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Hydrogen Storage for Energy Application

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1. Introduction

The rising population and increasing demand for energy supply urged us to explore more sustainable energy resources. The reduction of fossil fuel dependency in vehicles is key to reducing greenhouse emissions [1-2]. Hydrogen is expected to play an important role in a future energy economy based on environmentally clean sources and carriers. As a fuel of choice it is light weight, contains high energy density and its combustion emits no harmful chemical by-products. Moreover, hydrogen is considered as a green energy, because it can be generated from renewable sources and is non-polluting [3-5].

Nevertheless, there is a still remaining significant challenge that hinders the widespread application of hydrogen as the fuel of choice in mobile transportation, namely, the lack of a safe and easy method of storage. Vehicles and other systems powered by hydrogen have the advantage of emitting only water as a waste product. The efficient and safe storage of hydrogen is crucial for promoting the “hydrogen economy” as shown in Figure1 [6-9].

The United States’ Department of Energy (DOE) has established requirements that have to be met by 2015; regarding the reversible storage of hydrogen according to which the required gravimetric density should be 9 wt % and the volumetric capacity should be 81 g of H₂/L [10-11]. To fulfill such requirements there are main problems for hydrogen storage such as:

- reducing weight and volume of thermal components is required;
- the cost of hydrogen storage systems is too high;
- durability of hydrogen storage systems is inadequate;
- hydrogen refuelling times are too long;
- high-pressure containment for compressed gas and other high-pressure approaches limits the choice of construction materials and fabrication techniques, within weight, volume, performance, and cost constraints.

For all approaches of hydrogen storage, vessel containment that is resistant to hydrogen permeation and corrosion is required. Research into new materials of construction such as metal ceramic composites, improved resins, and engineered fibers is needed to meet cost targets without compromising performance. Materials to meet performance and cost requirements for hydrogen delivery and off-board storage are also needed [10].

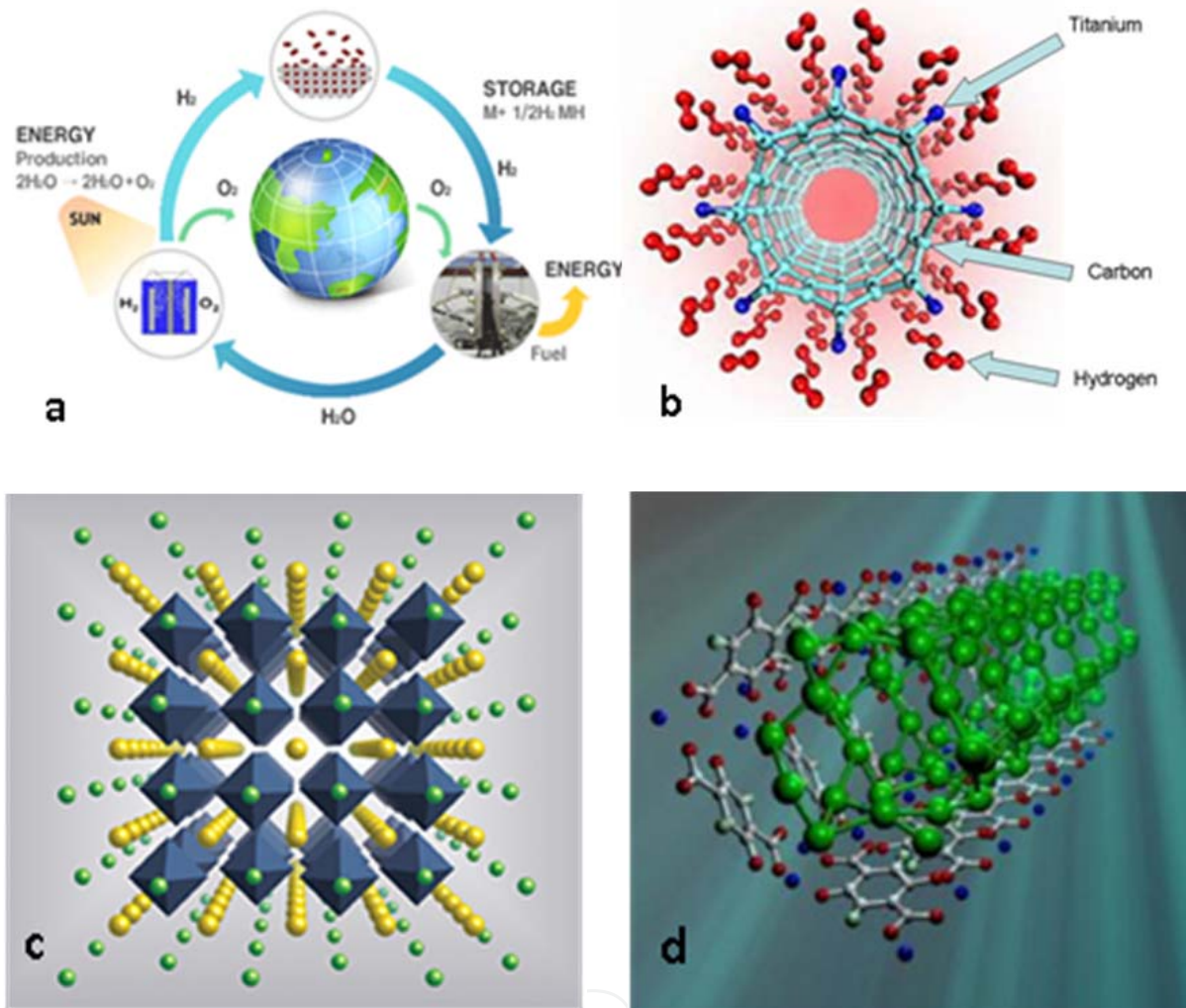


Figure 1. (a) Hydrogen production and storage by renewable resource [6], (b) hydrogen storage in metal doped carbon nanotubes [7], (c) storage in mesoporous zeolite: by controlling the ratio of different alkali metal ions (yellow and green balls), it is possible to tailor the pressure and temperature at which hydrogen is released from the material [8], (d) hydrogen storage in metal–organic framework (MOF)-74 resembles a series of tightly packed straws comprised mostly of carbon atoms (white balls) with columns of zinc ions (blue balls) running down the walls. Heavy hydrogen molecules (green balls) adsorbed in MOF-74 pack into the tubes more densely than they would in solid form [9].

Moreover, for all methods of hydrogen storage thermal management is a key issue. In general, the main technical challenge is heat removal upon re-filling of hydrogen for compressed gas and onboard reversible materials within fuelling time requirements. Onboard reversible materials typically require heat to release hydrogen. Heat must be

provided to the storage media at reasonable temperatures to meet the flow rates needed by the vehicle power plant, preferably using the waste heat of the power plant. Depending upon the chemistry, chemical hydrogen approaches often are exothermic upon release of hydrogen to the power plant, or optimally thermal neutral. By virtue of the chemistry used, chemical hydrogen approaches require significant energy to regenerate the spent material and by-products prior to re-use; this is done off the vehicle.

2. Methods and problems of hydrogen storage

At the moment, several kinds of technologies of hydrogen storage are available. Some of them will be briefly described here.

1. The simplest is compressed H₂ gas. It is possible at ambient temperature, and in- and out-flow are simple. However, the density of storage is low compared to other methods.
2. Liquid H₂ storage is also possible: from 25% to 45% of the stored energy is required to liquefy the H₂. At this method the density of hydrogen storage is very high, but hydrogen boils at about -253°C and it is necessary to maintain this low temperature (else the hydrogen will boil away), and bulky insulation is needed.
3. In metal hydride storage the powdered metals absorb hydrogen under high pressures. During this process heat is produced upon insertion and with pressure release and applied heat, the process is reversed. The main problem of this method is the weight of the absorbing material – a tank's mass would be about 600 kg compared to the 80 kg of a comparable compressed H₂ gas tank.
4. More popular at this time is carbon absorption: the newest field of hydrogen storage. At applied pressure, hydrogen will bond with porous carbon materials such as nanotubes.

So, it can be summarized that even mobile hydrogen storage is currently not competitive with hydrocarbon fuels; it must become so in order for this potential environmentally life-saving technology to be realized on a great scale.

3. High pressure hydrogen storage

The most common method of hydrogen storage is compression of the gas phase at high pressure (> 200 bars or 2850 psi). Compressed hydrogen in hydrogen tanks at 350 bar (5,000 psi) and 700 bar (10,000 psi) is used in hydrogen vehicles. There are two approaches to increase the gravimetric and volumetric storage capacities of compressed gas tanks. The first approach involves cryo-compressed tanks as shown in Figure 2 [12]. This is based on the fact that, at fixed pressure and volume, gas tank volumetric capacity increases as the tank temperature decreases. Thus, by cooling a tank from room temperature to liquid nitrogen temperature (77 K), its volumetric capacity increases. However, total system volumetric capacity is less than one because of the increased volume required for the cooling system. The limitation of this system is the energy needed to compression of the gas. About 20 % of the energy content of hydrogen is lost due to the storage method. The energy lost for hydrogen storage can be reduced by the development of new class of lightweight composite

cylinders. Moreover, the main problem consisting with conventional materials for high pressure hydrogen tank is embrittlement of cylinder material, during the numerous charging/discharging cycles [13-14].



Figure 2. Hydrogen storage in tanks presently used in hydrogen-powered vehicles [12].

4. Liquefaction

The energy density of hydrogen can be improved by storing hydrogen in a liquid state. This technology developed during the early space age, as liquid hydrogen was brought along on the space vessels but nowadays it is used on the on-board fuel cells. It is also possible to combine liquid hydrogen with a metal hydride, like Fe-Ti, and this way minimize hydrogen losses due to boil-off.

In this storage method, first gas phase is compressed at high pressure than liquefy at cryogenic temperature in liquid hydrogen tank (LH₂). The condition of low temperature is maintained by using liquid helium cylinder as shown in Figure 3 [15]. Hydrogen does not liquefy until -253 °C (20 degrees above absolute zero) such much energy must be employed to achieve this temperature. However, issues are remaining with LH₂ tanks due to the hydrogen boil-off, the energy required for hydrogen liquefaction, volume, weight, and tank cost is also very high. About 40 % of the energy content of hydrogen can be lost due to the storage methods. Safety is also another issue with the handling of liquid hydrogen as does the car's tank integrity, when storing, pressurizing and cooling the element to such extreme temperatures [10,16-19].

