**HYDROGEN STORAGE USING MOFs**

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1. **BACKGROUND:**

Hydrogen is the most swarming component within the universe. It is a gift on earth present in good quantities combined with different parts. Therefore, it should be extracted from these parts to get chemical element gas, which has several sensible applications.

At the origin of the Universe,  
More than thirteen billion years past,  many minutes after  the large Bang, the protons that compose the nuclei of H came into existence. At this stage within the formation of the Universe, the temperature was extraordinarily high—close to a billion degrees.  
The Universe then began a section of growth and cooling. Once many million years, it absolutely was sufficiently cold to permit H molecules to make. These molecules gave rise to Brobdingnagian clouds referred to as “nebulas” that initiate the formation of the celebrities.  
The four large volatilized planets in our star system—Jupiter, Saturn, Uranus and Neptune—are conjointly in the main shaped out of H.  
Hydrogen was discovered in 1766 by British man of science Cavendish. It absolutely was by combining metals with robust acids that Cavendish noticed the formation of a gas that he referred to as “inflammable air” as a result, it absolutely was flammable. This extraordinarily light-weight gas was if truth be told H. He then noticed that burning it created water vapour (steam).  
Hydrogen is that the smallest and lightest molecule within the Universe. it's 50000 times smaller than the thickness of a hair and one litre of H gas weighs ninety mg beneath traditional conditions of pressure and temperature; this can be adequate to 3 postage stamps  
The H molecule (H2), that is usually referred to as “dihydrogen”, is that the oldest and simplest molecule in our Universe. It’s found in each star, together with the Sun, which pulls its energy from the transformation of H into argon throughout a fusion.

It is created from 2 H atoms that measure primary 2 parts to possess the shaped quite thirteen billion years past.  
• Name: H  
• Symbol: H  
• Number: one  
• Chemical series: Non-metal  
• Group: 1  
• Period: one  
• Block: s  
For many years, H has been used for multiple industrial applications in terribly various sectors of activity. It is in the main accustomed create fuel cleaner by eliminating the sulphur that is naturally found in fossil oil.

Once H is combined with an electriccell, it is conjointly a supply of property energy, a field that is developing chop-chop.

**1.1 Physical and Chemical Properties:**

The extremely low melting and boiling points result from weak forces of attraction between the molecules. The existence of those weak intermolecular forces is additionally revealed by the very fact that, when hydrogen gas expands from high to low at temperature, its temperature rises, whereas the temperature of most other gases falls. Consistent with thermodynamic principles, this suggests that repulsive forces exceed attractive forces between hydrogen molecules at room temperature—otherwise, the expansion would cool the hydrogen. In fact, at −68.6° C attractive forces predominate, and hydrogen, therefore, cools upon being allowed to expand below that temperature. The cooling effect becomes so pronounced at temperatures below that of nitrogen (−196° C) that the effect is employed to realize the liquefaction temperature of hydrogen gas itself.

**1.2 Ortho-hydrogen and para-hydrogen:**

Two sorts of molecular hydrogen (ortho and para) are known. These differ within the magnetic interactions of the protons due to the spinning motions of the protons. In ortho-hydrogen, the spins of both protons are aligned within the same direction—that is, they are parallel. In para-hydrogen, the spins are aligned in opposite directions and are therefore antiparallel. The connection of spin alignments determines the magnetic properties of the atoms. Normally, transformations of 1 type into the opposite (i.e., conversions between ortho and para molecules) do not occur and ortho-hydrogen and para-hydrogen are often considered two distinct modifications of hydrogen. The 2 forms may, however, interconvert under certain conditions. Equilibrium between the 2 forms are often established in several ways. One among these is by the introduction of catalysts (such as activated carbon or various paramagnetic substances); another method is to use a discharge to the gas or to heat it to a heat.

