

Hydrogen Sorption Studies on Microporous and Mesoporous Materials

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Abstract:

Hydrogen storage has been envisaged as one of the challenging tasks to accomplish the goals for hydrogen economy. In this context, many systems are being investigated to improve the maximum hydrogen storage capacity (reversible), kinetics of sorption and desorption, moderate equilibrium pressure and/or decomposition temperature and better cyclability. This paper briefly reviews various on-going efforts to develop hydrogen storage technology in general and summarizes attempts made till date using microporous and mesoporous materials for hydrogen storage.

Keywords: Hydrogen storage, Zeolites, Zeo-type materials, Microporous materials, Mesoporous materials.

Introduction:

Owing to the dramatic environmental impact on emission norms and limited available stocks of fossil fuel, search for alternative clean fuel is becoming increasingly important [1]. As a result, Hydrogen has been identified as a future clean energy carrier [1].

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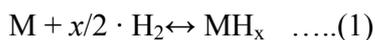
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However, use of hydrogen as an energy carrier involves many concerns which include a) production, b) storage, c) transportation, and d) safety issues [2]. In particular, hydrogen storage is envisaged as a major concern for meeting DOE targets both in terms of volumetric as well as gravimetric density for vehicular applications [2]. The major challenges in the development of new hydrogen storage materials are improved energy storage density, kinetics and cycle life, using readily available elements at a reasonable cost [2]. Thus numerous efforts are being undertaken to develop hydrogen storage system other than liquefaction and compression approaches. This includes use of metal hydrides, complex hydrides, chemical storage, carbon based nanoporous materials and microporous and mesoporous sorbents for hydrogen storage.

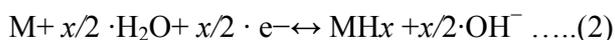
In the present paper, we briefly summarize aforementioned approaches and more particularly review the use of microporous and mesoporous media in hydrogen storage.

Metal hydrides:

Hydrogen is a highly reactive element and is known to form hydrides and solid solutions with numerous of metals and metal alloys [3]. Most of the natural elements adsorb and release hydrogen under specific temperature conditions to form metal hydrides either through dissociative chemisorption as per the following reaction.



where M represents the metal or by means of electrochemical splitting of water using a catalyst such as such as palladium / platinum, to break down the water as per the following reaction



The storage of hydrogen in the form of metallic hydrides offers several advantages, e.g. (i) relatively large hydrogen storage capacity, compared with the gaseous, liquid and even the solid form; and (ii) good reversibility of hydrogenation/ dehydrogenation with many metallic hydrides [3].

For optimum hydrogen storage, metal hydrides should meet the following criteria: high storage capacity, low dissociation temperature, moderate dissociation pressure, low heat

of formation in order to minimize the energy necessary for hydrogen release (and also less heat to dissipate during the exothermic hydride formation), low cost, light weight (in particular for transport applications such as electric vehicles) and high stability against O₂ and moisture for long cycle life [4].

In view of the above, numerous efforts have been reported to investigate the hydrogen storage potential for LaNi₅ and TiFe compounds, Zr- and Ti-based Laves phases, Mg₂Ni- and Mg-based materials, and composites based metal hydrides [5]. The formation of metal hydrides is an exothermic reaction. Significant heat is released during absorbing hydrogen and the same amount of heat is required in order to release hydrogen from the hydrides. More stable the hydride is, more heat is needed to desorb hydrogen. Typically, approximately 25% higher amount of energy is required to release hydrogen from MgH₂. Therefore, adsorption and desorption of hydrogen usually takes place at elevated temperatures and pressures [5].

On the other hand, metal hydrides which could absorb and desorb hydrogen at ambient temperature and near atmospheric pressure, offer high volumetric density for hydrogen for storage, but limited gravimetric density (about 3 wt%). For example, a volumetric density of 115 kg/m³ has been reported for LaNi₅H₆ system compared to gravimetric density of 1.4 wt% [6]. Recent attention turns to the hydrides formed by light metals, and Mg becomes the focus of attraction. But, it is still a challenge to find out an appropriate hydride of light metals with high hydrogen capacity.

Complex hydrides

If metal hydrides are to become important hydrogen storage materials in mobile applications, the mass of the system needs to be reduced from today's devices, such as FeTi. This puts strong constraints on the chemical elements which can be used. In such scenario, Group I, II, and III elements, e.g. Li, Mg, B, Al, which are known to build a large variety of metal–hydrogen complexes with about 2 hydrogen atoms per metal atom become ideal choice. For example, the hydride, MgH₂, can store up to 7.6 wt.% of hydrogen [7,8]. Such complexes show the highest volumetric density, 150 kg/m³, as in

Mg_2FeH_6 and $\text{Al}(\text{BH}_4)_3$. Among the complex hydrides, LiBH_4 shows the highest gravimetric density (18 wt%) at room temperature [9-18]. Some of the lightest elements NaAlH_4 , LiBH_4 and NaBH_4 commonly known as alanates can absorb hydrogen at moderate temperatures and has attracted recent attention. However, the low dynamics of the hydrogen releasing process at moderate temperatures is a major problem for practical utilization. Hence, a high temperature (623-873 K) for hydrogen desorption is essential. Furthermore, the reversibility of the hydrogen storage is not yet clear for all systems. Recently, it has been shown that desorption temperature for hydrogen release could be brought down in the range of 543-573 K by doping the hydride with TiO_2 [19-22].