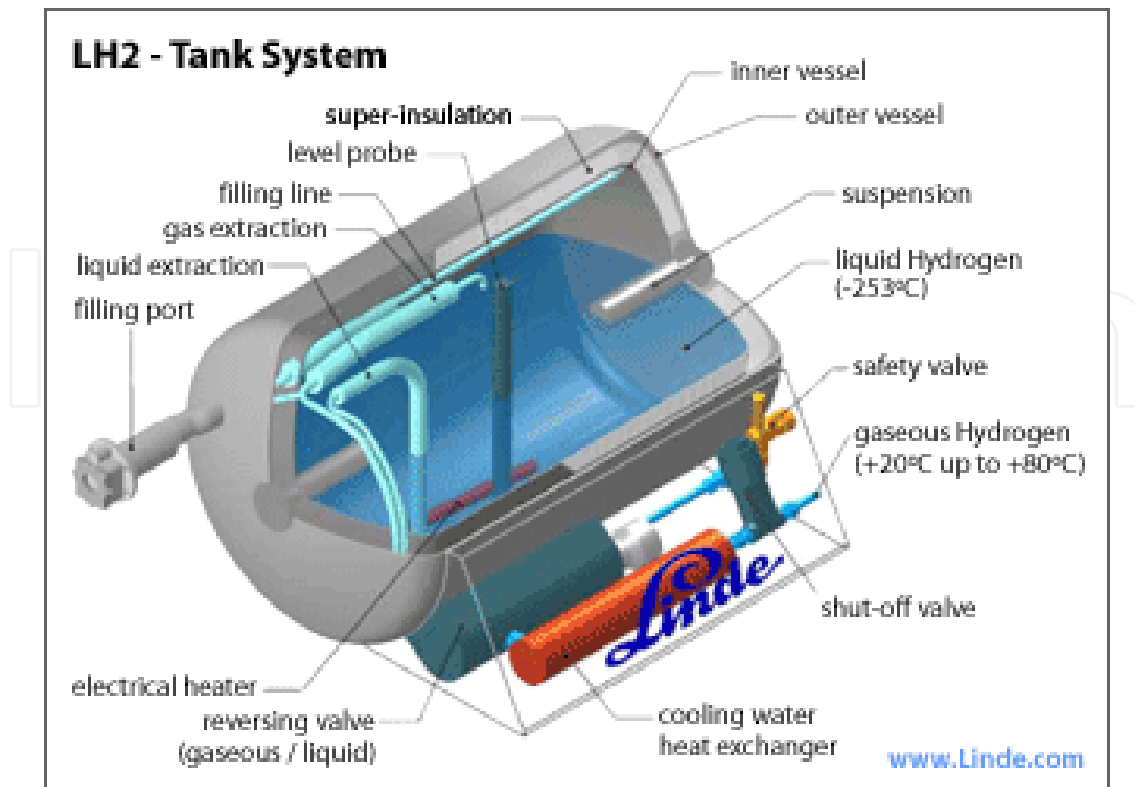


Figure 3. Liquid hydrogen storage tank system, horizontal mounted with double gasket and dual seal [15].

5. Solid state hydrogen storage

As mentioned above, certainly some practical problems, which cannot be circumvented, like safety concerns (for high pressure containment), and boil-off issues (for liquid storage), both are challenging for hydrogen storage. There is a third potential solution for hydrogen storage such as (i) metal hydrides and (ii) hydrogen adsorption in metal-organic frameworks (MOFs) and carbon based systems [10,17,18].

In these systems, hydrogen molecules are stored in the mesoporous materials by physisorption (characteristic of weak van der Waals forces). In the case of physisorption, the hydrogen capacity of a material is proportional to its specific surface area [20-22]. The storage by adsorption is attractive because it has the potential to lower the overall system pressure for an equivalent amount of hydrogen, yielding safer operating conditions. The advantages of these methods are that the volumetric and cryogenic constraints are abandoned. In recent decades, many types of hydrogen storage materials have been developed and investigated, which include hydrogen storage alloys, metal nitrides and imides, ammonia borane, etc.

Currently, porous materials such as zeolites, MOFs, carbon nanotubes (CNTs), and graphene also gained much more interest due to the high gravimetric density of such materials [23-24]. The corresponding hydrogen storage capabilities of these materials are displays in Figure 4 [25].

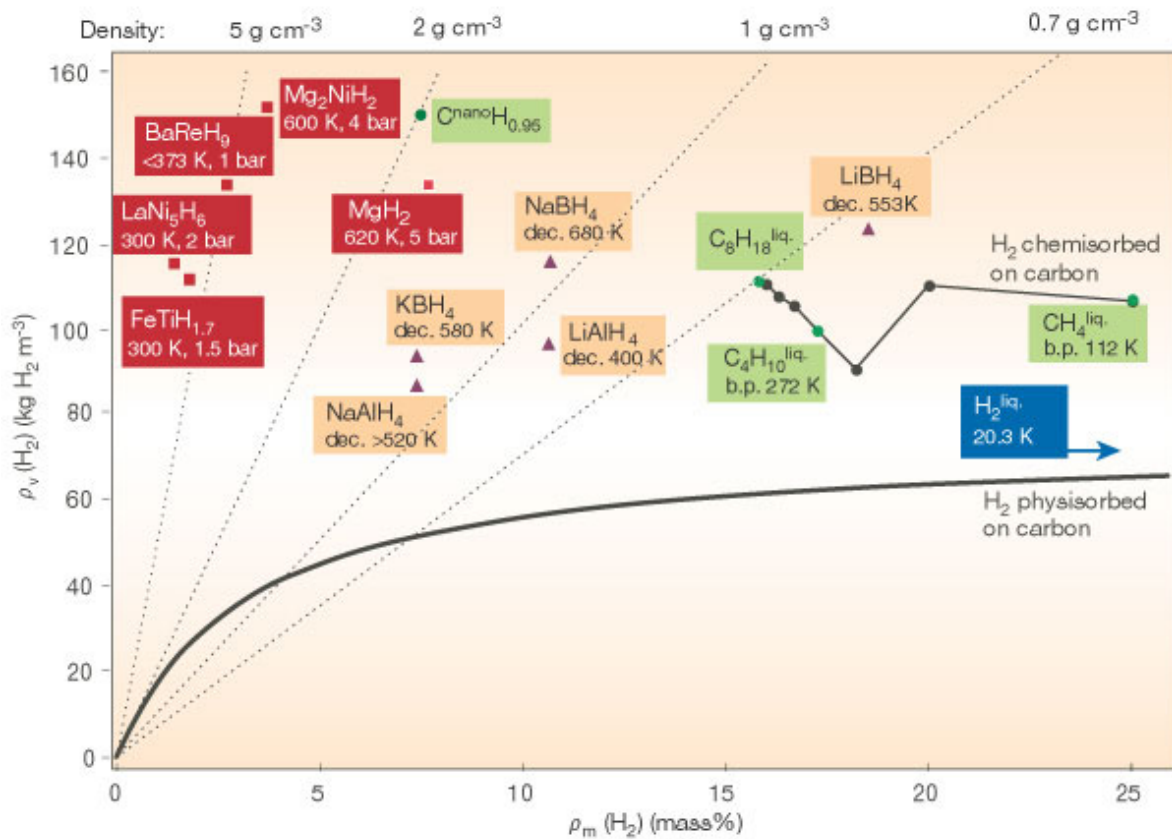


Figure 4. A complete survey plot of hydrogen storage in metal hydrides and carbene-based materials [25].

5.1. Hydrogen storage in metal hydrides

Initially, metal alloys, such as LaNi₅, TiFe and MgNi [10] were proposed as storage tanks since by chemical hydrogenation they form metal hydrides as previously shown in Figure 2 (compressed tank) [12]. Latter, hydrogen can be released by dehydrogenation of metal hydrides with light elements (binary hydrides and complex hydrides) because of their large gravimetric H₂ densities at high temperature [10,17]. Regarding vehicle applications, metal hydrides (MHs) can be distinguished into high or low temperature materials [26]. This depends on the temperature at which hydrogen absorption or desorption is taking place. Normally, in MHs hydrogen uptake and release kinetics is considered as above or below of 150 °C, respectively [27]. La-based and Ti-based alloys are examples of some low temperature materials with their main drawback as they provide very low gravimetric capacity (<2 wt %). The corresponding hydrogen storage capabilities of metal hydrides are displays in Figure 5 [13].

The analysis of above plot LiAlH₄ (LAH) (Fig.5) shows that the gravimetric weight ratio of hydrogen is 10.6 wt%; thereby LAH seems a potential hydrogen storage medium for future fuel cell powered vehicles. But, in practice the hydrogen storage capacity is reduced to 7.96 wt% due to the formation of LiH + Al species as the final product. Due to this, a substantial research effort has been devoted to accelerating the decomposition

kinetics by catalytic doping in the MHs [10]. The high hydrogen content, as well as the discovery of reversible hydrogen storage is reported in Ti-doped NaAlH_4 . In order to take advantage of the total hydrogen capacity, the intermediate compound LiH must be dehydrogenated as well. Due to its high thermodynamic stability this requires temperatures higher than $400\text{ }^\circ\text{C}$ which is not considered feasible for transportation purposes [13]. Another problem related to hydrogen storage is the recycling back to LiAlH_4 due to its relatively low stability, requires an extremely high hydrogen pressure in excess of 10000 bar [27].

