the manifold (from which the gas expands into the cell). Both sample cell and manifold volumes must be known and the temperature of the system must be measured with sufficient accuracy and precision to warrant reliable results.

There are two main error sources to account for: the volume of the manifold and the presence of leaks. Concerning the former, since all calculations refer to this volume, it is essential to calibrate it with high accuracy. On the latter, a very small leak can be interpreted as gas adsorption if the equilibrium time is larger than the rate of gas release due to the leak. Given the small size and high diffusivity of Hydrogen, this source of error is also of high relevance.

There is a common source of error shared by both methods which is incorrect data analysis. For example, in the volumetric system, the use of a suitable EOS is essential to obtain reliable data (the higher the pressure, the greater the importance of the EOS selection). As shown in Fig. 2, important differences exist in the same experimental adsorption data depending on the EOS used, being the Lee-Kesler and mBWR equations the recommended by NIST^[2]. In any high pressure adsorption study, it is very important to mention the EOS used when reporting hydrogen storage data. This will avoid reporting unrealistic values of hydrogen storage since the data may experience a variation that may be fourfold, which is of course critical given the end-user application intended for the resulting devices.

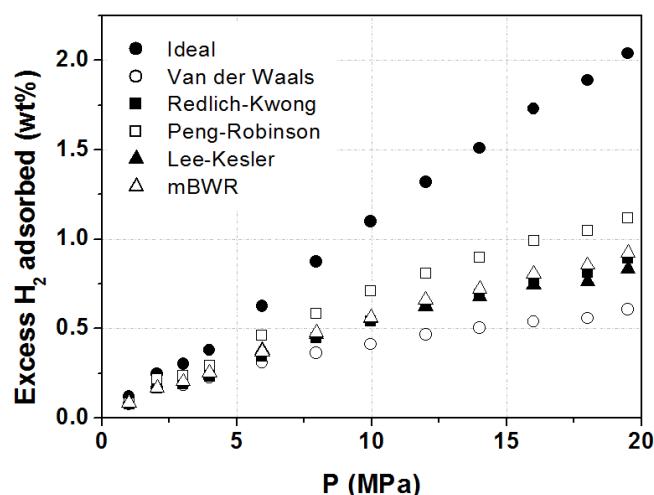


Figure 2. Excess hydrogen adsorption isotherms at 298 K and up to 20 MPa (200 bar) for an activated carbon obtained using different EOS indicated in the figure legend.

Last, but definitely not least, another key parameter must be mentioned that enables a correct interpretation of the adsorption data as well as correctly determining the volumetric adsorption capacity and total amount of stored Hydrogen, which is the density of the material used. A thorough description of the different definitions of density used in the literature is detailed in ^[2], but in brief these densities are (in growing order):

- Bulk density and tap density
- Packing density
- Crystal density
- True (skeletal or Helium) density

As it will be shown below, the density used will have a great influence in the calculation of the amount of adsorbed hydrogen in volumetric basis and, hence, in the resulting total hydrogen storage capacity.

3. Hydrogen storage in porous materials: State of the art

Carbon materials raised great expectations following on the reports of Dillon et al.^[13] who predicted gravimetric adsorption values for Single-Wall Carbon Nanotubes (SWCNTs) between 5 and 10 wt% in samples containing very low amounts of this carbon nanomaterial. The anticipation surged even further when Chambers et al.^[14] reported hydrogen adsorption capacities at 11.2 MPa on different Carbon Nanofibers (CNFs) which surpassed the energy density of liquid gasoline. These findings spurred the initial efforts on H₂ storage in carbon nanomaterials, including CNTs, CNFs, carbide-derived carbons, templated carbons, etc. As minutely reviewed by Cazorla-Amorós et al.^[2], the results on the adsorption capacities of different carbon-based materials, from classical activated carbons to nanostructured carbons, can be plotted in terms of their hydrogen adsorption capacity versus their textural properties

giving good correlations, provided that the effect of impurities from either the sample or the gas used are discarded and a reliable equipment is used. In this respect, a good correlation may be found between BET surface area or narrow microporosity volume and hydrogen uptake at 77K and up to 30 bar or 298K up to 200 bar, respectively. Nevertheless, when it comes to the “record” values reported in the literature, the influence of the aforementioned experimental (including material and gas purities) and analytical results has produced a large scattering of the values, which makes these advanced carbon materials significantly less reproducible than the so-called “classical” carbon materials such as activated carbons (ACs) or activated carbon fibers (ACFs).