Unlike the metallic hydrides, hydrogen is released via cascade decompositions from the complex hydrides, and the step reactions call for different conditions. Therefore, there is a large difference between the theoretical and the practically attainable hydrogen capacities. Besides, significant changes in the particle morphology and elemental distribution were induced by hydrogen desorption. Repeated absorption/desorption cycles have to be tested before the conclusion regarding the potential application being made. $\text{Al}(\text{BH}_4)_3$ also has very high gravimetric hydrogen density (17 wt%). It has a melting point of $-65\text{ }^\circ\text{C}$ and is liquid at room temperature. However, very little is known about it today.

Chemical Storage:

Chemical storage option for hydrogen is one of the options being explored. Among such approach, the feasibility of using aminoborane (NH_3BH_3) as an on-board hydrogen storage medium has been identified as promising route. This is because the aminoborane molecule has 19.6% by weight of hydrogen in its molecular formula and thus has potential to meet DOE's year 2015 targets of gravimetric (0.09 kg H_2 /kg of system weight) as well as volumetric (0.081 kg H_2 /L of system volume) energy densities [23-26]. The studies show that if the cost of ammonia-borane production were to be reduced, it would be realized to use it for on-board hydrogen applications such as fuel cells.

Chemical compounds containing hydrogen can also be considered as a kind of hydrogen storage. These include e.g. methanol CH_3OH , ammonia NH_3 , and methylcyclohexane $\text{CH}_3\text{C}_6\text{H}_{12}$. At STP, all of these compounds are in liquid form and thus the infrastructure for gasoline could be used for transportation and storage of the compounds. The hydrogen storage capacity of these chemical compounds is quite good – 8.9 wt% for CH_3OH , 15.1 wt% for NH_3 , and 13.2 wt% for $\text{CH}_3\text{C}_6\text{H}_{12}$ [27]. These figures do not include the containers in which the liquids are stored. The containers can be made of light-weighted composites or even plastic in some cases making the effect of container weight on the overall weight negligible, especially with larger systems.

Chemical storage of hydrogen has also some disadvantages. The storage method is non-reversible, i.e. the compounds cannot be “charged” with hydrogen reproducibly. The compounds must be produced in a centralized plant and the reaction products have to be recycled somehow. This is difficult especially with ammonia, which produces highly pollutant and environmentally unfavorable nitrogen oxides. Other compounds produce carbon oxides, which are also quite unfavorable.

Microporous and Mesoporous media:

The discovery of carbon and boron nitride nanotubes [29, 30] and their successful evaluation for hydrogen storage has recently attracted much attention for microporous and mesoporous materials as storage media. According to IUPAC classification, materials are classified as microporous, having pore size less than 2 nm, mesoporous, having pore size between 2-50 nm, and macoporous with pore size above 50 nm [31]. The hydrogen has been reported to store over these materials by means of van der Waals forces exerted by walls of nanotube on hydrogen molecule via physisorption mode. Thus, uptake of hydrogen is often found to be reversible. Because of which, H_2 storage by molecular adsorption over microporous and mesoporous media could represent an advantage with respect to dissociative processes, where kinetic effects during the charging and discharging processes are present.

As the physisorption of any gas is carried out at or above 77 K due to practical limitations, the gas can be physisorbed on to the solid surface either by capillary condensation provided the pore size of the solid is more than 2 nm or by volume filling mechanism for solids having pore size of less than 2 nm at or near critical temperature of the gas. However, hydrogen, whose critical temperature is 33 K, is under super critical conditions at 77 K. Thus the hydrogen is physisorbed by monolayer coverage over the solid surfaces irrespective of their pore dimensions. Therefore, solids with high surface area and having specific affinity for hydrogen molecule are highly essential for hydrogen storage. In the following sections, the hydrogen uptake studies on various microporous and mesoporous structures are reviewed.

Carbon Materials:

Among, carbon based materials; the best performance in hydrogen storage is envisaged for those structures having high surface area in the form of the highest effective porosity. Such criteria is met by two advanced carbon structures namely, fullerenes and nanotubes with special properties. Typically, fullerenes are made up of multiple layers of graphite which are wrapped together into very stable ball (Fig. 1a). Like wise, wrapping of multilayers of graphite into tubular shape leads to formation of single-wall carbon nanotube (SWCT), Fig. 1b.

Fullerenes:

Fullerenes are a new class of carbon aromatic compounds with unusual structural, chemical and physical properties which, in turn, is foreseen as an ideal candidate for novel and unexpected applications [32, 33]. They are synthesized by electric arc discharge method in which carbon is vaporised between two graphite electrodes to obtain C₆₀ / C₇₀ fullerenes having football shape. They are able to hydrogenate through the reaction:



According to theoretical calculations, the most stable of these are C₆₀H₂₄, C₆₀H₃₆ and C₆₀H₄₈, latter of which corresponds to 6.3 wt.% of adsorbed hydrogen. This has been indeed observed at 180 °C and at about 25 bar [32, 33]. However, desorption of hydrogen

is only possible above 400 °C as the bonds between C and H atoms are very strong. Despite the quite high hydrogen-storing ability, the cyclic tests of fullerenes have shown poor properties of storing hydrogen.

Carbon nanotubes:

These structures were discovered accidentally in 1991, while synthesizing fullerenes. Owing to the unique porous tubular carbon structure of nanotubes, this microporous carbon form has been predicted to have many interesting properties capable of numerous applications in mechanical, electrical and many other domains [29]. Due to this, numerous synthesis methodologies are being developed. The most commonly practiced route employs a hydrocarbon source such as acetylene, methane, which is carbonized at elevated temperature in the presence of transition metals such as nickel, cobalt to form nanotubes. Nanotubes so obtained are classified into two different species, characterized by the structure of their wall: the single-walled nanotubes (SWNT) and the multi-walled nanotubes (MWNT). SWNT consist of a graphene sheet rolled up into a cylinder of a few nanometers diameter and several microns length. Most of them are aligned and packed together to form ropes of 10–100 parallel tubes. Their synthesis in significant quantities is yet a challenge to take up especially to obtain a pure material. On the other hand, a MWNT is an arrangement of coaxial tubes of graphite sheets ranging in number from two up to about fifty. The synthesis, purification, and characterization of such type of materials have recently been reviewed [34].