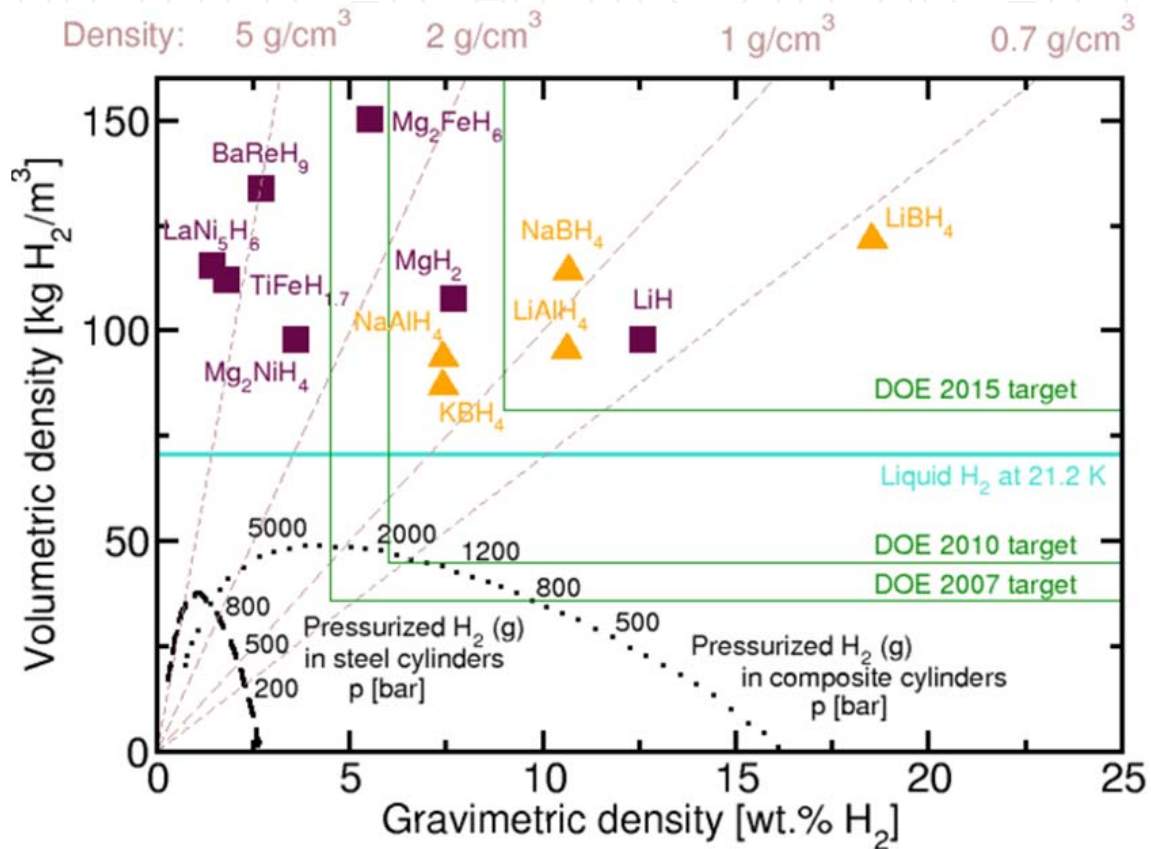


Figure 5. Volumetric and gravimetric hydrogen storage densities of different hydrogen storage methods. Metal hydrides are represented with squares and complex hydrides with triangles. BaReH_9 has the highest known hydrogen to metal ratio (4.5), Mg_2FeH_6 has the highest known volumetric H_2 density, LiBH_4 has the highest gravimetric density. Reported values for hydrides are excluding tank weight. DOE targets are including tank weight, thus the hydrogen storage characteristics of the shown hydrides may appear too optimistic [13]. Controversially, high temperature materials like Mg-based alloys can reach a theoretical maximum capacity of hydrogen storage of 7.6 wt%, suffering though from poor hydrogenation / dehydrogenation kinetics and thermodynamics [10,18,23].

Thus, the high work temperature and the slow reaction rate (high activation energy) limit the practical application of chemical hydride systems. Those properties can be improved by the nanocomposite materials (Fig.6) [28].

The nanocomposite materials for hydrogen storage encompass a catalyst and composite chemical hydrides at the nanometer scale. The catalyst increases reaction rate. The

thermodynamic stability of the nano-composite materials can be controlled by the composite chemical hydrides having protide (hydride) ($H\delta^-$) and proton ($H\delta^+$). In addition, the hydrogen absorption kinetics is accelerated by the nanosize materials and they may change the thermodynamic stability of the materials [28].

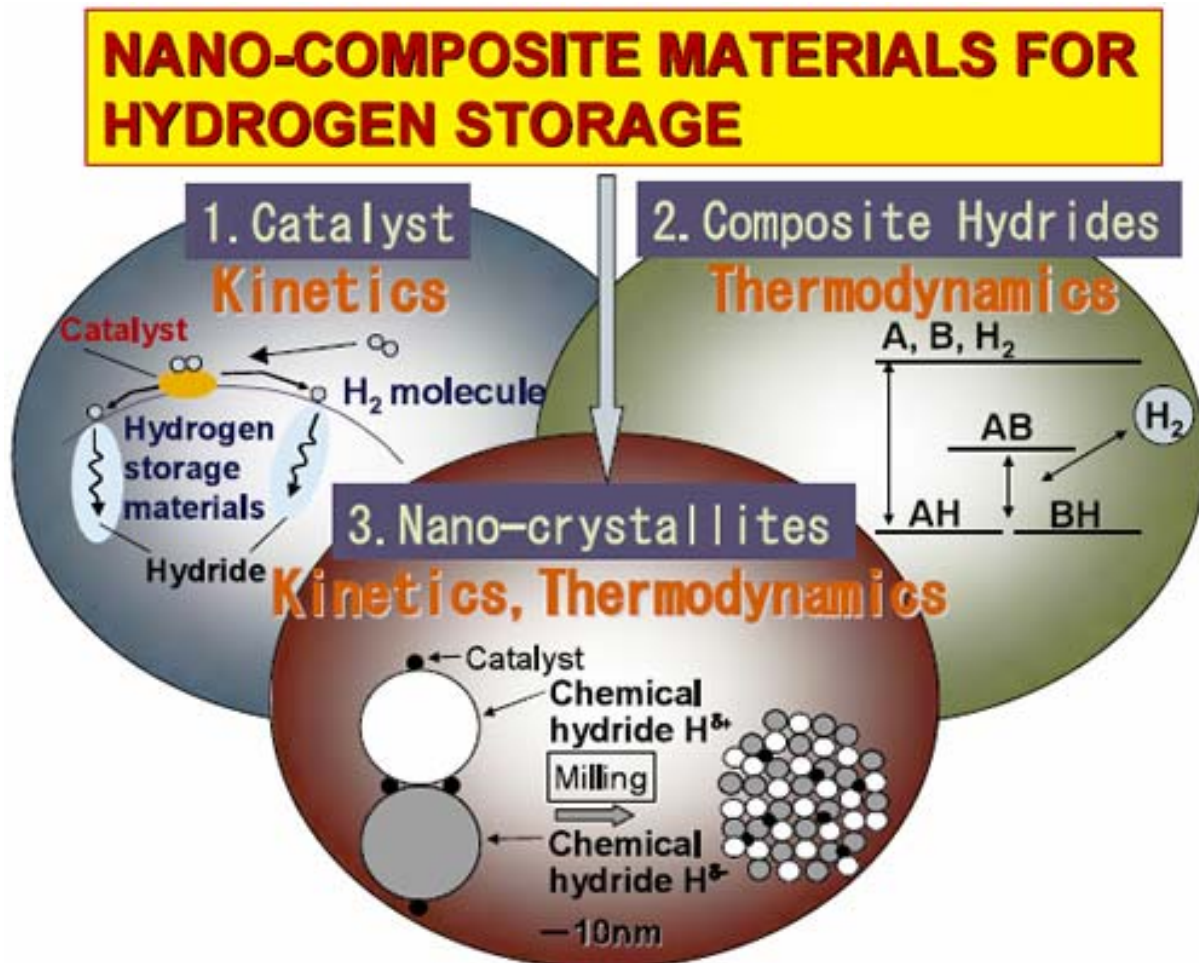


Figure 6. Design concept of nano-composite materials for hydrogen storage [28].

Another strategy to increase the interaction energy refers to the modifications of the chemical properties: surface treatment, ion exchange, doping, etc. It was observed that the capacity of hydrogen adsorption in metal oxide increased remarkably when Pt was introduced into mesoporous nickel oxide and magnesium oxide [29].

The analyse of hydrogen storage property of Ni-nanoparticles with cerium shell structure showed that the quantity of hydrogen released gradually increased with increasing temperature up to a maximum of $400\text{ }^\circ\text{C}$, then gradually decreased at temperatures above $400\text{ }^\circ\text{C}$. The catalytic activity of nanoparticles in the gas phase hydrogenation of benzene was related to their hydrogen storage properties and it reached the maximum value when the maximum amount of bulk H was released. By comparing the catalytic activity of nano-Ni particles with and without Ce shell structure, the higher activity of nano-Ni with Ce shell was attributed to the property of hydrogen storage and the synergistic effect of Ce and Ni in

the shell structure, which was also illustrated by the result of gas phase benzene hydrogenation over supported nano-NiCe particles [30].

5.2. Hydrogen storage in nanostructured / porous material

It is well known that there are three categories of porous materials: microporous with pores of less than 2 nm in diameter, mesoporous having pores between 2 and 50 nm, and macroporous with pores greater than 50 nm. The term “nanoporous materials” has been used for those porous materials with pore diameters of less than 100 nm. Many kinds of crystalline and amorphous nanoporous materials such as framework silicates and metal oxides, pillared clays, nanoporous silicon, carbon nanotubes and related porous carbons have been described lately in the literature. It will be focused here on microporous zeolites, nanoporous metal organic frameworks (MOFs) and carbon-based materials.

5.2.1. Zeolites

Zeolite is a type of microporous solid used commercially in catalysis and gas separation [31]. Zeolites are prominent candidates for a hydrogen storage medium, due to their structural and high thermal stability, large internal surface area, low cost and adjustable composition [32].

Zeolites contain well defined open-pore structure, with often tunable pore size, and show notable guest-host chemistry, with important applications in catalysis, gas adsorption, purification and separation [33]. Additionally, this material is cheap and has been widely used in industrial processes for many decades. The extensive experimental survey depicts the hydrogen storage capacity of zeolites to be <2 wt% at cryogenic temperatures and <0.3 wt% at room temperatures and above [34]. Figure 7 shows that the structure of these minerals is most commonly based on a framework of alternating AlO_4 and SiO_4 species, with charge balancing (hydroxyl or cationic) entities, forming networks of cavities, channels and openings of varying dimensions [35].