**1.3 Hydrogen:**

**Reactivity of hydrogen:**  
One molecule of hydrogen dissociates into two atoms (H2 → 2H) when an energy adequate to or greater than the dissociation energy (i.e., the quantity of energy required to interrupt the bond that holds together the atoms within the molecule) is supplied. The dissociation energy of molecular hydrogen is 104,000 calories per mole—written 104 kcal/mole (mole: the relative molecular mass expressed in grams, which is 2 grams within the case of hydrogen). Sufficient energy is obtained, for instance, when the gas is brought into contact with a white-hot tungsten filament or when an electrical discharge is established within the gas. If atomic hydrogen is generated during a system at low, the atoms will have a big lifetime—e.g., 0.3 second at a pressure of 0.5 millimetre of mercury. Atomic hydrogen is extremely reactive. It combines with most elements to make hydrides (e.g., hydride, NaH), and it reduces metallic oxides, a reaction that produces the metal in its elemental state. The surfaces of metals that don't combine with hydrogen to make stable hydrides (e.g., platinum) catalyse the recombination of hydrogen atoms to make hydrogen molecules and are thereby heated to incandescence by the energy that this reaction releases.  
Molecular hydrogen can react with many elements and compounds, but at temperature the reaction rates are usually so low on be negligible. This apparent inertness is partially associated with the very high dissociation energy of the molecule. At elevated temperatures, however, the reaction rates are high.  
Sparks or certain radiations can cause a mix of hydrogen and chlorine to react explosively to yield acid, as represented by the equation H2 + Cl2 → 2HCl. Mixtures of hydrogen and oxygen react at a measurable rate only above 300° C, consistent with the equation 2H2 + O2 → 2H2O. Such mixtures containing 4 to 94 percent hydrogen ignite when heated to 550°–600° C or when brought into contact with a catalyst, spark, or flame. The explosion of a 2:1 mixture of hydrogen and oxygen is particularly violent. Most metals and non-metals react with hydrogen at high temperatures. At elevated temperatures and pressures hydrogen reduces the oxides of most metals and lots of metallic salts to the metals. for instance , hydrogen gas and ferrous oxide react, yielding metallic iron and water, H2 + FeO → Fe + H2O; hydrogen gas reduces palladium chloride to make palladium metal and acid , H2 + PdCl2 → Pd + 2HCl.  
Hydrogen is absorbed at high temperatures by many transition metals (scandium, 21, through copper, 29; yttrium, 39, through silver, 47; hafnium, 72, through gold, 79); and metals of the actinoid (actinium, 89, through lawrencium, 103) and lanthanoid series (lanthanum, 57, through lutetium, 71) to make hard, alloy-like hydrides. These are often called interstitial hydrides because, in many cases, the metallic space lattice merely expands to accommodate the dissolved hydrogen with none other change.

**1.5 Hydrogen Bond:**

Some covalently bonded hydrides have an atom bound simultaneously to 2 separate electronegative atoms, which are then said to be hydrogen bonded. The strongest hydrogen bonds involve the tiny, highly electronegative atoms of fluorine (F), oxygen, and nitrogen. Within the bifluoride ion, HF2−, the atom links two fluorine atoms. Within the crystal structure of ice, each oxygen atom is surrounded by four other oxygen atoms, with hydrogen atoms between them. A number of the hydrogen bonds are broken when ice melts, and therefore the structure collapses with a rise in density. Hydrogen bonding is vital in biology due to its major role in determining the configurations of molecules. The helical (spiral) configurations of certain enormous molecular chains, as in proteins, are held together by hydrogen bonds. Extensive hydrogen bonding within the liquid state explains why fluoride (HF), water (H2O), and ammonia (NH3) have boiling points much above those of their heavier analogues, acid (HCl), sulfide (H2S), and phosphine (PH3). Thermal energy required to interrupt up the hydrogen bonds and to allow vaporization is out there only at the upper boiling temperatures.  
The hydrogen during a strong acid, like hydrochloric (HCl) or nitric (HNO3), behaves quite differently. When these acids dissolve in water, hydrogen within the sort of a proton, H+, separates completely from the charged ion, the anion (Cl− or NO3−), and interacts with the water molecules. The proton is strongly attached to at least one water molecule (hydrated) to make the oxonium ion (H3O+, sometimes called hydronium ion), which successively is hydrogen-bonded to other water molecules, forming species with formulas like H(H2O)n+ (the subscript n indicates the amount of H2O molecules involved). The reduction of H+ (reduction is that the chemical process during which an atom or ion gains one or more electrons) are often represented because the half reaction: H+ + e− → 1/2H2. The energy needed to cause this reaction are often expressed as a discount potential. The reduction potential for hydrogen is taken by convention to be zero, and every one metals with negative reduction potentials—i.e., metals that are less easily reduced (more easily oxidized; e.g., zinc: Zn2+ + 2e− → Zn, − 0.763 volt)—can, in theory, displace hydrogen from a robust acid solution: Zn + 2H+ → Zn2+ + H2. Metals with positive reduction potentials (e.g., silver: Ag+ + e−→ Ag, + 0.7995 volt) are inert toward the aqueous proton.