Hydrogen storage on nanotubes can occur by both physisorption and chemisorption mode. However, the methods of trapping hydrogen are not known very accurately but density functional calculations have shown some insights into the mechanisms. The nanotubes considered in molecular simulations are open tubes, well structured, without amorphous carbon and impurities, having well determined and chosen diameters and geometrical location in the bundles.

These calculations indicate that hydrogen can be adsorbed at the exterior of the tube wall by H-C bonds with a H/C coverage 1.0 or inside the tube by H-H bonds with a coverage

up to 2.4. In view of this, hydrogen uptake as a monolayer at the surface of the nanotube or as a condensate in the cavity with same density as that of liquid hydrogen at 20 K is anticipated [34].

The adsorption into the interior wall of the tube is also possible but not stable. The hydrogen relaxes inside the tube forming H-H bonds. Multi-wall nanotubes, in which two or more single tubes are rounded up each other with van der Waal's attraction, can adsorb hydrogen between the single wall nanotubes because of which the radius of the tubes increases leading to instability for a multi-wall nanotube during hydrogen storage. In nanotube bundles hydrogen can also be adsorbed in the middle of different tubes. The density functional calculations have shown that theoretically in proper conditions a single-wall nanotube can adsorb over 14 wt.% and a multi-wall nanotube about 7.7 wt.% of hydrogen [34].

The uptake value in the range of 5-10 wt% has been indeed noticed. Furthermore, alkali doped nanotubes are reported to store even 20 wt.% under ambient pressure, but are unstable or require elevated temperatures for storage. This result has been found to be ambiguous in the literature. Recently an uptake of 7 wt% at 0.67 bar and 600 K, on a single wall nanotube is noticed with a good cycling stability. Another result at ambient temperature and pressure shows that 3.3 wt.% hydrogen can be adsorbed and desorbed reproducibly and 4.2 wt.% hydrogen with a slight heating. Recent evidence surfaced to show the feasibility of semiconducting carbon tubes as being better suited for hydrogen storage applications [34].

Although nanotubes are envisaged as promising candidate for hydrogen storage, difficulties of elaboration and purification, has limited their potential use for device fabrication for hydrogen storage and reported capacities are still questionable.

Activated carbon:

This form of carbon is microporous in nature and has high surface area. In general, activated carbon is produced by mixing a chemical agent such as phosphoric acid with a

carbonaceous material obtained from walnut / coconut shells, sawdust (CS) and carbonising the resultant mixture at elevated temperature under inert atmosphere. The resulting very porous carbon structure is filled with activation agent, which removed from carbon by washing to form porous predominately a microporous carbon network. The pores in activated carbons are scattered over a wide range of size and shape. Owing to the pore dimension, the hydrogen sorption in such material takes place either at high pressure or at cryogenic conditions (77 K). The pores are classified by their sizes usually into three groups: (i) macropores having average diameter more than 50 nm, (ii) mesopores with diameter 2–50 nm and (iii) micropores having average diameter less than 2 nm. These are further divided into supermicropores (0.7–2.0 nm) and ultramicropores of diameter less than 0.7 nm [31]. The pore structure in wood derived carbons is a memory of the texture of the precursor wood and hence differ based on the type of wood/plant. In some wood carbon, these are of similar shape and size and are equally distributed, whereas in coal they are of very different shapes and sizes and are organized in circular fashion. These macropores are in turn connected to mesopores and micropores. For microporous carbons, the details of the pores (size and shape) apparently affect the specific H₂ uptake to a large extent.

Thus, storage capacity ranging from about 0.5 to 2.2 wt% has been achieved at cryogenic temperatures and 1 atm (Table 1). However, such capacity is found to be poor at ambient temperature [35].

Research and development efforts are continuing for more and more efficient applications of these materials. Carbon molecular sieves (CMS), are a special class of active carbons having small pore sizes with a sharp distribution in a range of micropores, as compared with other activated carbons. The pore size in CMSs is comparable to the size of adsorbate molecules, such as nitrogen and hydrogen. But less information is available on their use as hydrogen storage media. Like wise, the potential of recently discovered mesoporous carbons is yet to be investigated.

Boron Nitride nanotubes:

Boron nitride (BN) is one of the most interesting materials of the Group III-V compounds with a potentially bright future in advanced materials design [30]. In recent years, much research interest was focused on BN nanostructures represented by BN nanotubes [30]. The investigations aiming to probe certain properties of BN nanotubes for potential applications are becoming more and more important. In general, BN nanotubes are prepared through a chemical vapor deposition process by pyrolyzing the B-N-O precursor at ~ 2000 K under N_2/NH_3 atmosphere. The morphologies of the nanotubes are controlled by varying the oxygen contents in the B-N-O precursors. Specifically, multiwall nanotubes are obtained with $B_4N_3O_2H$ precursor (oxygen content 27%). On the other hand, bamboo-like nanotubes (bamboo purity $\sim 90\%$) are produced with BN powder precursor enriched with oxygen (oxygen content $\sim 10\%$). On the basis of TEM characterizations, multiwall nanotubes generally have a narrow diameter distribution from 10 to 30 nm and lengths of a few micrometers and the tubes are capped at each end [30].