The specific structural configuration of the zeolite provides great influence for their properties with respect to adsorption, selectivity and mobility of the guest molecules. An important property of zeolites is their high ion-exchange capacity, which allows for the direct manipulation of the available void space inside the material, as well as the chemical properties of the binding sites, greatly influencing their storage capacity [36]. Theoretical modelling also provides a close insight of the hydrogen storage capacity of zeolite materials [37-38].

A hydrogen capacity equal to 1.28 wt% was obtained at 77 K and 0.92 bar for H-SSZ-13 zeolite [39]. Also at cryogenic temperatures and 15 bar gravimetric storage capacities of 2.19 wt% was reported for Ca exchanged X zeolite [32]. However, hydrogen adsorption on zeolites at room temperature and 60 bar was reported less than 0.5 wt% [34,40]. It was shown that the amount of hydrogen adsorbed on zeolites depended on the framework structure, composition, and acid–base nature of the zeolites [32].

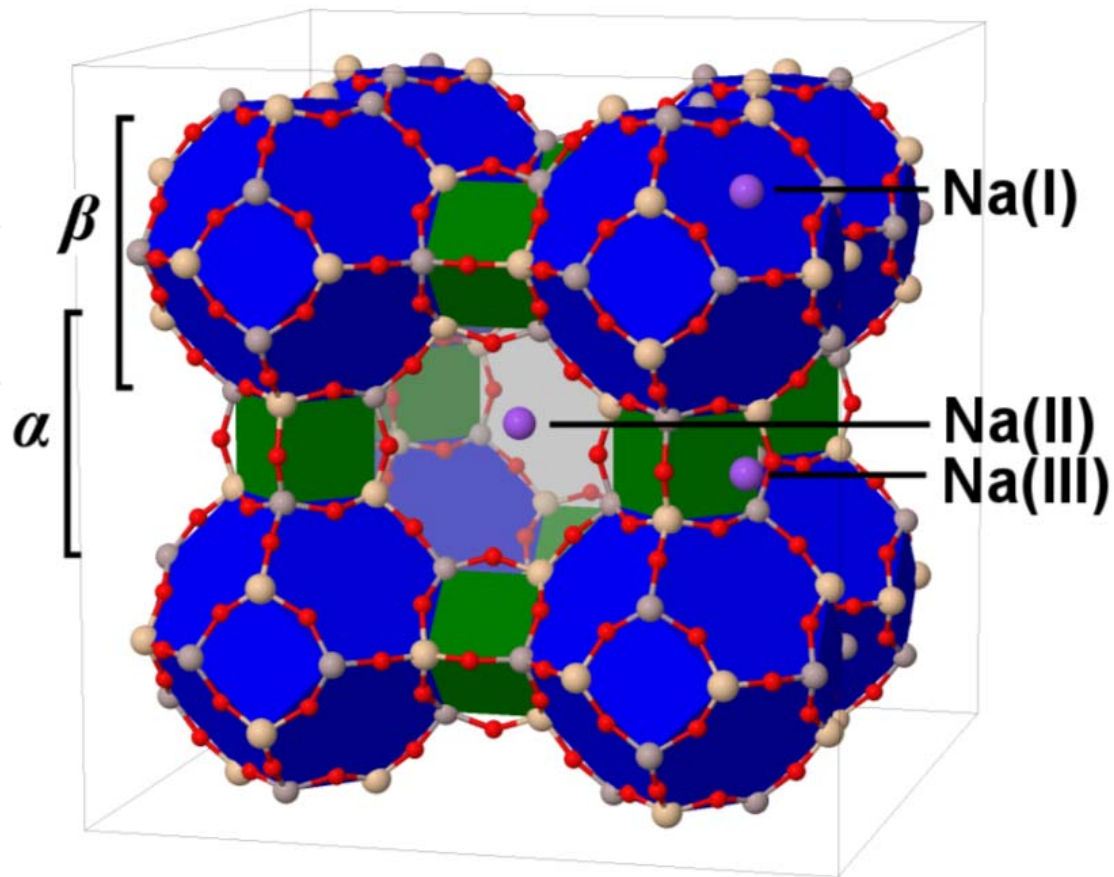


Figure 7. An unit cell of sodium zeolite with cage and cavity [32].

5.2.2. Metal organic frameworks

Lately, novel nanoporous materials like metal organic frameworks (MOFs) is have been targeted to the hydrogen storage problem [14,24,41]. MOFs are porous materials constructed by coordinate bonds between multidentate ligands and metal atoms or small metal-containing clusters. MOFs can be generally synthesized via self-assembly from different organic linkers and metal nodules. Due to the variable building blocks, MOFs have very large surface areas, high porosities, uniform and adjustable pore sizes and well-defined hydrogen occupation sites. These features make MOFs (some type of MOF is called IRMOF) promising candidates for hydrogen storage. As usually, MOFs are highly crystalline inorganic-organic hybrid structures that contain metal clusters or ions (secondary building units) as nodes and organic ligands as linkers (Fig.8) [42].

When guest molecules (solvent) occupying the pores are removed during solvent exchange and heating under vacuum, porous structure of MOFs can be achieved without destabilizing the frame and hydrogen molecules will be adsorbed onto the surface of the pores by physisorption. Compared to traditional zeolites and porous carbon materials, MOFs have very high number of pores and surface area which allow higher hydrogen uptake in a given volume [43]. The research interests on hydrogen storage in MOFs have been growing since 2003 when the first MOF-based hydrogen storage material was introduced [44]. Since there

are infinite geometric and chemical variations of MOFs based on different combinations of secondary building units (SBUs) and linkers, many researches explore what combination will provide the maximum hydrogen uptake by varying materials of metal ions and linkers as shown in Figure 9 [45].

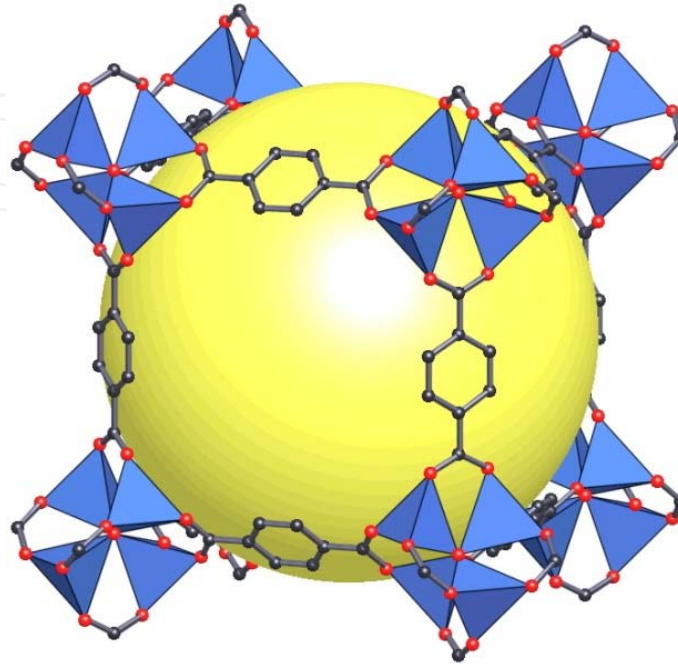


Figure 8. Eight units surround this pore (yellow ball represents space available in pore) in the metal-organic framework called MOF-5. Each unit contains four ZnO_4 tetrahedra (blue) and is connected to its neighboring unit by a dicarboxylic acid group [42].

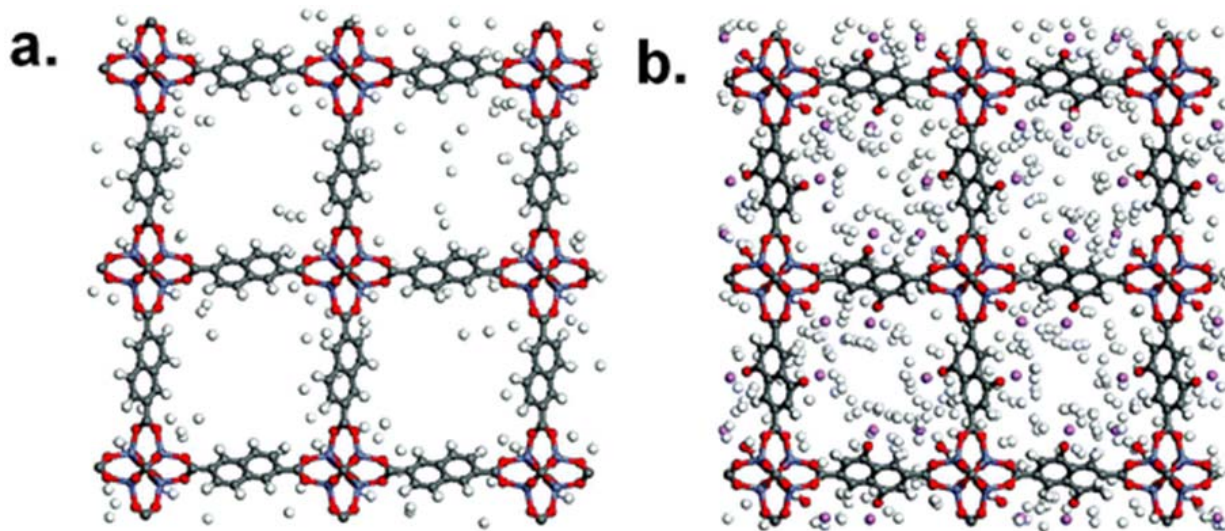


Figure 9. Snapshots of the IRMOF-8 cage with adsorbed H_2 at 77 K and 1 bar: (a) unmodified IRMOF-8 and (b) Li-alkoxide modified IRMOF-8 [45].

The effects of surface area, pore volume and heat of adsorption on hydrogen uptake in MOFs were discussed and in result the extensive work was directed toward the synthesis of MOFs with high surface areas and pore volumes [46].

As example, it was reported about storage capacity of 3.1 wt% at 77 K under 1.6 MPa in the formed 1D lozenge-shape tunnels, with pores of 8.5 Å and average surface area of 1100 m²/g in the nanoporous metal-benzenedicarboxylate $M(OH)(O_2C-C_6H_4-CO_2)$ ($M=Al^{3+}, Cr^{3+}$), MIL-53 systems (Fig. 10) [44].