**1.5.1Production and Applications of Hydrogen:**

The most important industrial method for the assembly of hydrogen is that the catalytic steam–hydrocarbon process, during which gaseous or vaporized hydrocarbons are treated with steam at high over a nickel catalyst at 650°–950° C to supply carbon oxides and hydrogen: CnH2n+2 + nH2O → nCO + (2n + 1)H2; CnH2n+2 + 2nH2O→ nCO2 + (3n + 1)H2. The first reaction products are processed further in various ways, counting on the specified application of the hydrogen. Another important process for hydrogen production is that the noncatalytic partial oxidation of hydrocarbons under elevated pressures: CnH2n+2 + (n/2) O2→ nCO + (n + 1) H2. This process requires a feed system for delivering precise rates of fuel and oxygen, burners of special design to offer rapid mixing of the reactants, a refractory-lined reactor, and a cooling system to recover heat from the effluent gases. The latter process is exothermic (heat producing), in contrast to the endothermic (heat absorbing) steam–hydrocarbon process.  
In a third process, called the pressure catalytic partial oxidation method, the 2 preceding processes are combined to take care of the specified reaction temperature without external heating of the catalyst bed. Superheated steam and hydrocarbons are mixed, preheated, and blended with heated oxygen during a diffuser at the highest of the catalytic reactor. The oxygen reacts with the hydrocarbons during a space above the catalyst. The reactants then undergo a bed of nickel catalyst during which the steam–hydrocarbon reactions proceed almost to equilibrium.  
Before 1940 most of the planet production of hydrogen was made by processes supported coal or coke, the principal one being a water–gas reaction between steam and red-hot coke: H2O + C → CO + H2. By 1970, however, relatively little hydrogen was being produced by such processes. For several years relatively, small amounts of hydrogen had been produced by the electrolysis of aqueous solutions of salt or caustic soda, the electrode reaction being H2O + e− → 1/2H2 + OH−. The reaction between sulfuric or acid and a lively metal like zinc is employed to liberate hydrogen within the laboratory, but such hydrogen usually contains trace quantities of volatile hydrides, like arsine (AsH3) and phosphine (PH3), produced by impurities within the metal. These volatile impurities could also be removed by bubbling the mixture of gases through an answer of a robust oxidant, like permanganate of potash.  
A commercial method was developed for separating hydrogen from carbon monoxide gas synthesis gas by diffusion. The gas flows struggling through bundles of small hollow polyester fibres through whose walls the hydrogen passes.  
The largest single use of hydrogen within the world is in ammonia manufacture, which consumes about two-thirds of the world’s hydrogen production. Ammonia is manufactured by the so-called Haber process, during which hydrogen and nitrogen react within the presence of a catalyst at pressures around 1,000 atmospheres and temperatures around 500° C: N2 + 3H2 → 2NH3. Large amounts of hydrogen are utilized in the preparation of methanol by the reaction CO + 2H2 → CH3OH. This process is administered within the presence of certain mixed catalysts containing flowers of zinc and chromium oxide at temperatures between 300° and 375° C and at pressures between 275 and 350 atmospheres.Another major application of hydrogen is within the catalytic hydrogenation of organic compounds. Unsaturated vegetable and animal oils and fats are hydrogenated to form margarine and vegetable shortening. Hydrogen is employed to scale back aldehydes, fatty acids, and esters to the corresponding alcohols. Aromatic compounds are often reduced to the corresponding saturated compounds, as within the conversion of benzene to cyclohexane and of phenol to cyclohexanol. Nitro compounds are often reduced easily to amines.  
Hydrogen has been used as a primary rocket propellant for combustion with oxygen or fluorine and is favoured as a propellant for nuclear-powered rockets and space vehicles. Another increasing use of hydrogen is within the direct reduction of iron ores to metallic iron and within the reduction of the oxides of tungsten and molybdenum to the metals. A hydrogen (reducing) atmosphere is used within the pouring of special castings, within the manufacture of magnesium, within the annealing of metals, and for the cooling of huge electric motors. Hydrogen was once used for inflating lighter-than-air vessels, like dirigibles and balloons, but now helium is usually used because it is inflammable. The barrage balloons utilized in England during war II, however, were crammed with hydrogen. Liquid hydrogen is employed within the laboratory to supply low temperatures.