While carbon materials spearheaded the research on hydrogen storage in its early stages, other materials have also attracted significant attention, such as zeolites^[18], MOFs (metal organic frameworks)^[19], PCPs (porous coordination polymers), or COFs (covalent organic frameworks)^[20]. Given the highly promising results obtained for these two latter kinds of materials (see for example ^[21]), research on gas storage has focused on them to a very significant degree. This can be clearly seen by plotting the number of published items on hydrogen storage per material as Figure 3 shows. It must be mentioned that the large entry for “graphene” (which the reader may consider surprising since this material is not intrinsically porous, let alone microporous) is because under this term you may find works related to graphite oxide, graphene oxide, or more generally „graphene-like materials“, and thus the term labelled as “graphene” can be misleading, hence the clarification. Furthermore, it should also be noted that in a significant portion of these works graphene (or graphene-like materials) is used as part of a composite or as support. If we combine all the entries related to carbon-based materials their number is higher than that of MOFs. Nevertheless, it is undeniable that these materials have shown great promise in gas storage applications. It must be noted, however, that this consideration is true for storage on gravimetric basis, but as we will show in a later section, the picture changes dramatically when storage is considered on a volumetric basis.

While they are not the object of the current work, mention must also be made to other Hydrogen storage materials in which storage takes place by absorption (as it is the case of certain alloys made of light elements) or chemically (as in ammonia borane or formic acid). The reader is referred to a recent review on such materials for further reading^[22].

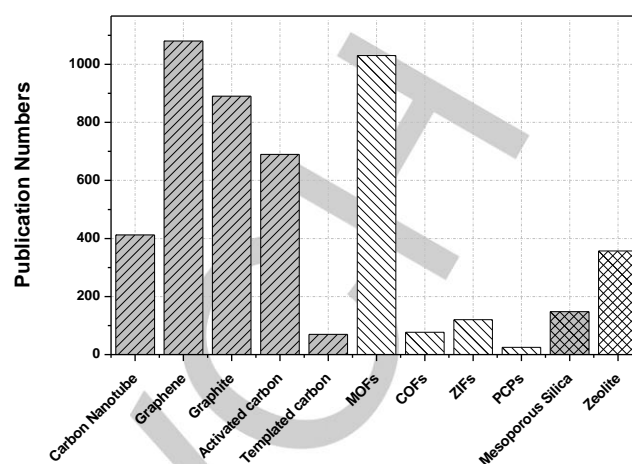


Figure 3. Publications under topics “hydrogen storage” and “various adsorbent names” from 1997 to May 2017 (source: ISI Web of Knowledge).

In this personal account, we will focus on the results obtained in our previous works, which have dealt with a wide range of porous materials comprising different chemical composition, structural characteristics and porous texture, as will be detailed below. This analysis will be extended to other (novel) materials. Thus, in the following sections, the hydrogen adsorption values found in the literature for those materials at different temperatures and pressures conditions will be compared with our results.

3.1. Hydrogen adsorption at 298K.

Under “high” temperature conditions (at least as compared to cryogenic Hydrogen storage), a wide range of pressure has been analyzed for energy storage. In this sense, the pressure range from 5 to 50 MPa at 298K has been the dominant trend to analyze the behavior of many different materials. Focusing first on (nano)porous carbon materials, which have hitherto been the main source of our expertise, some valuable general considerations may be drawn^[2]. At room temperature, a good correlation can be established between the amount of hydrogen adsorbed (in wt%) and the total micropore volume obtained from the Nitrogen adsorption isotherm performed at 77K, being the best for the amount of hydrogen adsorbed at 50 MPa. What should be remarked is that this stands for materials as diverse as “classical” activated carbons, ACFs, nanotubes, nanofibers, KOH-activated nanotubes, activated amorphous CNFs, and zeolite templated carbons which serves to establish the general validity of the statement. However, as the adsorption pressure decreases (e.g. below 20 MPa), significant deviations to this general trend exist. The samples with the largest porosity development do not present the highest Hydrogen uptake. In this lower pressure range the highest Hydrogen adsorption capacity corresponds to samples with lower micropore volume but with narrower micropore size, which are those quantified by CO₂ adsorption at 273K. As an example Fig. 4 shows the correlation between the amount of adsorbed Hydrogen at room temperature and 20 MPa and the narrow micropore volume for a