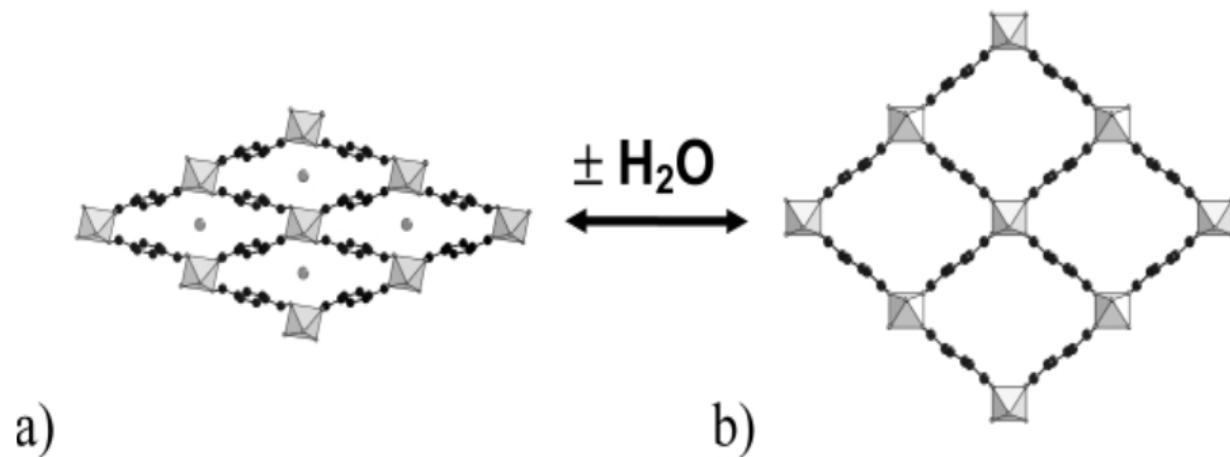


Figure 10. Representation of the structure of MIL-53 showing the expansion effect due to the removal of a water molecule, (a) hydrated (left), (b) dehydrated (right); octahedra: $MO_4(OH)_2$, $M=Al^{3+}, Cr^{3+}$. The dehydrated form of MIL-53 was tested for the hydrogen adsorption experiment [44].

A series of isorecticular (meaning having the same underlying topology) metal organic frameworks, $Zn_4O(L)$, were constructed by changing the different linking zinc oxide clusters with linear carboxylates L , so as to get a high porosity. Recently, MOF-177 ($Zn_4O(BTB)_2$) was formed by linking the same clusters with a trigonal carboxylate. MOF-177 was claimed to have a high Langmuir surface area of 5640 m² g⁻¹, and the highest hydrogen storage of 7.5 wt% H₂ at 77 K and 70 bar. The more meaningful surface area, BET surface area (calculated by well known Brunauer-Emmett-Teller method), for MOF-177 is around 3000 m² g⁻¹. More recently, it was reported a nanoporous chromium terephthalate-based material (MIL-101) with the highest Langmuir surface area (4500–5900 m² g⁻¹) among all MOFs [44]. It was reported that the hydrogen storage capacities in this material at 8 MPa were 6.1 wt% at 77 K, and 0.43 wt% at 298 K. Although these MOFs have remarkable hydrogen capacities at 77 K, no significant hydrogen storage capacities were obtained with the MOFs at room temperature [11].

5.2.3. Carbon-based materials

Among the vast range of materials, carbon-based systems have received particular research interest due to their light weight, high surface area and chemical stabilities. Early experimental data for hydrogen storage in carbon nanomaterial's was initially promising, indicating high hydrogen storage capacities exceeding DOE targets [17,18]. Therefore, hydrogenation of carbon-based materials e.g., activated carbon, graphite, carbon nanotubes and carbon foams, have gained large technological and scientific interest for hydrogen storage and were included in the group of hydrogen storage materials as shown in Figure 4 [25].

It was already mentioned stored hydrogen in the liquid form requires large energy consumption for liquefaction at 20 K and it also suffers from the “boil-off” problem. At the

same time, carbon materials, as well as MOFs and other nanostructured and porous materials, have high surface areas and have exhibited promising hydrogen storage capacities at 77 K. However, among the currently available candidate storage materials, none is capable of meeting the DOE criteria for personal transportation vehicles at moderate temperatures and pressures. The hydrogen adsorption capacities at the ambient temperature on all known sorbents are below 0.6–0.8 wt% at 298 K and 100 atm. This is true for all sorbent materials including the MOFs and templated carbons [11].

Hydrogen storage by spillover has been proposed as a mechanism (i.e., via surface diffusion) to enhance the storage density of carbon-based nanostructures as well as MOF structures. This approach relies on the use of a supported metallic catalyst to dissociate molecular hydrogen, relying on surface diffusion through a bridge to store atomic hydrogen in a receptor.

The term hydrogen spillover was coined decades ago [47] to describe the transport of an active species (e.g., H) generated on one substance (activator, Act) to another (receptor, Rec) that would not normally adsorb it. Common in heterogeneous catalysis, the activator is metal and the receptor can be a metal or a metal oxide, $H_2 - Act \rightarrow 2H$, $H + Rec \rightarrow H@Rec$ [47].

The number of adsorbed H atoms can exceed that of the activator by orders of magnitude and approach the number of receptor atoms. This feature makes the spillover attractive for H storage: if a receptor is made from light elements, notably C, then the gravimetric fraction of the “spilled” H may be large and approach the DOE’s goals in its use as an onboard energy source [48].

Obviously, in order for the spillover process to take place, next processes need to occur: (i) H atoms migrate from the catalyst to the substrate via physical adsorption (physisorption), when the adsorbate molecules are attracted by weak van der Waals forces towards the adsorbent molecules, or chemical adsorption (chemisorption), when the adsorbate molecules are bound to the surface of adsorbent by chemical bonds; (ii) H atoms diffuse from the adsorption sites at the vicinity of the catalyst to the sites far away from the catalyst. Thus the process of physisorption results in the H_2 molecule remaining intact. And, in opposite, chemisorption leads to H_2 bond dissociation, with the resulting H atoms forming chemical bonds with the storage substrate [49]. Physisorption can occur as a preliminary state to chemisorption.

It was already reported that a hydrogen spillover induced increase of hydrogen storage capacity for activated carbon and single-walled carbon nanotubes by factors of 2.9 and 1.6, respectively [50]. It has been suggested that the stored hydrogen atoms in the carbon-based materials are “loosely adsorbed” on surfaces of substrates via spillover upon H_2 dissociation on nickel catalyst. It was explained that at a given pressure of H_2 gas, the H_2 molecules undergo dissociative chemisorption upon interacting with a supported transition metal catalyst, e.g. nanoparticles of platinum. The generated H atoms then migrate from the catalyst particles to the storage material through a “bridge” built of carbonized sugar molecules and further diffuse throughout the entire bulk solid. Obviously, in order for the spillover process to occur to any significant extent in solid materials, it is essential that the H

atoms should be able to move from the vicinity of catalyst particles to substrate sites far from where the catalysts reside (Fig.11) [50].

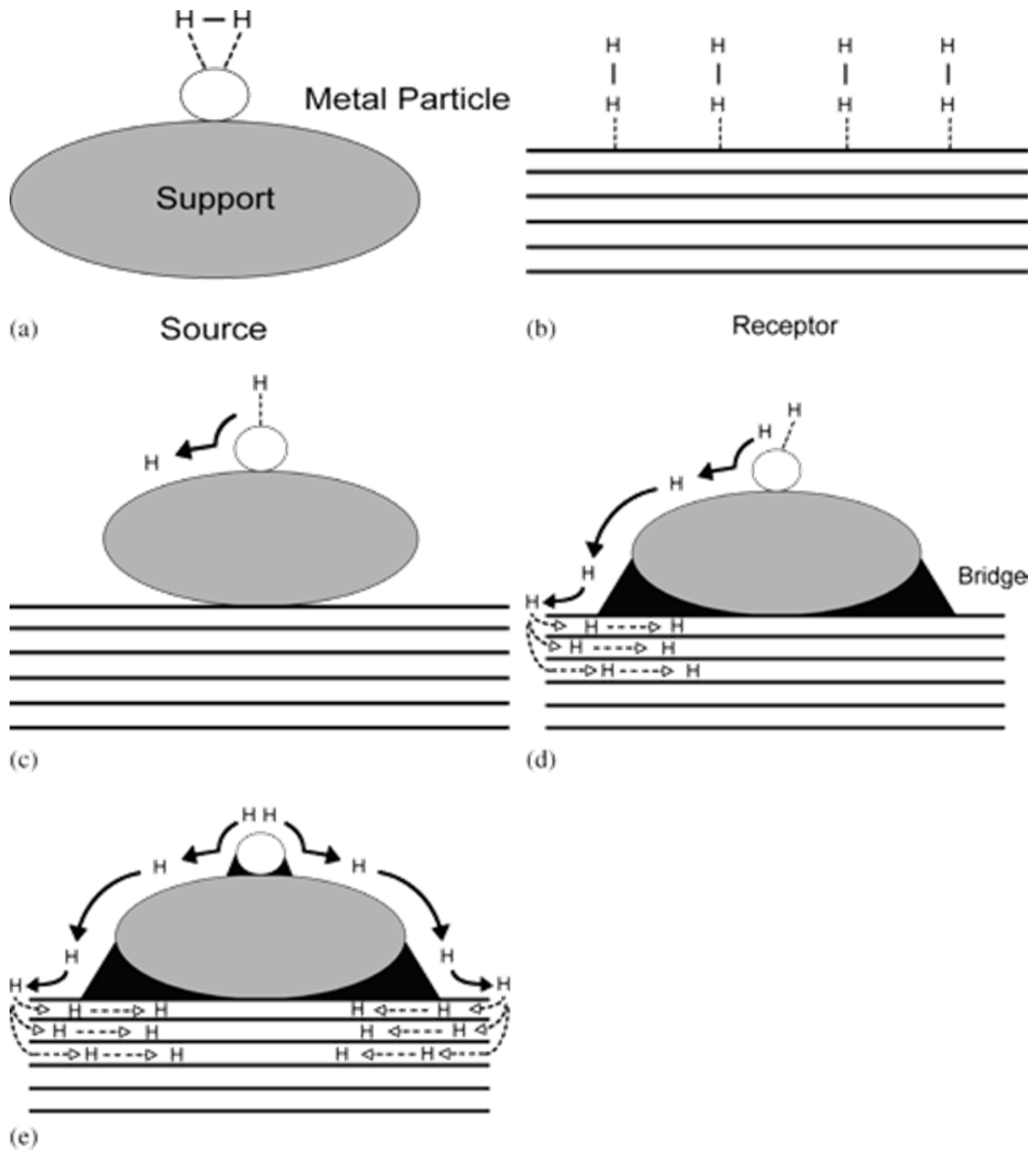


Figure 11. Hydrogen spillover in a supported catalyst system: (a) adsorption of hydrogen on a supported metal particle; (b) the low-capacity receptor; (c) primary spillover of atomic hydrogen to the support; (d) secondary spillover to the receptor enhanced by a physical bridge; (e) primary and secondary spillover enhancement by improved contacts and bridges [50].