1. **LITERATURE**

The icurrent iglobal ienergy iconsumption iis irapidly iincreasing itogether iwith ithe idemand ifor iprimary ienergy isources/fossil ifuels, ithereby icausing irapid idepletion iof ithese ilimited isources.iThe ienvironmental ipollution iis ialso iincreasing iwith ithe iconsumption iof ifossil ifuels, iwhich iis iaffecting ithe ihealth iof iliving ibeings ion ithe iearth.iThe iinfluence iof igreenhouse igas iemission ion iglobal iwarming iis ialso iwell idocumented.iThus, ienergy isecurity iand ienvironmental idegradation iare iof iglobal iconcern.iThe iconventional i/ icommercial ienergy isources i iare inot ilikely ito imeet ithe ienergy idemand iwhich inecessitates ialternate ienergy isources.iThis ihas icompelled ito itake iinitiatives ito ishift ifrom icarbon ibased ito icarbon ineutral itechnologies ilike isolar, ihydro, iwind, ibiomass i& ibiofuel ibased itechnologies, ietc.

Hydrogen ihas ibeen iwidely irecognizedias ian ialternate ienergy icarrier ito iaddress ithe ithree imain iconcerns iviz.ienergy isecurity, ienvironmental iissues iand ipeak ienergy idemand.iCurrently, iglobal ihydrogen iproduction iis i48% ifrom inatural igas, i30% ifrom ioil, i18% ifrom icoal iand i4% ifrom iwater ielectrolysis.iSeveral iindustries, iespecially ithe ichlor-alkali, iproduce isubstantial iamounts iof ihydrogen ias ibyproduct.iHydrogen imay ialso ibe iproduced ifrom idifferent ikinds iof iurban iand iindustrial iwastes ietc.

Safe iand iefficient istorage iand idelivery iof ihydrogen iis iessential ifor ithe isuccess iof ihydrogen ieconomy. Hydrogen ican ibe istoredthe ifollowingiways: -

1. High-pressure igas icylinders i(up ito i800 ibar)
2. Liquid ihydrogen iin icryogenic itanks i(at i21oK)
3. Physi-sorbed ihydrogen ion imaterials iwith ia ilarge ispecific isurface iarea
4. Chemi-sorbed ion iinterstitial isites iin ihost imetals iand iInter-metallics
5. Chemically ibonded iin icovalent iand iionic icompounds
6. Oxidation iof ireactive imetals isuchias.iLi,iNa, iMg, iAl, iZn iwith iwater.

##### 2.1 STORAGE iTECHNOLOGIES

**2.1.1 Gas iStorage**

Hydrogen iis igenerally istoredias igas iin icompressed iform ibecause iit iis ivery ilight iwith ilow idensity iof i0.084 ikg/m3.iThe ienergy icontent iof ihydrogen igas iat iambient ipressure iand itemperature iis i10 iMJ/m3, iwhich idemands iextremely ilarge ivolume ifor ihydrogen istorage.iThe iconventional ihydrogen istorage itank iis isignificantly iheavier ithan ihydrocarbon istorage itank ifor istoring ithe iequal iamount iof ienergy.i

Hydrogen istorage ineeds ispecial iattention idue ito iembrittlement (causediby ihydrogen idiffusion ibeing ismallest imolecule iin isize) iof imaterials iof iconstruction iof ipressure ivessels.iTherefore, iit ibecomes inecessary ito iuse ispecial ialloys ior icomposite ifiber ireinforced icontainers.i

Compressed igas istorage ialso iposes iissues iof ihigh ipotential ienergy iand isafety ihazards idue ito ipossibility iof iexplosion iof ipressure ivessels.iHowever, iit iis ipossible ito ihave inecessary isafety ipractices iwith isuitable iblast iwalls iand imonitors/sensors iand iensure icompatible iand isafe ihigh ipressure istorage ibottles.iHydrogen iis ibeing istored iin igaseous iform ion-board ifor itransportation iapplications, iwith ifocus iprimarily ion ithe idriving irange iof i500 ikm.iSome iautomakers ihave idemonstrated itheir iprototype ivehicles iqualifying ithis irange.