series of carbon-based samples both in powder and monolith form. The adsorption of CO₂ has long been established as an excellent tool to characterize porous materials with narrow microporosity (pore size below about 0.7 nm), not only carbon materials^[23], but also zeolites^[24] and ordered mesoporous materials^[25]. In any case, taking in the results reported as a whole highlight the importance of balancing high micropore volumes together with narrow microporosity for pressures below 20 MPa at room temperature. The specific weight of the contribution of the micropore size distribution (MPSD) becomes more relevant as the storage pressure is decreased, as we have observed in previous reports^[2].

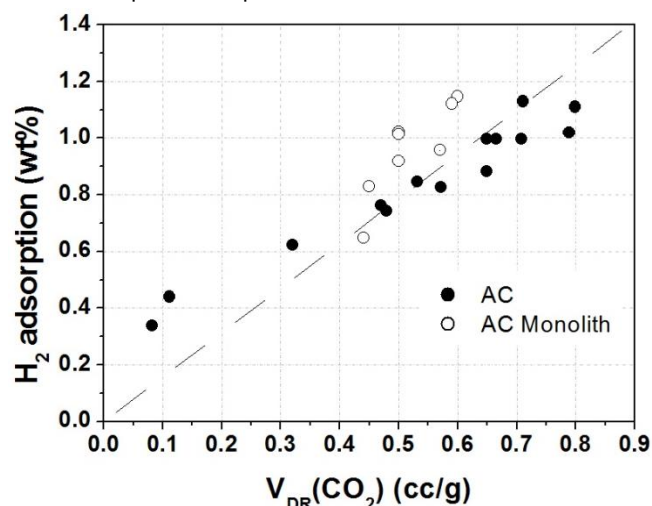


Figure 4. Amount of hydrogen adsorbed at 298 K at 20 MPa in a wide range of carbon-based materials versus their narrow micropore volume.

Our expertise in this field started with the analysis of different carbon materials which ranged from “classical” ACs to nanostructured carbon materials. These materials included KOH-activated carbons, commercial ACs (Maxsorb-A and AX21), ACFs, carbon nanotubes, carbon nanofibers, KOH-activated nanotubes, and activated amorphous CNFs and they were later expanded to MOFs^[26-32]. More recently, we have considered the possibilities of either improving Hydrogen storage in carbon materials from a different perspective, or by selecting new materials altogether, some of which are not related to carbon. In order to complete this subsection, we shall comment each case separately.

While the first logical approach to increase the Hydrogen uptake in a porous sample would be to increase, as already mentioned, the micropore volume with a suitable MPSD, there is a lot of ground for improvement in different directions. For example modifying carbon materials to give rise to pillared graphene layers, in which the strength of adsorption of the hydrogen molecules could be increased, is one interesting option. The isosteric heat of adsorption of hydrogen is usually around 5 kJ/mol which means that the interaction is weak and explains the need of using low temperatures and high pressures to get adequate hydrogen storage values. Using graphite oxide silylated with methyltrichlorosilane, we obtained samples which despite having a comparatively low narrow micropore volume

(around 0.2 cm³/g measured by CO₂ adsorption at 273K) adsorbed 0.6 wt% of Hydrogen at room temperature and 20 MPa, which is almost 50% above the expected value^[33]. The heat of adsorption measured was around 10 kJ/mol for hydrogen adsorption in these materials and it was attributed to the small pore size in which the strength of the interaction is higher compared to wider pores.

Our results using other types of hybrid materials also showed interesting results. In this respect, we also analyzed the adsorption capacity of different graphene-clay materials in which two different natural silicates such as montmorillonite and sepiolite, were impregnated with commercial caramel and heat treated under different conditions to give rise to graphene-clay hybrids.^[34,35] At room temperature, the materials showed promising Hydrogen storage values not in terms of exceedingly high values, but in terms of showing strong stabilization of the H₂ molecule upon adsorption, which was attributed to a beneficial effect arising from the presence of a functionalized fibrous silicate (i.e. sepiolite). This might be ascribed to the fact that since fibrous materials show a high aspect (surface-to-volume) ratio, this results in a large external surface area thus facilitating surface diffusion of any adsorbed (in this case Hydrogen) species. These materials were especially interesting since its preparation using commercial caramel and silicates (which can be purchased at affordable prices) resulted in environmentally friendly and cost-effective synthesis.