Synthesized carbon nanotubes feature highly complex electronic properties owing to their diversity in diameter and helicity. This is one of the probable reasons for the “hydrogen storage controversy” in carbon nanotubes, i.e., highly different results reported from different groups. Conversely, BN nanotubes are semiconducting with the gap of ~ 5.5 eV nearly independent of the tube diameter and helicity. BN nanotubes also have a preferential nonhelical or “zigzag” orientation (the tube axes along the $[10\bar{1}0]$ direction). Taking into account the chemical and thermal stability, BN nanotubes ultimately may be stable lightweight hydrogen gas accumulators [30]. It is thus rather reasonable and of great interest to look into the hydrogen uptake capacity in BN nanotubes. Recently, a total hydrogen concentration of 2.6 wt % has been reported for mechanically milled h-BN powders under a hydrogen pressure of 10 bar [36]. This offers some perspective for the (de-) hydriding properties of BN. On the other hand, multiwall BN nanotubes have been reported to show uptake in the range of 1.8-2.6 wt % ~ 100 bar at room temperature. Attempts have been made to prepare BN fullerene materials and evaluate their potential for hydrogen storage. It is proposed that BN fullerene would be a good candidate for

hydrogen storage applications with its better resistance to heat and calculated hydrogen storage capacities show that BN stored H₂ easier than carbon fullerenes [37].

In view of this further efforts are needed for the mass production of BN nanotubes and optimization of post production treatment protocols for a thorough investigation of the hydrogen adsorption/desorption mechanism.

Sulfide based nanotubes:

The transition-metal dichalcogenide TiS₂ has been originally of interest as insertion materials of the positive electrode of lithium batteries. Structurally, atoms within a S-Ti-S sheet are bound by strong covalent forces, while individual S-Ti-S layers are held together by van der Waals interactions. This enables the introduction of foreign atoms or molecules between the layers by intercalation. Therefore, to exploit such mechanism for hydrogen storage, considerable research has been devoted to the synthesis and characterization of transition-metal disulfide nanotubes in the past decade. Significant breakthrough is obtained for preparation of WS₂ and MoS₂ nanotubes through gas-solid reaction at elevated temperatures (1073-1273 K) [38]. Single-wall MoS₂ nanotubes bundles with long length are prepared by a C₆₀-catalyzed transport reaction. Like wise, Groups IVB and VB transition-metal disulfide nanotubes with multiwalls are obtained through the thermal decomposition of metal trisulfides in a hydrogen atmosphere at 1073-1273 K. MoS₂ nanotubes have been demonstrated to store hydrogen via. electrochemical process [39]. Recently, the high-purity multiwalled TiS₂ nanotubes with open-ended tips, have been shown to efficiently store 2.5 wt % hydrogen at the temperature of 298 K and under the hydrogen pressure of 40 bar through physisorption and chemisorption mode [40].

Zeolites and zeo-type materials:

Crystalline aluminosilicates, commonly known as zeolites, are microporous in nature [41]. Wide spread applications of zeolites in the filed of catalysis and separation science has led to the discovery of zeo-type materials. Zeo-type materials such as crystalline microporous aluminophosphate molecular sieves frameworks offer flexibility to modify the microporous framework properties via. hetero-atom substitution like zeolitic

framework. Till date numerous aluminosilicate and aluminophosphate based compositions have been successfully prepared and their applicative potential in the area of catalysis and separation science is being exploited. Efforts are also being continuously made to prepare novel microporous frameworks. Typically, these materials have large surface area in terms of their micropore volume and are ideal hosts for guest molecule via sorption phenomena. In view of this, zeolites and zeo-type materials are envisaged as ideal candidate to investigate the hydrogen storage. The presence of charge balancing extraframework cations and flexibility of ion-exchange has offered unique opportunities for sorbent development for gas separation. Typically, sorption potential (ϕ) for any guest molecule within the micropores of zeolite is governed by

$$\phi = \phi_D + \phi_R + \phi_P + \phi_{F-\mu} + \phi_{F-Q} \text{-----(4)}$$

Where, ϕ_D , ϕ_R , ϕ_P , $\phi_{F-\mu}$, and ϕ_{F-Q} correspond to contribution from dispersion, repulsion, polarization, dipole moment and quadrupole interactions [42]. The physical properties of hydrogen (Table 2) illustrates absence of interactions such as dipole and quadrupole interaction and the only possibility of weak physisorption during hydrogen sorption within micropores. Thus, hydrogen sorption in zeolite pores is governed mainly by physisorption mechanism and hence is highly reversible which is advantageous. In view of this, attempts have been made to explore the sorption potential of zeolites and zeo-type materials for hydrogen storage.

The feasibility of the sodalite-type (SOD) structures, $\text{Si}_6\text{O}_{12}:(\text{all-Si})$, $\text{Na}_3\text{Si}_3\text{Al}_3\text{O}_{12}:(\text{Na-AlSi}(3:3))$, $\text{Al}_3\text{P}_3\text{O}_{12}:(\text{AlP}(3:3))$, and $\text{Ge}_6\text{O}_{12}:(\text{all-Ge})$, as hydrogen storage media is assessed by calculating the hydrogen uptake isotherms by means of grand canonical Monte Carlo (GCMC) calculations for the range 73–773 K and 0–3000 bars. A structural representation of SOD framework is shown in Figure 2. Typically, a Type I Hydrogen sorption isotherm is observed over these materials thus indicating the presence of micropore filling phenomena while hydrogen sorption. At 573 K and 100 bar, a storage capacity of around 0.1 wt% is expected for each SOD-type. This lies far below the required capacity for a technically feasible H_2 storage medium. The more technologically

interesting capacities of >4 wt% are only found to be achieved under extremely low temperature and/or extremely high pressure conditions [43].