Hydrogen iin icompressed imode ihas ibeen iwidely iused iin ion-board imobile iapplications ilike iin ithe ivehicles ifor iroad itransportation, istationary iapplication ifor idispensing ihydrogen iat ire-fueling istations iand iat isites ifor istationary ipower igeneration.iHydrogen, iwhile istoring iat ihigh ipressures ireacts iwith ithe imaterials i iof iconstruction iof icontainers iand imakes ithem ibrittle; itherefore, ithe i icontainers iare imade iof ispecial ialloys iand ialso iwith ireinforced icomposite icarbon ifiber.iCurrently, ihydrogen iis ibeing istored iin icompressed iform iat i350 ibar i(5,000 ipsi) iin ion-board iin idemonstration ivehicles iand i700 ibar i(10,000 ipsi) iin iType iIV icarbon icomposite icylinders.iCarbon icomposite icylinders ito istore ihydrogen iat i700 ibar i(10,000 ipsi) iare inot ibeing imanufactured iin ithe icountry.

##### 2.1.2 Liquid iStorage:

Storage iand itransportation iof ihydrogenias ia iliquid iis ianother ipossibility.iThe icryogenic ihydrogen iis ito ibe istored iin ispecially iinsulated ivessels iat i(-) i252.880C.iThe ienergy irequired ito iliquefy ihydrogen i(gas iat i300oK iand i1 ibar ipressure) iis iabout i47 iMJ i/ ikg iof ihydrogen.iThe ienergy ialso iis idependent ion ithe isize iof ithe iplant.iWith iimproved itechnologies iand ismall iplants iinvolving i imagnetic iregenerative iliquefaction iabout ihalf iof ithis ienergy imay ibe iadequate.iThus, ienergy irequired ifor ibulk istorage iand itransport icryogenic iliquid ihydrogen igas ican ibe iabout i10 ito i20% ilower.iLike ihydrogen iin igaseous iform, ithe iliquid ihydrogen ialso ihas itendency ito idiffuse iinto ithe imaterial iof iconstruction iat ihigh ipressures iand imake ithem ibrittle.iTo icheck ithis iproblem iof iembrittlement, ithe istorage ivessels imay ibe imade iof iFCC i(as imaterial iof iconstruction) iwith ispecial iinsulation, icomprising idouble iwalled iwith ivacuum iin ibetween, iopacifiers iand imulti-layer iinsulations.

Hydrogen ican ibe istored iin iliquid iform iin icryogenic iconditions.iSo ifar, iLH2 iapplication ihas ibeen imainly iin ispace iapplication.iThese iforms iof istorage iare inot isuitable ifor iwidespread icommercial iapplication.iLiquid iorganic ihydrides iare ialso ipotential icandidates ifor ihydrogen istorage iand idelivery.iThe iconcept ihas ibeen idemonstrated isuccessfully iat ilaboratory ilevel.i iPilot ilevel istudies idemonstrate i ithe iefficacy iof ithe isystem iand ipossibilities iof iup-scaling.iConsiderable iwork ihas ialso ibeen icarried iout iat iNational ilevel ileading ito igeneration iof iIPR ifor icountry.iFurther iwork iis ibeing iconducted iand iexpected ito ibe isupported iby igovernment/industry imay ilead ito idevelopment iof ia itechnology ifor isafe ihydrogen istorage iand idelivery iat inear iambient iconditions ifor ilong idistance itransportation.iIn iorder ifor ithe ihydrogen iprogram ito ibe isuccessful iin iIndia, idevelopment iof irequired itesting ifacilities, istandards icodes iand iregulations ifor icylinders, icomponents, ivehicles iand ifuel ineed ito ibe ideveloped iin iline iwith iinternational iregulations.