Moving into non-carbon related samples but still delving on hybrid materials, we analyzed the adsorption capacity of layered titanosilicates synthesized on commercial glass fibers with a high aspect ratio at different temperatures.^[36] The prepared materials proved to be robust and upon incorporating very small amounts of Pd (<0.1 wt%), it was possible to obtain promising H₂ adsorption capacities. Another layered material that we tested recently was based on different stannosilicate samples that showed very promising results in terms of Hydrogen adsorption at 298K^[37]. The best results were obtained for a delaminated stannosilicate which presented a H₂ uptake equivalent to materials possessing 10 times its specific surface area, which denoted a very significant adsorption enhancement in this layered material. This points out not only the relevance of the porous texture, as detailed above, but also the morphology and chemical composition of the solid, which have a strong influence in the adsorption strength. This was also observed for zeolite imidazolate framework (ZIF) samples in which the final morphology, was strongly influenced by the preparation method.^[38] In this particular paper, the preparation of ZIF-11 with very small crystal size resulted in an impoverishment in their adsorption performance.

Since, in general, the interaction between the hydrogen molecules and the adsorbent is weak, in order to increase the amount of Hydrogen stored in a given porous sorbent, the most widely studied alternative is to decrease the adsorption temperature. This means the use of cryogenic conditions, which is discussed in the next section.

3.1. Hydrogen adsorption at 77K.

One of the advantages of working under cryogenic conditions is that significantly lower adsorption pressures are required and higher Hydrogen loadings are reached. Thus, pressures ranging from 0.1 to 6 MPa have been reported in the literature when using 77K, reaching adsorption values which have gone over the 8 wt% barrier on a materials basis. The most widespread results are those obtained up to 0.1 MPa due to the relatively easy access to the required instrumentation. As described in the previous section, the good correlation between the Hydrogen uptake and the micropore volume still applies at 77K. In our previous review^[2], we already mentioned that, at low pressure (0.1 MPa), the contribution of the narrow microporosity becomes more relevant (i.e. pores with size below 0.7 nm) and the correlation is better when the amount of H₂ adsorbed is plotted versus the narrow micropore volume^[26]. On the other hand, when the working pressure is 4 MPa very little effect of the MPD is observed and samples with high total micropore volumes are desired. In this respect, Fig. 5 shows the correlation between the excess H₂ stored in different porous materials and their total micropore volume^[31]. In addition, as observed in Fig. 5, this relationship is independent of the adsorbent used, showing that hydrogen storage at these conditions occurs through a physical adsorption process.

In order to understand the observed trend, which applies to both adsorption temperatures, we need to consider the fundamentals of supercritical adsorption. H₂ has a critical pressure (P_c) equal to 1.28 MPa and a critical temperature (T_c) of 33.1 K. Under these conditions, hydrogen behaves as a supercritical fluid under the given conditions. Thus, no valid approximation may be made concerning the density of the adsorbed phase since this value will depend on the pressure and the pore size^[39]. Nevertheless, it is possible to give an estimate of the "saturation pressure" under supercritical conditions by using different empirical equations. For example, Dubinin proposed a simple equation ($P_s = P_c \cdot (T/T_c)^2$),^[40] which may be used to obtain qualitative interpretation of the experimental data. Using this equation, the estimated relative pressure (P/P₀) for H₂ at 77K under 0.1 MPa and 4 MPa of pressure would be 0.014 and 0.56, respectively. This evidences how the narrow microporosity is dominant at 0.1 MPa and at 4 MPa the MPD becomes less relevant. At 298K, the obtained relative pressures for 50 and 20 MPa are 0.47 and 0.19, which once again explains the same trend. This correlation between the Hydrogen storage capacities at 77 K (0.1 MPa) and 298 K (10-20 MPa) and the narrow micropores has been also recently discussed by other authors^[41]. It was reported that H₂ adsorption occurs preferentially in smaller micropores (diameters <1 nm) at both 77 K (0.1 MPa) and 298 K (10 MPa), irrespective of the adsorbent (comparing MOFs and microporous carbons). They found an empirical correlation between the H₂ adsorption capacities at 77 K (0.1 MPa) and 298 K (10 MPa) which offers a simple method for predicting adsorption capacities under otherwise unapproachable conditions by many researchers for a given porous material.