While active research efforts are being made to understand the hydrogen spillover processes, to date, there has been no general consensus on the spillover mechanisms that can

satisfactorily explain the observed large storage capacity (up to 4 wt% of H₂) or facile hydrogen desorption kinetics from the carbon-based storage compounds at near-ambient temperatures. Hydrogen spillover on solid-state materials is not a newly discovered phenomenon. The concept of hydrogen spillover has its genesis in fundamental studies with heterogeneous metal catalysts, particularly with such systems as are used for chemical hydrogenation reactions.

On another way, in catalytic processes, the metal has the role of “activating” hydrogen by reversibly dissociating H₂ into metal-H atom (hydride) species on its surface. It has been observed that, for instance, by heating Pt dispersed on carbon at 623 K, Pt/Al₂O₃ at 473–573 K, Pd/C at 473 K, and Pt/WO₃, under hydrogen pressure the amount of H₂ absorbed is in excess of the known H₂-sorption capacity of the metal alone. While the concept of hydrogen spillover is normally associated with solid-state materials such as activated carbon (or transition metal oxides), there have been a small number of reports of the solid-state hydrogenation of organic compounds that appear to implicate hydrogen spillover as the mechanism for hydrogenation [49].

Thus, the hydrogen spillover process includes three consecutive steps. In the first step, H₂ molecules undergo dissociative chemisorption upon interacting with metal catalysts. Subsequently, H atoms on the catalyst surfaces migrate to the substrate in the vicinity of the catalyst particles. Finally, H atoms near the catalysts diffuse freely to the surface or bulk sites far from where the catalyst particles reside [49].

So, as it was mentioned before, hydrogen can be stored in the light nanoporous carbon materials by physisorption and the interaction between H₂ and host material is dominated only by weak van-der Waals forces, and only a small amount of H₂ can be stored at room temperature. Thus, high surface area and appropriate pore size are key parameters for achieving high hydrogen storage. The nanoporous carbon structures fulfill this criterion, placing them since the beginning among of the best candidates for hydrogen storage media.

5.2.3.1. Carbon nanotubes

Because of unique hollow tubular structure, large surface area, and desirable chemical and thermal stability carbon nanotubes (CNTs) are considered as a promising candidate for gas adsorption (Fig.12) [51].

The experimental results on hydrogen storage in carbon nanomaterials scatter over several orders of magnitudes. It was reported in 1997 that single-walled CNTs (SWCNTs) could store ~10 wt% hydrogen at room temperature, and predicted a possibility to fulfill the benchmark set for on-board hydrogen storage systems by DOE [26].

Soon after this work, other optimistic results of hydrogen storage in CNTs were reported [52,53]. A few years later, very low hydrogen storage capacity of CNTs started to emerge, in particular, those experimentally obtained at room temperature: lower than 0.1 wt% at room temperature and 3.5 MPa [54]. It was also pointed that “the application of CNTs in hydrogen storage is clouded by controversy” [55], the reproducibility is poor, and the

mechanism of how hydrogen is stored in CNTs remains unclear. In summary, it was mentioned that amount of hydrogen can be stored in CNTs, the reliable hydrogen storage capacity of CNTs is less than 1.7 wt% under a pressure of around 12 MPa and at room temperature, which indicates that CNTs cannot fulfill the benchmark set for onboard hydrogen storage systems by DOE [56]. However, higher values hydrogenation of carbon atoms in the SWCNTs (approximately 5.1 ± 1.2 wt%) was also demonstrated as well as reversibility of the hydrogenation process [57].

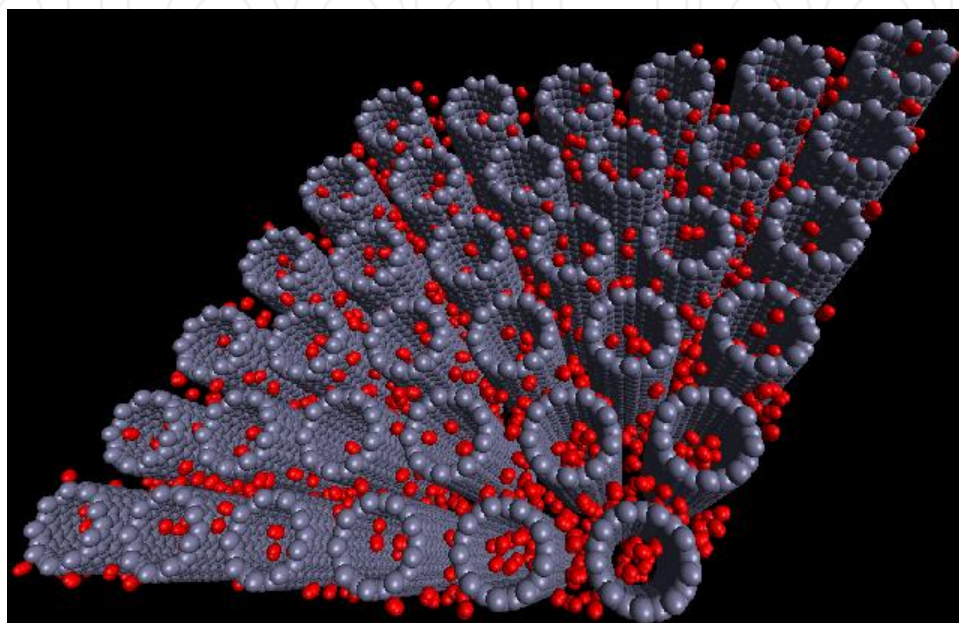


Figure 12. Hydrogen gas (red) adsorbed in an array of carbon nanotubes (grey). The hydrogen inside the nanotubes and in the interstitial channels is at a much higher density than that of the bulk gas [51].

All these results suggest that pure CNTs are not the best material for investigating hydrogen uptake. However, CNTs can be an effective additive to some other hydrogen storage materials to improve their kinetics. For example, the hydrogen storage capacity of CNTs can be increasing by the doping effect: potassium hydroxide (KOH) to increase the capacity of hydrogen storage on multi-walled carbon nanotubes (MWNTs) from 0.71 to 4.47 wt%, respectively, under ambient pressure [58]. Also, experimental results revealed that the structure of CNTs became destructive after being activated by KOH at 823 K in H_2 atmosphere [58].

Metal doping (Pt catalyst) influence on electronic structure and hydrogen storage of SWCNT was also studied [59]. It was represented that the spillover mechanism is responsible for hydrogenation of Pt-SWNT composites using molecular hydrogen (Fig.13). Moreover these materials store hydrogen by chemisorption, that is, the formation of stable C-H bonds. The hydrogen uptake indicates 1.2 wt% hydrogen storage for LB-film composites (monolayer assemblies of SWNT films prepared by the Langmuir-Blodgett method) and 1 wt% for chemical vapour deposition (CVD)-grown CVD composites. This maximum hydrogen storage was possible only after obtaining a uniform dispersion of monolayer thick unbundled SWNTs, doped with optimal size and density of Pt catalyst particles (~ 2 nm, which corresponds to nominal thickness of 6 Å) [59]. This storage capacity may be increased by improving the

kinetics of atomic-hydrogen diffusion from the Pt catalyst to the SWNT support and also by employing nonbundled CNTs with an increased Pt-to-C dispersion [59].

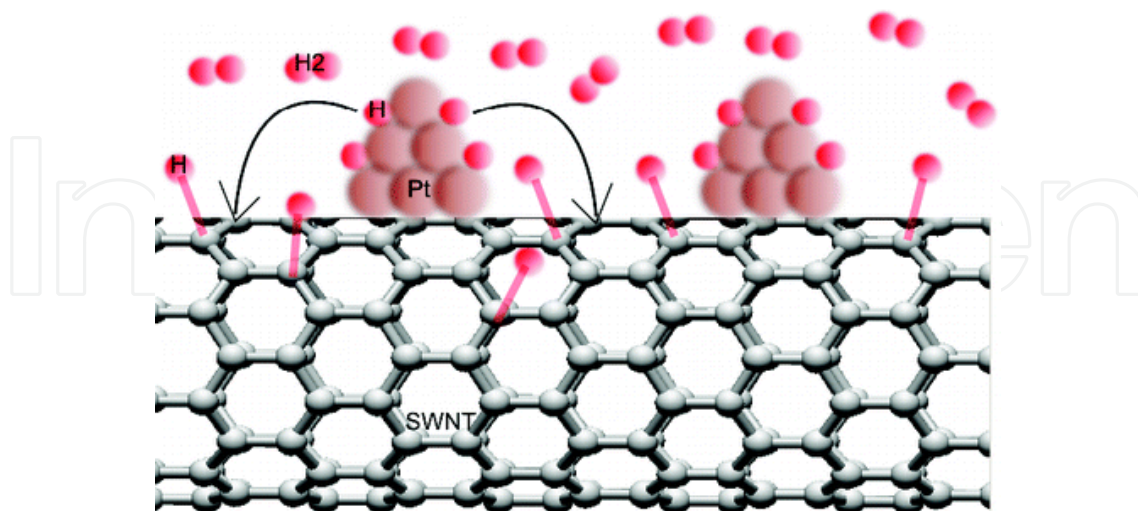


Figure 13. Schematic spillover mechanism: hydrogen uptake of single-walled carbon nanotubes is influenced by the addition of Pt nanoparticles [59].