##### 2.1.3 Solid iState iStorage

Solid istate istorage iof ihydrogen iisia imuch isafer iand iefficient imethod ithan ipressurized cryogenic istorage iof ihydrogen.iThe ibasic iparameters iof ihydrogen istorageimaterials asI targetediby iDepartment iof iEnergy(DoE),

The inew i“Ultimate iFull iFleet” itargets iare isimilar iin iphilosophy ito ithe iprevious i2015 itargets iin ithat ithey irepresent ithe ihydrogen istorage isystem iperformance ithat iis irequired ifor ifull ivehicle ipenetration iinto Ithe ilight-duty imarket iacrossia ibroad irange iof imakes iand imodels.iThe i“Ultimate iFull iFleet” itargets ialso iapproximate icurrent igasoline iICE ivehicle isystems ifor ipackaging ivolume iacross ithe imost idemanding ivehicle iplatforms.iWhile ithe i“Ultimate iFull iFleet” itargets iallow iincreases iin iweight iand ivolume icompared ito icurrent ivehicle ifuel itank isystems, ithese iincreases iare imanageable iacross ithe irange iof ilight-duty ivehicle iplatforms.iStorage isystems ithat ican imeet ithe i“Ultimate iFull iFleet” itargets iwould itherefore ihave idriving iranges ithat iare icompetitive iwith imost iof ithe icurrent iICE ivehicle ifleet.

While iliterally ihundreds iof iintermetallic ialloys ihave ibeen iprepared iand itheir ihydrogenation ipotentials iassessed, irelatively ifew ihave ithe iright icombinationof iproperties ithat ipermit itheir iuse ifor ihydrogen istorage ior i iother i iapplications.iThe imost iviable icandidates iinclude ialloys iwith ithe ifollowing icompositions: iA2B i(e.g., iMg2Ni), iAB i(e.g., iTiFe), iAB2 i(e.g., iZrMn2) iand iAB5 i(e.g., iLaNi5).iA ikey iadvantage iof imany iintermetallic ialloys iis ithe iability ito ialter itheir ihydrogen isorption ibehavior iby isubstitution ifor ieither ior iboth ithe iA iand iB imetals ithat ioften iimprove itheir iperformance iin ivarious iapplications.

A ivariety iof isolid-state ihydrogen istorage imaterials iviz. iMgH2, iMg2NiH4, iNaAlH4, iother ialanates, iborohydrates i(gravimetric icapacity iof i>7wt%), icommercial ihydrides isuch ias iFeTiH2 iand iLaNi5H6, iadsorbents ilike icarbon, inano- istructured icarbons i(including iCNTs) iMoFs iand ihydrogen iclathrate ihydrate ihave ibeen iinvestigated ifor ihydrogenation iand idehydrogenation ireaction iconditions iand itheir ikinetics, iretention iof icycling icapacity, isusceptibility ito iimpurities iand ireversible icapacities. iThe ineed ifor imaterial iwith ipractical ioperative iconditions iof ipressure i(1-10 ibar) iand itemperature i(300C-1000C) ihas isimulated ithe iinterest iof imany iresearchers. iOther imajor iareas iof iresearch iare iimprovement iof ikinetics iof ihydrogen iuptake/release iand ienhancement iof icycling icapacity.

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Nanostructured isystems iincluding icarbon inanotubes, inano-magnesium ibased ihydrides, icomplex ihydride i/ icarbon inanocomposites, iboron initride inanotubes, isulphide inano-tubes iof ititanium iand imolybdenum, ialanates, ipolymernanocomposites, iand imetal iorganic iframeworks iare iconsidered ito ibe ipotential icandidates ifor istoring ilarge iquantities iof ihydrogen.iThe isynergistic ieffects iof inanocrystalinity iand inanocatalyst idoping ion ithe imetal ior icomplex ihydrides iimprove ithermodynamics iand ihydrogen ireaction ikinetics.iIn iaddition, ivarious icarbonaceous inanomaterials iand inovel isorbent isystems i(e.g. icarbon inanotubes, ifullerenes, inanofibers, ipolyaniline inano-spheres iand imetal iorganic iframeworks ietc.) iand itheir ihydrogen istorage icharacteristics iare iconsidered.iIn ispite iof ithese iconsistent iand ipersistent iefforts, ithese imaterials iare iyet ito isatisfy ithe irequired icharacteristics ilike istorage icapacity iof iaround i6 iweight ipercent, ifavourable iand ituning ithermodynamics iaround i30-55 iKJ/mol iof ihydrogen iand itemperature iof ioperation iaround i373 iK iwith iabout i1000s iof icycles iof ioperation.