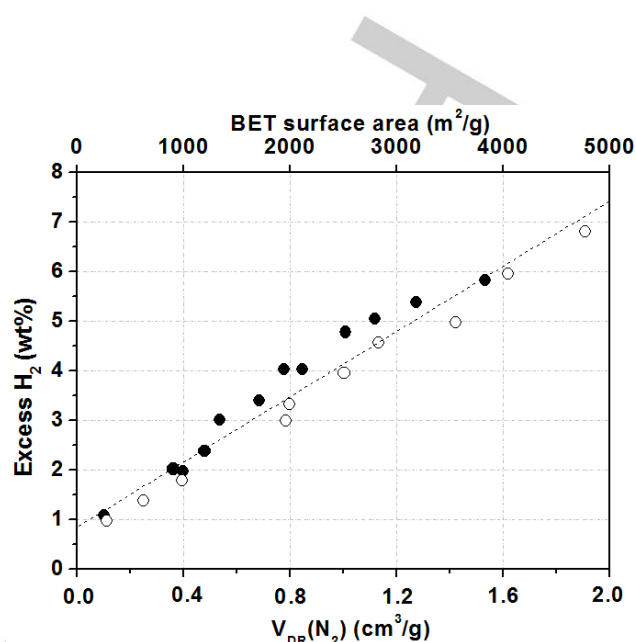


Figure 5. Excess H₂ adsorption on two well characterized series of activated carbons (black dots) and MOFs (white dots) at 77K up to 4MPa as a function of their surface areas and micropore volumes.

In the case of hybrid materials, the graphene-clay materials which we studied^[34] revealed that graphene supported on sepiolite produced structures that bring forth beneficial effects affecting Hydrogen storage capacity at low temperatures, and this might be further improved by favouring Hydrogen spill-over by adding a suitable dopant to the fibrous material which may add up to the aforementioned surface diffusion enhancement^[36]. Deepening into this concept, we observed that delaminated stannosilicate samples could adsorb Hydrogen up to over 4 wt% at 77K despite the fact that these materials only have BET surface areas around 250 m²/g. For other non-fibrous materials which we have analyzed recently^[38], namely a ZIF material (ZIF-11) versus its nanoparticulate counterpart, a detrimental effect was observed when the particle size was reduced. These results point out that working with nanostructure, morphology and chemical composition, optimized materials can be designed for this application.

3. Hydrogen Storage Capacity.

3.1 Volumetric versus Gravimetric basis.

While the ultimate goal concerning Hydrogen storage in porous materials is clear (to reach a sufficiently high value to make Hydrogen powered devices economically viable), the underlying matter is that the fuel tank (filled with the long-sought material) must fit into the device if it is meant for mobile applications. This is crucial, especially where mobile devices and vehicles are

concerned. In this respect, it must be noted that adsorption isotherms are normally expressed on gravimetric basis (amount of gas adsorbed per weight of sample). However, from a purely practical point of view, hydrogen adsorption capacities should be expressed on a volumetric basis. This in turn should make comparison between different samples a simpler and more straightforward task. However, providing storage capacity values requires knowing a suitable sample density (see Section 2). In the literature reporting hydrogen adsorption, data are expressed on gravimetric basis, and data on volumetric basis or density of the material are harder to find (whenever reported which is hardly the case).

The relevance of presenting Hydrogen storage in volumetric basis was already pointed in our earlier report^[2], but the first papers highlighting its importance date back from the 1990s. Chahine and Bose^[42] reported it back in 1994 and other researchers followed suit a decade later^[43,44]. Despite the importance of reporting the gas storage capacity in volumetric terms, this value is not frequently reported in the literature. In order to accurately report such value the only requirement is to know the material density with sufficient precision, which might be not altogether straightforward.