Recently, the H₂ adsorption isotherms at 77 K in H-SSZ-13, HSAPO-34 and H-ZSM-5 have been reported for the pressure range 0–0.9 bars. They show a linear increase for pressures up to 0.005 bar after which the isotherms start to flatten a little. The measured H₂ uptakes at 1 bar and 77 K depend on the exact structures but all lie around 1 wt% which is in quantitative agreement with the calculated uptakes in SOD at 1 bar and 77 K. Furthermore, it is noticed that, the calculated H₂ adsorption isotherm of all-Si SOD and the experimentally measured isotherm of HSSZ-13 are shown to illustrate the good qualitative agreement of the curves [43]. Like wise attempts have been made to measure hydrogen sorption potential for many zeolitic frameworks as list in Table 3 . However, the capacity is found to be low (about 1 wt%) at 1 bar and 77 K.

Attempts are being made to overcome the problem of slow kinetics with metal hydride systems, by growing nanostructured metal grids (about 1 nm metal thickness) with about 50% micro porosity (about 1 nm wide pores) using zeolite as a host. This has been anticipated to increase the overall hydrogen dissociation reaction rate (since the external metal area is greatly enhanced) and decrease the diffusion time constants (since the diffusion path is greatly reduced). In addition, the high mass transfer rates through the pores and hydrogen dissociation dispersed throughout the metal will enhance the energy transport in the metal. The flexibility of such a grid is expected to lower decrepitation caused by cycling. Hydrogen storage capacity may also increase due to contributions by physical adsorption and through possible quantum effects. Thus, successful attempts are made to prepare metal grids through electrochemical approach in faujasite pores where the faujasite was crystallized in-situ on flat anodized titanium cathodes [44].

Unlike aluminosilicates, aluminophosphates are yet to be explored as a storage media. The work in our laboratory on such materials is being carried out. The hydrogen sorption on SSZ-51, a novel aluminophosphate framework is found to sensitive toward its framework composition. The measured sorption isotherms are found to be reversible at

77 K. The pure aluminophosphate framework is demonstrated to sorb hydrogen up to 1.1 wt% at 77 K and 1 bar pressure (Fig. 3). On the other hand, isomorphous substitution by Cobalt ion, in place of framework aluminum ion, found to lower its sorption capacity [45]. Furthermore, attempts are also made to measure H₂ over various silica gel samples.

Novel microporous frameworks:

In order to identify the best suitable Hydrogen storage media, attempts are being made to synthesize novel materials. This has led to successful synthesis of Nickel phosphate based microporous frameworks called VSB-1, and -5 [46, 47]. These frameworks are prepared under hydrothermal conditions with varying Ni/P framework ratio from 1.0, 1.66, and 2.5 [48]. The structural elucidation for such materials has revealed the presence of unsaturated Ni²⁺ sites in the microporous framework [46]. Such sites are anticipated to offer unique site for hydrogen uptake. Thus, attempts have been made to evaluate the hydrogen sorption potential for VSB-5 at 77 K [50]. The measured capacity is found to be about 0.33 wt% at 77 K. In our laboratory, we have synthesized VSB-5 framework with varying Ni/P ratio of 1.0, 1.66, and 2.5, respectively, under microwave-hydrothermal conditions. The measured hydrogen sorption isotherms (Fig. 4) demonstrated the highest capacity for framework having Ni/P ratio of 1.66 even though the higher density of unsaturated Ni²⁺ sites is envisaged with framework having Ni/P ratio of 2.5 [45]. This result illustrates the need for understanding the hydrogen sorption mechanism over such microporous solids.

Microporous metal coordination materials (MMOMs):

Porous metal coordination structures represent a promising new entry to the field of hydrogen storage materials. To fully exploit this new field, relationships between structure and storage properties must be developed to guide the further rational design and synthesis of tailored materials with significantly improved hydrogen adsorption capability. In view of the above, attempts are being made to synthesize new type of sorbents called microporous metal coordination materials (MMOMs) with pore dimensions comparable to the length scale of the molecular diameter of hydrogen [50].

The MMOMs share physical characteristics similar to those of single-walled carbon nanotubes (SWNTs) that have been under intense investigation as storage materials. Both are lightweight and composed of open channels based on aromatic carbon. In addition, MMOMs possess several advantageous features over SWNTs that are particularly promising for improving hydrogen adsorption. For example, the MMOMs incorporate metals that can bind hydrogen much more strongly than graphitic carbon, but not as strongly as when a true chemical bond forms as in the case of metal hydrides. Furthermore, the organic components can be modified to induce stronger interactions with H₂. The open channels in MMOMs are perfectly ordered, allowing effective access of hydrogen to the interior space. The internal surfaces of MMOMs can easily be modified to change the channel curvature, thus enhancing the H₂- sorbent interactions. They are synthesized by “one-pot” synthesis approach which is simple, cost effective, and highly reproducible. More importantly, the structures of these materials, including the metal building unit, pore dimension, shape, size, and volume, can be systematically tuned for the purpose of modifying and improving hydrogen uptake and adsorption/desorption properties [51].

This has led to successful synthesis of mesoporous MOF-5 [50], Cu-(hfipbb)(H2hfipbb)_{0.5} [H2hfipbb= 4,4-(hexafluoroisopropyl idene)- bis(benzoic acid) framework [52], Scandium terephthalate [Sc₂(C₈H₄O₄)₃] framework [54]. MOF framework is observed to sorb 1.65 wt %hydrogen at 48 atm at room temperature in spite of having accessible volume of about 76.8 % based on its framework density. On the other hand, Cu- (hfipbb)(H2hfipbb)_{0.5} [H2hfipbb= 4,4-(hexafluoroisopropyl idene)- bis(benzoic acid) framework is found to sorb about 1 wt % at 48 atm and room temperature. It may be noted that Cu- (hfipbb)(H2hfipbb)_{0.5} [H2hfipbb= 4,4-(hexafluoroisopropyl idene)- bis(benzoic acid) framework has accessible volume of 11.6% based on framework density calculations. This suggests that pore volume is not the sole factor that determines the amount of gas adsorbed. The quality of the pores that contribute to the pore volume must be considered as well. One critical aspect of pore quality is the relative size of the pores with regard to the gas that is taken in.