|  |  |  |  |
| --- | --- | --- | --- |
| Hydrogen Storage Method | | | Efficiency,  100% |
| Compressed Gas | 300 bar | | 91.5 |
| 700 bar | | 90.5 |
| Liquid | | | 62.5-77 |
| Activated Carbon(77K) | | | 91.7-93.3 |
| Hydrides | | Low Temperature  (<100 celcius) | 90-93.3 |
| High Temerature  (>300 celcius) | 79-83 |

##### 2.1.4 Emerging iStorage iTechnologies:

Liquid iorganic ihydrides iconsisting iof ivarious icycloalkanes ican iconveniently ibe itransported ifrom ione iplace ito ianother.iThese ihydrides imay ibe iprepared iby ithe ireaction iof ihydrogen iwith itoluene iunder ispecific iconditions.iHydrogen iand itoluene imay ibe irecovered iby ithe idehydrogenation iof ithe icyclohexane iat ior inear ifueling istations ifor idispensing ihydrogen iinto ivehicles i/ iother iapplications.iToluene iis itransported iback ifor ireuse.iThe iadvantage iassociated iwith ithese iorganic ihydrides iis ihigher istorage icapacity iof ihydrogen, iwhich iis imore ithan i6 iwt% iand i60 ikg/m3.

Compressing ihydrogen iinside ihollow iglass imicrospheres ior imicrocapsules ihas ibeen isuggested ito igive ihigh ivolumetric istorage idensities.iLoading iand iunloading iof ihydrogen igas iin iand iout iis ibased ion ithe ifact ithat igas ipermeation ithrough ithe isolid ishell iincreases iexponentially iwith itemperature.iHollow imicrospheres iare ialso icalled imicrocapsules, imicrocavities, imicrobubbles, ior imicroballoons.iHydrogen istorage iin ihollow iglass imicrospheres ipresents iseveral iadvantages.iFirst, ihollow imicrospheres ihave ihigh igravimetric ienergy idensity.Hydrogen ican ibe istored iunder iinternal ipressure ihigher ithan ithat iinside

**Figure**

**2.**

**1**

**Chemical Storage options for hydrogen**

**:**

Chemical Storage

Reversible

Conventiona

l Metal

Hydrides



Complex

Hydrides

New

Emerging

Methods

Light

Element

Systems

Non reversible

Reformed

Fuel

Hydrolys

ed

Fuel

Decomposed

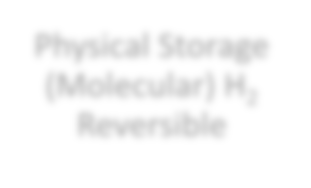
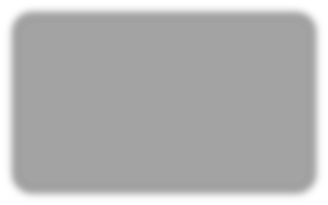
Fuel

**Figure**

**2.**

**Physical Storage options for Hydrogen**

**1:**



Physical Storage

Molecular) H

(

2

Reversible

Compressed

Gas

Hybrid Tanks

Liquid

Storage

### CHEMI-SORPTION THERMAL ENERGY STORAGE WITH iMETAL iHYDRIDES

A imajor iadvantage iof ireversible ithermochemical ienergy istorage isystems iis ithatithe iproducts iare istoredias istable ichemicals, ipreferably iat iambient itemperatures.iHence, ithey ican ibe istored iindefinitely iwithout iincurring ithermal ilosses, ithereby igreatly iincreasing ioverall isystem iefficiency.iAnother iadvantage iis ithat ithe iheat iis ireleased iat ia iconstant itemperature iif ithe iheat ican ibe iremoved ifast ienough ito iprevent iself-heating.