In order to illustrate this, we should consider Fig. 6 in which the excess Hydrogen adsorption isotherms at 77K are plotted up to a final pressure of 4 MPa in volumetric basis (i.e., g/l) using three different measurable densities.

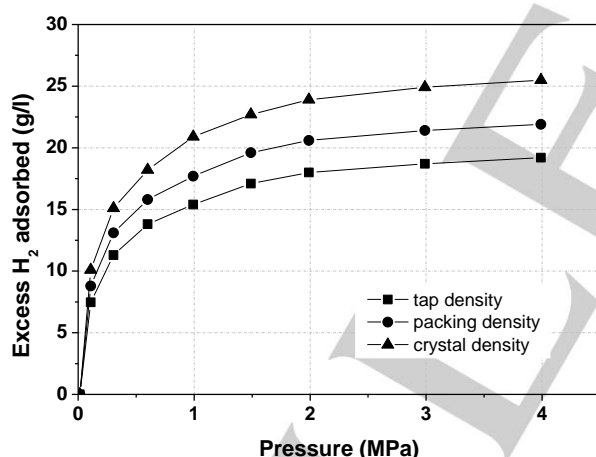


Figure 6. Excess hydrogen adsorption isotherm at 77K and up to 4 MPa for a commercial activated carbon (Maxsorb 3000) expressed in volumetric basis by using different densities.

From Figure 6, it becomes evident that the density of the material used for obtaining the isotherms on volumetric basis has a significant effect on the obtained values. Hydrogen adsorption capacities may range from under 20 to over 25 g/l depending on the type of density used. In this respect, it is important to elaborate on the fundamentals of adsorption at high pressure (Section 2). Bulk (ρ_{bulk}) and tap density (ρ_{tap}) are defined as the mass of solid divided by total volume occupied by

the solid. The two densities include the volume occupied by the solid atoms, the particle internal pore volume and the interparticle void space volume. They are determined by putting a solid mass in a container (e.g. in a measuring cylinder) and measuring the volume it occupies. The sample can be subjected to a specified compaction, usually involving vibration of the container, from which the tap density may be obtained. In the case of packing density (ρ_{packing}), it refers to a bulk density in which the sample is subjected to a compression process by applying uniaxial pressure in order to reduce the interparticle space. This density also includes the volume occupied by the solid atoms, the particle internal pore volume and the (now greatly reduced) interparticle space volume. In order to represent Figure 6 we also calculated the crystal density for the material according to the XRD diffraction pattern. This last value was merely used to show how the H₂ storage capacity might be overestimated by more than 25% by mistakenly using this latter density value, which would only be valid if a large (huge in fact) single crystal was used as adsorbent, which is obviously never the case. Only density values which include the interparticle void space should be considered in order to report volumetric capacity values. In this respect, and as we reported in an earlier study^[31] failure to do this results in incorrect data which initially favoured the MOFs versus “classical” activated carbons, but upon representing the H₂ capacity in volumetric basis using true packing density values, the activated carbon materials surpassed the MOFs by a very significant margin.

It must be remarked that recent studies have shed some additional light in this respect, predicting very high H₂ adsorption capacities in volumetric basis for a family of MOFs^[45]. Then again, their results were obtained at high pressure (10 MPa) under cryogenic conditions, which are significantly more demanding than the ones reported in this study. Other authors have also estimated that certain porous coordination polymers based on Nickel might have very promising Hydrogen uptake capacities^[46], but these studies have yet to be confirmed experimentally as they are based in computational calculations. It should be noted, however, that these values are based on calculated crystal densities, which, as discussed above, may give rise to overestimations in the final volumetric capacity.

It must also be remarked, due to its importance from an application point of view, that the packing density (or tap and bulk densities) of a material decreases with increasing the porosity development. This means that since the hydrogen uptake in volumetric basis is proportional to the density, an increase in porosity does not necessarily produce an increase in hydrogen uptake in volumetric basis and this parameter goes through a maximum^[2]. However, hydrogen uptake in gravimetric basis does increase with porosity development as we have already explained. Thus, it is very important from a porous material design point of view to produce an adequate balance between porosity development and packing (or tap/bulk) density to reach the highest hydrogen uptake in volumetric basis.