5.2.3.2. Graphene and graphane

After the discovery of graphene scientists move in that direction. Graphene has one of the highest surface area-per-unit masses in nature, far superior to even carbon nanotubes and fullerenes [33-37]. It can store individual hydrogen atoms in a metallic lattice, through chemical bonding to a metallic host. Besides the physisorption, the chemisorption of hydrogen in graphene is even more interesting for catalysis and electronic purpose. For the first time, it was possible to isolate two dimensional mono layers of atoms. A suspended single layer of graphene is one of the stiffest known materials characterized by a remarkably high Young's modulus of ~ 1 TPa. The high thermal conductivity ($3000 \text{ Wm}^{-1} \text{ K}^{-1}$), high electron mobility ($15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and high specific surface area of graphene nanosheet are also few amazing characteristics of this material. As an electronic material, graphene represents a new playground for electrons in 2, 1, and 0 dimensions where the rules are changed due to its linear band structure (Fig.14) [60].

Recently, graphene has triggered enormous interest in the area of composite materials and solid state electronics. When incorporated into a polymer, its peculiar properties manifest as remarkable improvements in the host material. The mechanical and thermal properties of these materials rank among the best in comparison with other carbon-based composites. For energy applications graphene is a very suitable candidate to produce ultra high charge capacitor or super capacitor. Here, storage capacity must be realized by rapid charging and discharging of composite materials. Therefore, the charge and discharge kinetics must be very high. Recently, it was reported that by using of different activation procedures other than heat treatment, such as chemical reduction, to remove unreacted functional groups the O/C ratio could be reduced and improve the surface area and adsorption capacity of graphene oxide frameworks (GOFs) increases significantly [61]. Moreover, doping effect also can increase the capacity of hydrogen storage in graphene: the maximum hydrogen

storage capacity in lithium ion doped pillared graphene material (Fig.15) around 7.6 wt% in the condition of 77 K and 100 bar pressure [10].

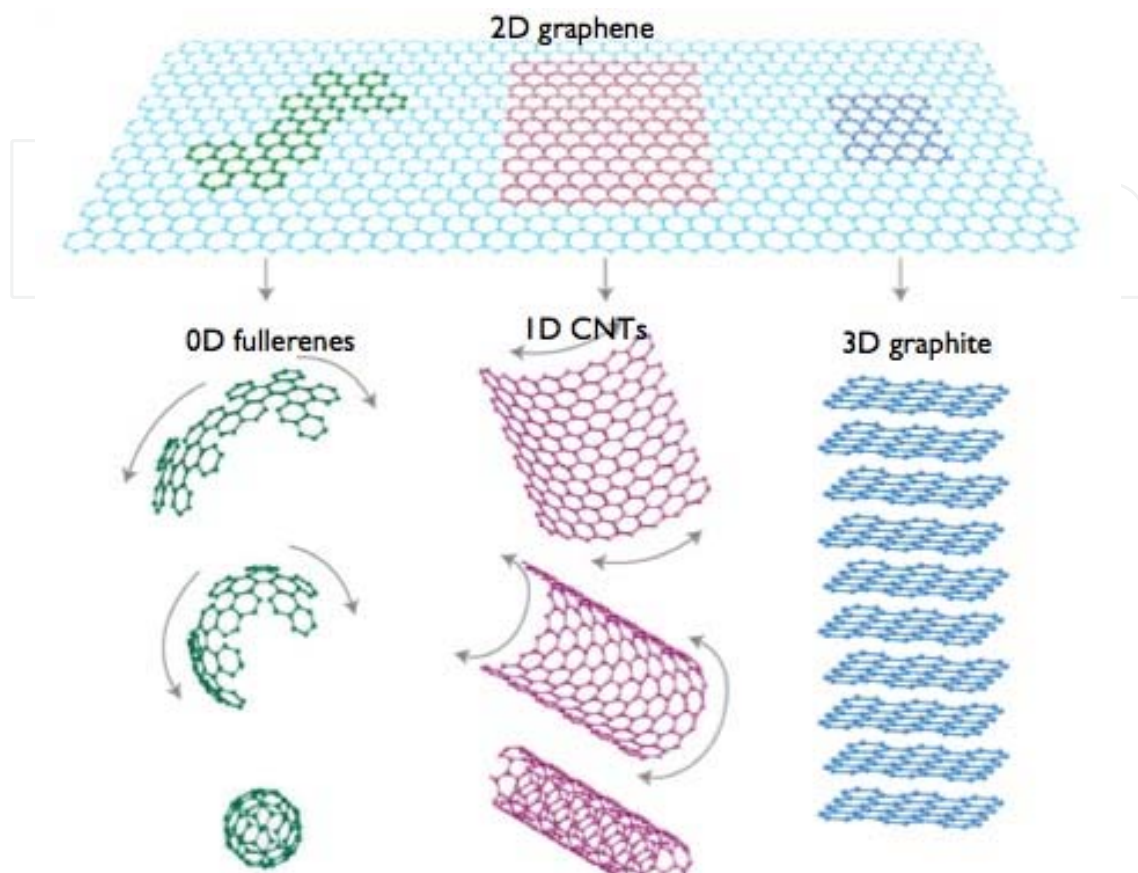


Figure 14. 2D Graphene can be transformed into CNTs, graphite, or fullerenes [60].

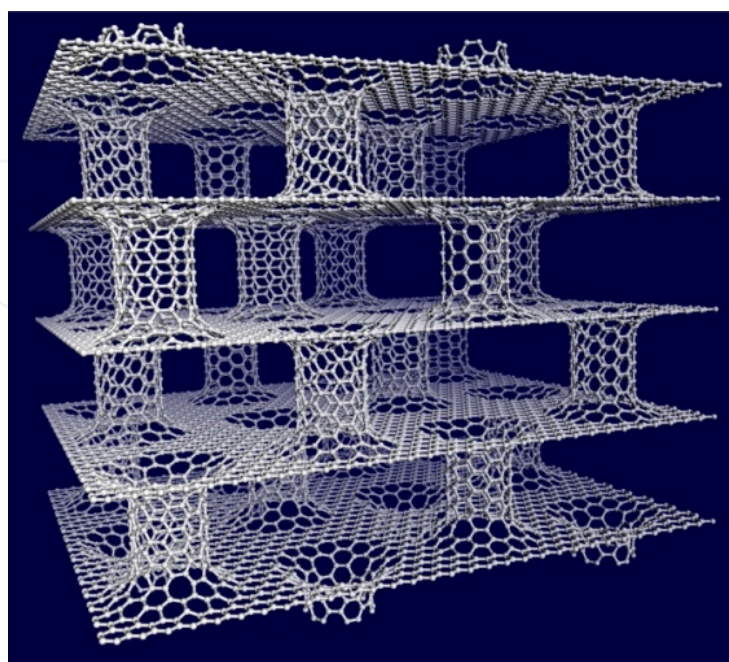


Figure 15. Pillared graphene structure, a theoretical approach [10].

Hydrogen storage is also dependent on number of layers of graphene. If graphene is single layer it can store more hydrogen as compare to bilayer or few layers. The analyse of multilayers of graphene on to the surface of Ru (0001) substrate by scanning tunnelling microscopy (STM) technique represented moiré patterns of superstructure as shown in Figure 16 [62]. Moiré pattern is generated due to the rotational misorientation between the layers. Graphene is one atom thick hexagonally arranged carbon material and whenever layers are stacking together (due to the van-der Waals forces) moiré pattern is observed. In the moiré pattern it was analyzed 12 stacking faults of graphene sheets with 2.46 Å typical lattices spacing of graphite [62].

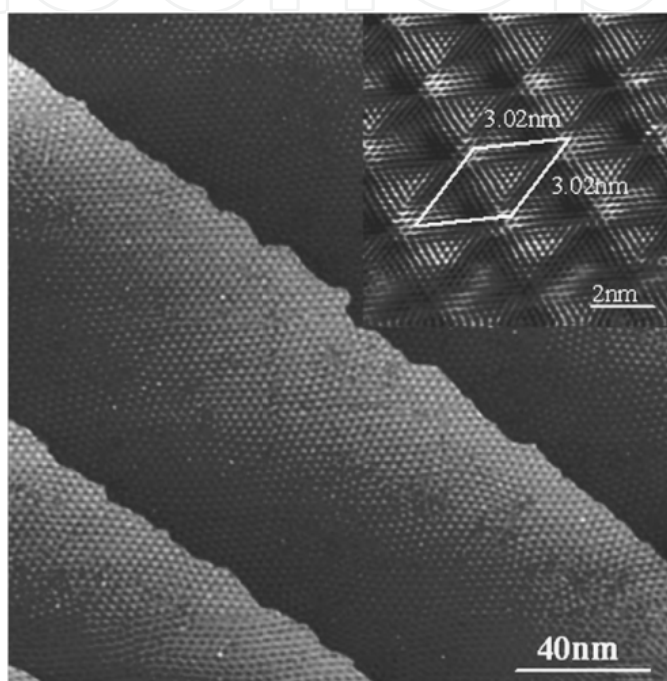


Figure 16. STM image (200 nm × 200 nm) of a monolayer graphene on Ru (0001). The moiré pattern with a periodicity of 30 Å is clearly visible. The inset shows the atomic structure of graphene/Ru (0001). The unit cell is marked as a rhombus [62].

The efficient hydrogenation of graphene can also be possible by catalytic conversion where catalyst provides a new reduction pathway of graphene through dissociation of graphene molecule [63]. The intercalated Ni nanoparticles inside of the alumina matrix with the flow of H₂ at 820°C demonstrated the catalytic hydrogenation of graphene films (Fig.17).

The degree of hydrogenation of graphene layers was also found 16.67 wt% and depended on the thickness of graphene [64]. Moreover, it was also reported about 100 % coverage of graphene by hydrogen atoms or each carbon atom has binding with hydrogen atoms. These results are very exciting that provides the future platform for hydrogenated graphene system [64].