Thus it is apparent that an optimal material would have pores that fit the size of the gas molecules well and have the largest possible pore volume. Positive evidence for a restricted pore size in Cu-(hfipbb)(H₂hfipbb)_{0.5} [H₂hfipbb= 4,4-(hexafluoroisopropylidene)-bis(benzoic acid) framework was found by comparing isotherms obtained for methane with those for hydrogen wherein the molar ratio of methane to hydrogen sorbed at 48 atm was 0.75, while for the larger pore size material of similar structure it was 1.7 [52].

More recently, metal-organic frameworks based on linking zinc oxide clusters with benzene-1,4-dicarboxylate, naphthalene-2,6-dicarboxylate, 4,5,9,10-tetrahydropyrene-2,7-dicarboxylate, 2,3,5,6-tetramethylbenzene-1,4-dicarboxylate, or benzene-1,3,5-tris(4-benzoate) were synthesized in gram-scale quantities to measure their hydrogen uptake properties. Hydrogen adsorption isotherms measured at 77 K showed a distinct dependence of uptake on the nature of the link. At 1 atm, the materials sorb between 4.2 and 9.3 molecules of H₂ per formula unit with an increase in number of rings in the organic moiety. Such study has given guidelines for optimization of pore size and adsorption energy by linker modification, impregnation, catenation, and the inclusion of open metal sites and lighter metals to enhance hydrogen sorption potential of MMOM framework [54].

The Scandium terephthalate [Sc₂(C₈H₄O₄)₃] framework is found to be microporous with a pore size of about 0.6 nm. Such material is reported to sorb 1.1 wt% hydrogen at 77 K and 1 atm [53].

More recently, An investigation of the hydrogen-adsorption properties of the two MMOFs [M₃(bpdc)₃bpy]·4DMF·H₂O [M = Zn(**1**), Co(**2**)] at low temperatures has revealed very interesting adsorption properties. The hydrogen uptakes (wt.-%) at 77 K (or 87 K) and 1 atm are 1.74 (1.32) and 1.98 (1.48) for **1** and **2**, respectively, among the highest values reported so far for metal-organic-based porous materials. The study also suggested that the difference in the H₂ uptake between the two structures can be attributed to their pore volumes (0.33 and 0.38 cm³ g⁻¹ for **1** and **2**, respectively), as well

as the extent of gas–solid interactions, which is indicated by the isosteric heats of adsorption [55].

Mesoporous and large pore materials:

The discovery of M41S and SBA-15 family of mesoporous silica family has offered unique opportunities to explore various applications in diverse field [56, 57]. This has also offered opportunity to investigate the sorption potential of these materials for hydrogen storage. Unfortunately, attempts made in this regard are scarce. Such material also offers unique opportunity to prepare mesoporous carbon [58], and organosilica frameworks [59]. However, these are yet to be proven as a hydrogen storage media. Like wise, large pore zeolite UTD-1 is yet to be explored [60].

Recently, the hydrogen adsorption of mesoporous carbon materials with different mesostructures, surface areas, and pore volumes has been investigated. Experimental results indicate that the hydrogen adsorption capacities are dominantly related to their surface areas. A hydrogen adsorption capacity of 1.78 wt % was obtained at 77 K and ambient pressure of about 1 bar for the mesoporous carbon with a surface area of 2314 m²/g [35]

In our laboratory, we have investigated the hydrogen sorption potential for SBA-15 mesoporous silica. Such material is found to sorb about 0.3 wt % at 77 K and 1 atm (Fig. 5) [45].

Summary:

Ongoing efforts for identifying the best suitable approach for hydrogen storage have led to numerous attempts in investigating the potential of metal hydrides, complex hydrides chemical storage. Although such systems hold promise but slow kinetics and high desorption temperature for hydrogen recovery limits their utilization. To overcome these limitations, efforts are being made to investigate the effect of dopants especially to reduce the hydrogen recovery temperature.

Alternatively, hydrogen sorption potential of microporous and mesoporous media, which offers reversibility, is being explored as a storage media. In this context carbon and boron nanotubes, fullerenes, zeolites, metal-organic microporous and mesoporous frameworks have been investigated. Among these, carbon nanotubes are judged as potential candidates. However, ambiguity on the reproducibility and cycle life has imparted interest in boron nitride nanotubes. However, efforts are required to address the issues related to cost effective mass production of boron nitride nanotubes. On the other hand, zeolites, activated carbon and related solids show highly reversible H₂ sorption, but the drawback with these materials is represented by their extremely weak interactions that require low temperature and high pressure to achieve high hydrogen storage capacity. Among the explored materials, MMOFs are promising candidates, but still lack in storage capacity to meet DOE targets. Thus, high surface area materials, hosting polarizing sites to achieve high packing density for adsorbed hydrogen molecules, can represent a viable way toward more favorable working conditions.

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Figures:

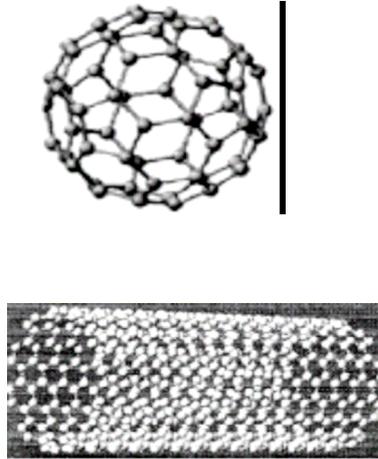


Fig.1. Structure of (a) fullerenes and (b) single wall carbon nanotube.