In short, a main point to maximize hydrogen storage in volumetric basis is to increase the packing density of the porous adsorbents. In the case of carbon materials, this might be done by a suitable selection of the carbon precursor, the activation method used and the variables of the activation protocol^[47] followed by making pieces, pellets or monoliths of these selected porous materials. It must be noted that from an application point of view, pieces offer advantages compared to powdered samples because they can present good mechanical properties, they are easier to handle than powder and appropriately prepared pieces, pellets or monoliths can give materials with density values around or above 1 g/cm³ while retaining a suitable porous texture. In the case of other types of materials, Yeon et al.^[48] prepared highly dense monoliths of Carbide-Derived Carbon (CDC) by treating titanium carbide plates, reaching very interesting Hydrogen storage results. In the case of MOFs, ZIFs, or PCPs, pressing or conforming the material may result in a collapse of the structure, as we have reported earlier^[31], and thus a flexible, shapeable framework is desired.

3.2. Total hydrogen storage capacity

The total hydrogen storage capacity refers to the total amount of hydrogen gas that can be stored in a tank filled with the adsorbent at a given conditions of pressure and temperature. This is probably the most important parameter from an application point of view and it includes the amount of gas adsorbed in the porous material and the gas that remains compressed in the inter-particle space. This means that the total amount of hydrogen stored in the tank, considering that the adsorption hydrogen excess is measured, corresponds to the sum of regions I, II, and III in Fig. 1.

From the experimental data that can be obtained, the total amount of hydrogen stored in the tank can be easily calculated^[2,27]. The packing (or tap/bulk) (ρ_p) and the true densities (ρ_t) can be used to obtain the volume of free space in the tank ($V_f = V_{\text{tank}}(1 - \rho_p/\rho_t)$). And then, the total amount of hydrogen stored in the tank can be calculated from the following equation, where n_s and n_e correspond to the total amount of hydrogen stored and to the excess hydrogen adsorption, respectively, both in volumetric basis.

$$n_s = n_e + \rho_{\text{gas}} \left(1 - \frac{\rho_p}{\rho_t}\right)$$

With this simple equation, the total amount of hydrogen stored by a material which is loaded in a tank can be easily calculated. For example, we can consider an activated carbon monolith (ACM) with a piece density of 0.61 g/cm³, a true density of 2.2 g/cm³ (i.e., helium density), an apparent surface area S_{BET} of 2374 m²/g, a micropore volume of 1.04 cm³/g and an excess hydrogen adsorption at 77K and 4MPa of 30 g/l^[27]. From these data it can be calculated that the total hydrogen storage capacity of a 1 l tank filled with this carbon monolith is 39.5 g H₂ at 77 K

and 4 MPa, which is around three times the amount stored in the same container just by compression (13.2 g of H₂). This concept can be applied to any experimental conditions and can be very useful to evaluate the interest of a material for this application. From an application point of view, it is desirable to prepare the porous material with the highest packing (or tap/bulk) density in order to maximize the storage due to adsorption.

4. Avenues towards improvement: Where to from where we stand?

At this point, and while very significant advancements have been and are being made in the field of Hydrogen storage towards its implementation for end-user applications, there is still a long way to go. The immediate answer to the question "How do we improve H₂ storage capacity?" would of course be to probe deeper into developing materials with an even more developed porosity but with highest packing density. Then again, as this has been under intense research for several decades (especially in the case of carbon materials), other avenues have appeared which pave new ways of boosting hydrogen storage capacity. In the first place, we have observed that it is possible to modify the heat of adsorption of Hydrogen by using carbon modified using silylated graphite oxide precursors^[33] which result in enhanced H₂ storage capacities. As mentioned above, modifying the morphology and outer surface structure of the different adsorbents, it is also possible to bring about very significant changes in their hydrogen storage capacity. In this respect, the preparation of different graphene-clay hybrids^[34,35] enabled us to identify a strong stabilisation of the H₂ molecule in the composite material, possibly arising from the fibrous morphology of the sepiolite material used in combination with the graphenic structure generated by the pyrolysis of commercial caramel. In this respect, the morphology of the adsorbent seemingly also plays a role in terms of Hydrogen accessibility and stability, as we have observed when using layered structures which upon delamination give rise to materials with rather high H₂ storage capacities.^[37] Concerning other possible ways for improvement, doping of the adsorbent material with the aim to improve H₂ spill-over to boost Hydrogen capacity is another alternative which we have reported recently^[36]. It must be noted that this surface structure modification does not always result in positive changes, since we have observed that when certain structures are obtained in nanocrystalline form, a detrimental effect is observed in absolute terms^[38].