The stability of a new extended two-dimensional hydrocarbon on the basis of first-principles total energy calculations was predicted [65]. The compound was called graphane and it was a fully saturated hydrocarbon derived from a single graphene sheet with formula CH. All of

the carbon atoms are in sp^3 hybridization forming a hexagonal network and the hydrogen atoms are bonded to carbon on both sides of the plane in an alternating manner (Fig.18). Graphane is predicted to be stable with a binding energy comparable to other hydrocarbons such as benzene, cyclohexane, and polyethylene.

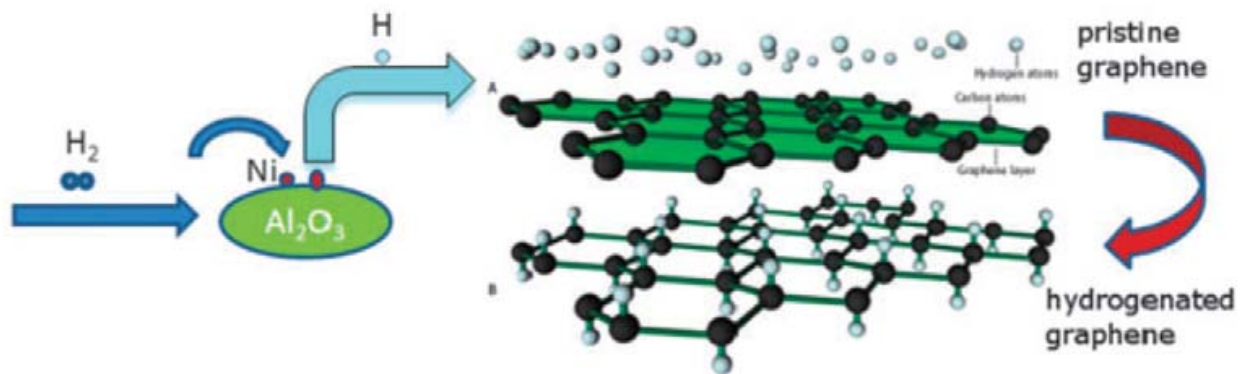


Figure 17. Schematic illustration for catalytic hydrogenation of graphene [63].

Thanks to its low mass and large surface area, graphane has also been touted as an ideal material for storing hydrogen fuel on vehicles. However, making graphane had proven to be difficult. The problem is that the hydrogen molecules must first be broken into atoms and this process usually requires high temperatures that could alter or damage the crystallographic structure of the graphene.

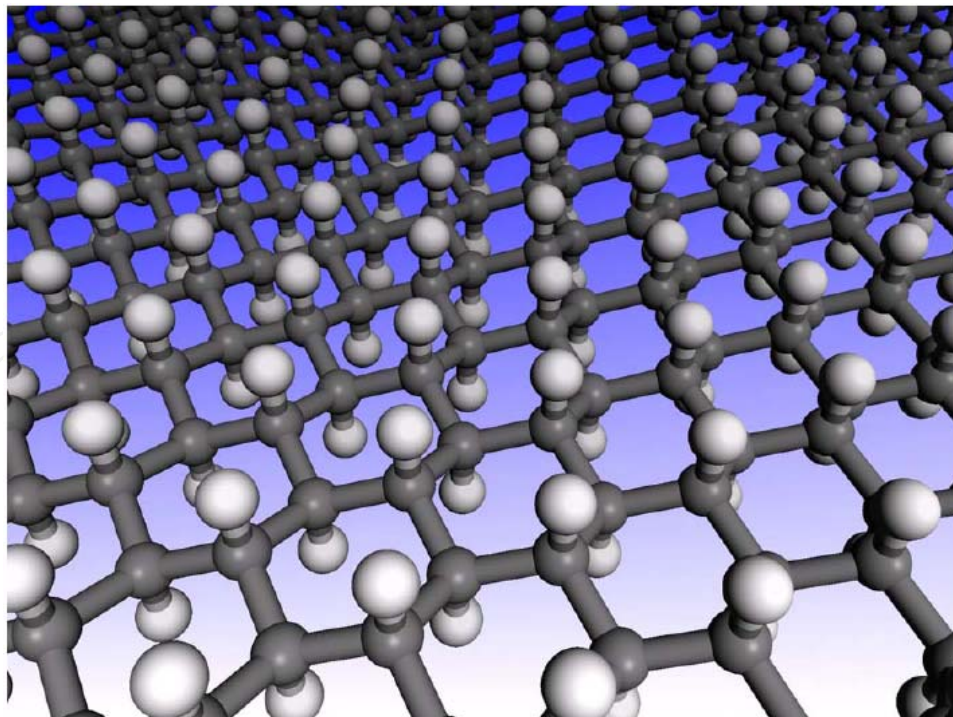


Figure 18. Structure of graphane in the chair conformation.

The carbon atoms are shown in gray and the hydrogen atoms in white.

The figure shows the hexagonal network with carbon in the sp^3 hybridization [65].

However, a team led by Geim and Novoselov has worked out a way to make graphane by passing hydrogen gas through an electrical discharge (Fig.19). This creates hydrogen atoms, which then drift towards a sample of graphene and bond with its carbon atoms. The team studied both the electrical and structural properties of graphane and concluded that each carbon atom is bonded with one hydrogen atom. It appears that alternating carbon atoms in the normally-flat sheet are pulled up and down - creating a thicker structure that is reminiscent of how carbon is arranged in a diamond crystal. And, like diamond, the team found that graphane is an insulator - a property that could be very useful for creating carbon-based electronic devices [66].

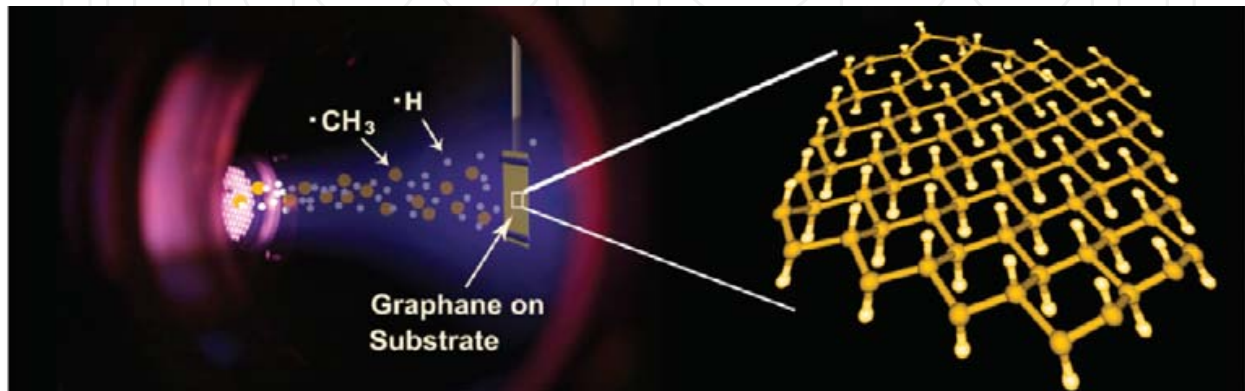


Figure 19. The growth of large-area graphane-like film by RF plasma beam deposition in high vacuum conditions. Reactive neutral beams of methyl radicals and atomic hydrogen effused from the discharged zone and impinged on the Cu/Ti-coated SiO₂/Si samples placed remotely. A substrate heating temperature of 650 °C was applied [67].

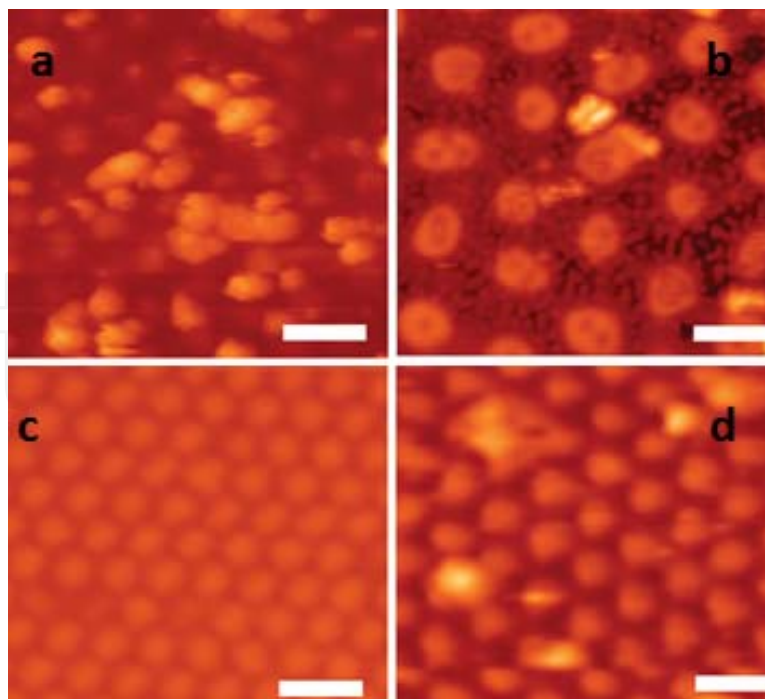


Figure 20. (a) STM images of graphane. The bright protrusions in the image are identified as atomic hydrogen clusters; (b) after annealing at 300 °C for 20 min; (c) after annealing at 400 °C for 20 min; (d) graphene recovered from graphane after annealing to 600 °C for 20 min. Scale bar 3 nm [67].

It was reported that the obtained graphane was crystalline with the hexagonal lattice, but its period was shorter than that of graphene. The reaction with hydrogen was found reversible, so that the original metallic state, the lattice spacing, and even the quantum Hall effect can be restored by annealing [67]. The degree of hydrogenation of graphene layers was analyzed by changing in moiré pattern and interconversion of graphane to graphene is presented in Figure 20.

6. Conclusion

The hydrogen revolution following the industrial age has just started. Hydrogen production, storage and conversion have reached a technological level although plenty of improvements and new discoveries are still possible. The hydrogen storage is often considered as the bottleneck of the renewable energy economy based on the synthetic fuel hydrogen. Different hydrogen storage methods and materials have been described already and need to be study more.

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