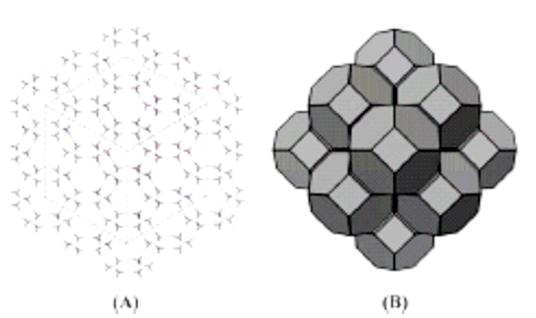


Fig. 2. Schematic representations of a super cell of sodalite: $3 \cdot 3 \cdot 3$ super cell with the viewing angle projected along the six-ring pores, black is a T-atom (T = Al, Si, Ge, P; cations are not shown) and grey is oxygen. The dashed cube is added to show how the cubical super cell is positioned in this representation of sodalite.

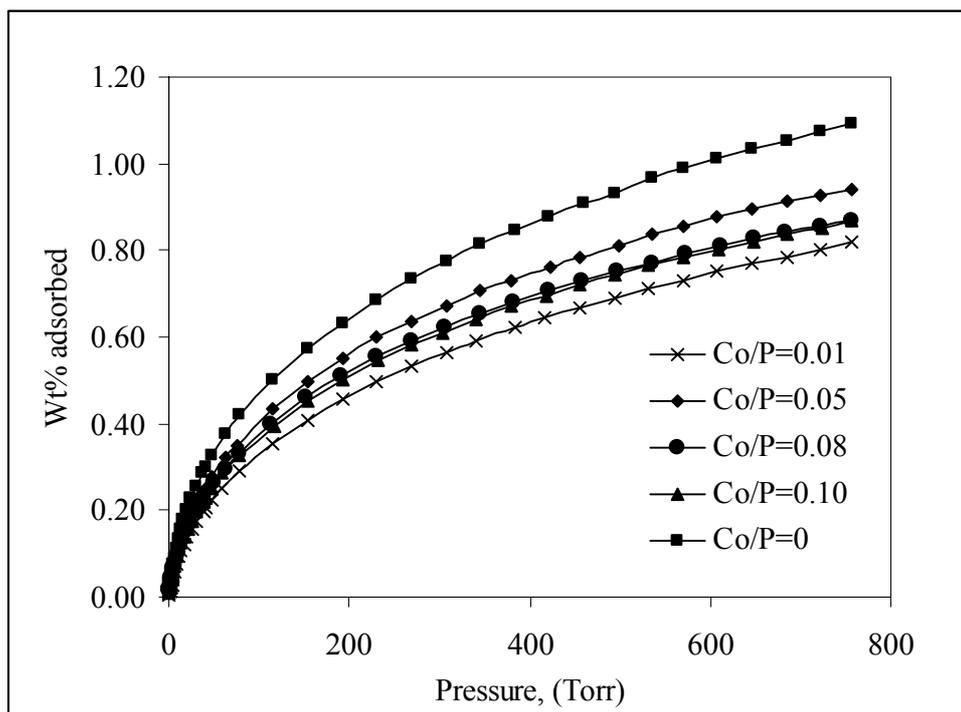


Fig. 3: Hydrogen sorption isotherms at 77 K for various SSZ-51 samples

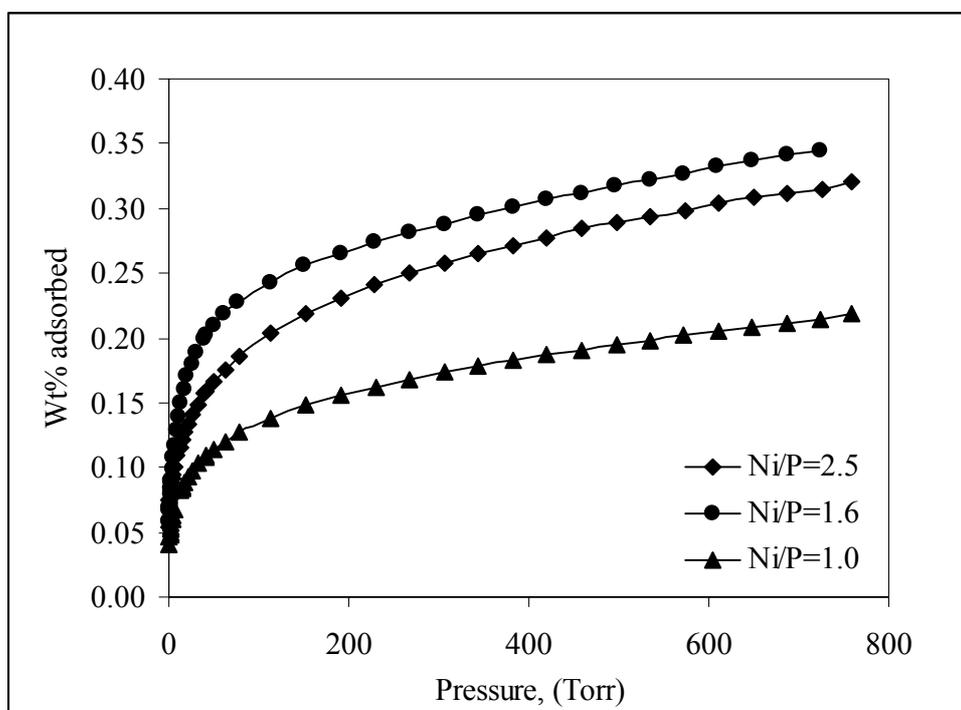


Fig. 4: Hydrogen sorption isotherms at 77 K for VSB-5 samples

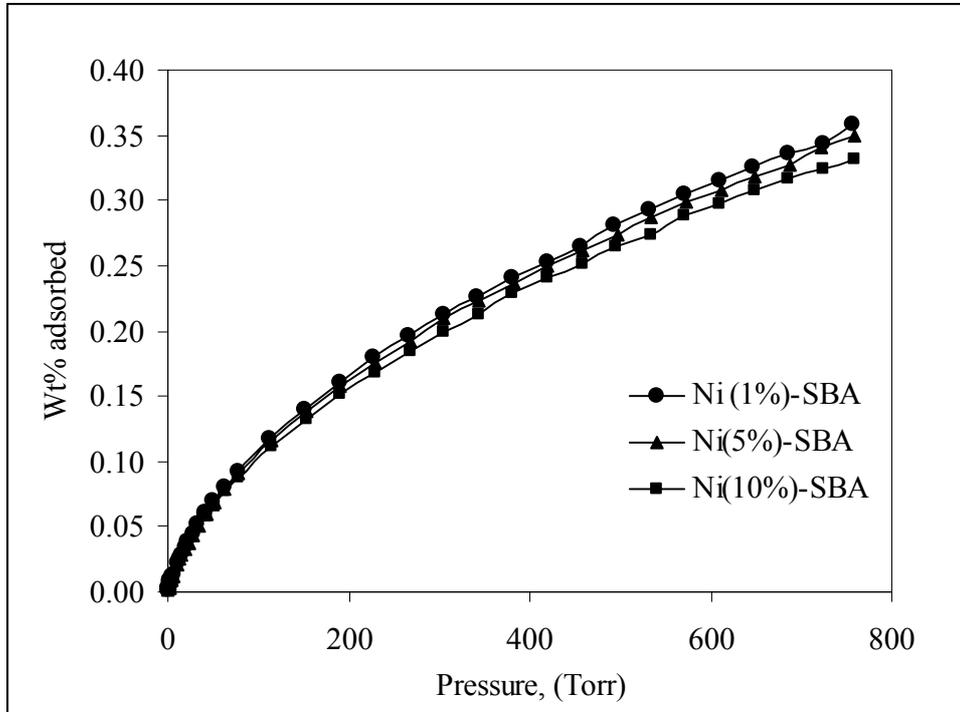


Fig. 5: Hydrogen sorption isotherms at 77 K for pure and nickel loaded SBA-15 samples

Tables:

Table 1: Textural properties and hydrogen adsorption capacities at 77 K and 1 bar for carbon adsorbents [35]

Material	PV(mg/g)	S _{BET} (m ² /g)	MPV(ml/g)	H ₂ total (ml/STP/g)
Synthetic graphite	0.04	7	0.0	0.00
Large diameter CNF	0.10	49	0.01	0.05
Activated graphite 100	0.26	119	0.02	0.12
Medium- diameter CNF 1	0.28	120	0	0.11
ACF 400	0.4	883	0.34	1.28
ACF 1200	0.42	899	0.37	1.64
AC Norit 990721	0.43	988	0.43	1.27
AC Norit ROZ 3	0.5	287	0.05	0.32
Activated graphite 300	0.51	287	0.05	0.32
Medium- diameter CNF 2	0.55	65	0	0.06