Concerning the design of the material itself, there are two key issues that must be considered, and these two are intimately related to the material stability. This stability must be understood from two different perspectives: mechanical stability and chemical stability. Concerning the former, it is important to note that while most carbon materials can withstand significant compression forces while retaining their adsorption capacity (with notable exceptions as discussed below), other inorganic materials (namely several MOFs which have been highlighted for their outstanding adsorption capacity) suffer from severe

drawbacks when under pressure. As we have reported in a detailed manner^[31], when adsorption capacities are reported in volumetric basis, unrealistically high values were reported for some MOFs which claimed superior H₂ capacities. As we reported, this was due to the fact that the packing density (critical in this aspect) was far larger than the reported crystal density, which ultimately gave rise to the observed anomalies. In this respect, and in agreement with other reports^[49], as the MOF sample was compressed at higher pressures, this gave rise to a collapse in its structure, resulting in diminished H₂ storage capacities. Several reports have highlighted that MOFs are largely flexible structures,^[50,51] being able to expand by over 300% depending on the solvent used (as is the case of the material known as MIL-53), but in the light of experimental evidence, this does not guarantee their mechanical stability.

On the latter, it must be noted that carbon materials are exceedingly stable except under strongly oxidizing conditions, which is sometimes not the case of other inorganic materials such as MOFs. In this respect, we reported that certain MOFs^[31] suffered severe decreases in their adsorption capacity when submitted to high humidity conditions for several days (denoted as “steaming” of the material) or even when stored under open bench conditions for prolonged periods of time. While this characteristic seems to have been overcome with recent reports^[45] in which the samples do not lose performance over time, their mechanical stability remains an issue.

Since the pore size becomes critical at specific adsorption conditions, the possibility of decreasing the pore size of the material under an exterior stimulus could be of great interest to maximize the adsorption (i.e., the density of the adsorbed phase increases with decreasing the pore size). The release of this stimulus could increase the pore size favouring the delivery of the gas. This could be a novel option for the design of materials for energy storage. In this sense, we have shown by using Synchrotron radiation that ACFs present a flexible porous network which pore size is modified by applying uniaxial tensile forces along the fiber main axis, being this change reversible.^[52] A recent report by Nishihara et al.^[53] has shown a highly flexible graphene mesosponge (GMS) which might be very interesting for H₂ storage applications considering that it has the possibility of tailoring the porosity.

5. Conclusions and Outlook

Whenever Hydrogen storage is considered, there are many aspects that must be considered, going from the very fundamentals of adsorption at high pressure down to (almost) the atomic arrangement of the material itself. Considerations and definitions about high-pressure adsorption under supercritical conditions and about the experimental procedures used to measure excess hydrogen adsorption isotherms (mainly gravimetric and volumetric methods) have been given in this Personal Account. We have also remarked the importance of properly measuring the material density in order to accurately

report the experimental data, since it is necessary to express the data in volumetric basis which is the most relevant from an application point of view in mobile applications. Comparison of the adsorption data at several temperatures and pressures on a wide range of materials allows us to draw some general conclusions: in absence of effects brought forth by certain modifications of the described materials, H₂ storage is governed by the microporous texture of the adsorbent, and the range of the microporosity playing a role in the adsorption process will be determined by the hydrogen pressure used. Combining both aspects, it can be concluded that materials with a proper balance between porosity development, pore size distribution and packing (or bulk/tap) density are the most useful for this application.

If we refer specifically to the materials, since from a strictly applied point of view, the sample density is a critical parameter that requires careful consideration, “classical” carbon materials seem to gain the upper hand thanks to their structure and mechanical properties. While novel MOFs, ZIFs, and PCPs show outstanding promise, they still have a significant amount of ground to cover in terms of overall performance and production costs. The design of the material with the highest porosity and packing density, with the adequate surface chemistry that assures a sufficiently high heat of adsorption and which pore size can be precisely modulated by an external stimulus like application of a stress, could be considered as a future goal to succeed in hydrogen storage in porous materials.

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