AC Norit ROZ SX2	0.6	841	0.27	1.34
ACF500	0.61	988	0.4	1.27
AC Norit UOK A	0.65	1195	0.47	1.68
AC Norit SX 1	0.67	922	0.31	1.50
AC Norit SX 1G AIR	0.68	1030	0.36	1.53
AC Norit GSX	0.78	933	0.26	1.44
AC Norit SX plus	0.79	1051	0.35	1.47
AC Norit SX G	0.83	1176	0.4	1.67
AC Norit 990293	1.03	2029	0.92	2.12
AC Norit Darco KB	1.39	1462	0.42	1.30
Hyper ion CNF	2.75	238	0	0.20

Table 2: Physical properties of Hydrogen

Properties	
Molecular weight	2.016 g/mole
Cross sectional area	0.104 nm ² / molecule
Critical Temperature	33.3 K
Critical density	0.031 g/cc
Melting point	13.86 K
Boiling point	20 K
Polarizability	0.817x10 ⁻²⁴ cm ³

Table 3: Textural properties and hydrogen adsorption capacities at 77 K and 1 bar for various adsorbents [35]

Material	PV(mg/g)	$S_{\text{BET}}(\text{m}^2/\text{g})$	MPV(ml/g)	H ₂ Capacity Wt%
SiO ₂ 90	0.23	79	0.01	0.04
Zeolite L	0.25	344	0.12	0.53
Zeolite ZSM5	0.28	431	0.16	0.71
Zeolite ferrierite	0.32	344	0.12	0.58
SiO ₂ D051 A	0.48	172	0	0.08
SiO ₂ 1614 E	0.51	97	0	0.08
SiO ₂ Caboxil M5	0.59	185	0	0.10
S980G	0.6	67	0	0.04
SiO ₂ Aerosil 200	0.66	167	0	0.00
SiO ₂ Becker AD 050	0.74	330	0	0.16
SiO ₂ -60-1	0.75	61	0	0.03
Al ₂ O ₃ preshaped	0.8	233	0	0.06
SiO ₂ 380	0.87	322	0.03	0.24
MCM-41	1.04	1017	0	0.58
S970SH	1.08	290	0.01	0.25