Metal ihydrides iprovideian iattractive ipossibility ifor ithermal ienergy istorage. Compared ito iconventional ithermo-chemical ireactions, imetal ihydride ibased isystems ioffer iseveral ifavorable ifeatures isuchias:

* + - Wide irange iof itemperatures iand ikinetics iare ipossible iby itailoring ithe ialloy icompositions
    - Temperature iupgradation iof ithe iheat isource ican ibe iachieved iby iheat ipump/heat itransformer ieffects
    - Better heat and mass transfer characteristics and amenable to iaugmentation itechniques
    - Comparable igravimetric i/ isometimes ibetter ivolumetric ienergy istorage idensities
    - Cyclingidegradationi (both iphysical iand ichemical) iis iminimal.
    - Volume ichanges iduring iabsorption i– idesorption iare iminimal.
    - Corrosion, itoxicity, ietc iare iavoided.iGenerally ienvironment ifriendly.iFlammability iof iH2 iisanissue ibut ican ibe ieasily ihandled.
    - Cost iis inot iprohibitive iif ione ichooses isuitable icomponents iand ialso idesigns ioptimally.Sizing iisian iimportant iissueA itypical iMH ibased ithermal ienergy storage isystem iis ishown iin iFigure i12.1.

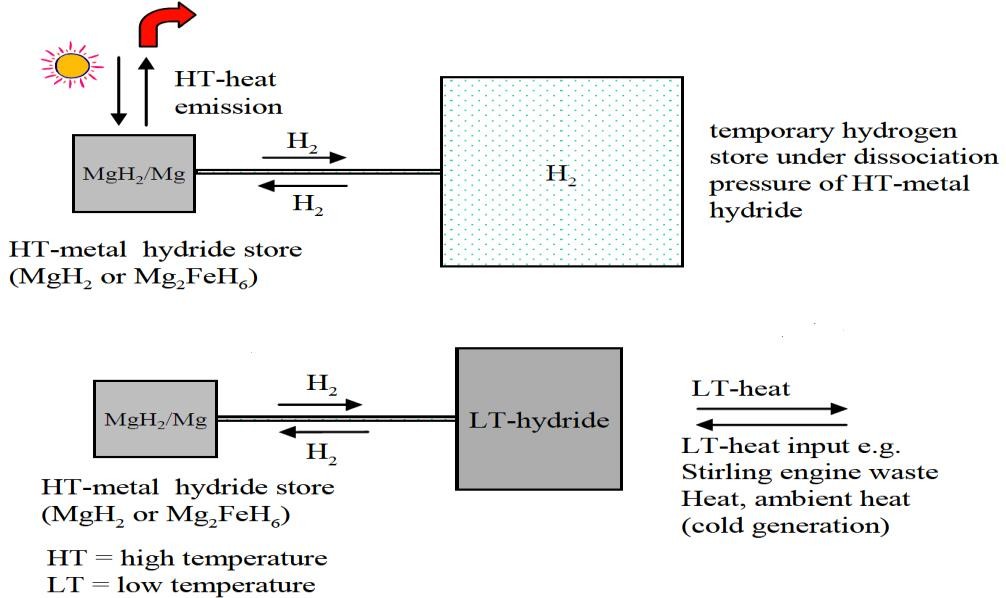


FIG 12.1 TYPICAL MH BASED THERMAL ENERGY SYSTEM

##### National iStatus:

Chemi-sorption ibased ithermal ienergy istorage iwork iis irather iscarce iin iIndia.iHowever, iover ithe ipast ithree idecades, iextensive istudies ion iheat iand imass itransfer iof imetal ihydride ibased ihydrogen istorage ialloys ihave ibeen ireported iin ithe icountry.iAt iIIT iMadras, iextensive iworks ion ithe idesign, idevelopment iand itesting iof imetal ihydride ibased ihydrogen istorage idevices.iSuch istudies iare ialso iextensively ireported ifrom iIIT iKharagpur, iIIT iGuwahati iand iIIT iIndore iin irecent iyears.iEven ithough iall ithese iworks iemphasize ion ithe ihydrogen istorage iaspects iof imetal ihydrides, ithe iresults ican ialso ibe iextrapolated ifor ithermal ienergy istorage.iHowever, iat iIIT iMadras iand iIIT iGuwahati isome ipreliminary istudies ion ithe iproperty irequirements iof imetal ihydrides ifor iheat istorage ihave ibeen icarried iout.iCurrently, ia iDST iproject ion idevelopment iof iMH ibased ithermal istorage isystems isuitable ifor iCSP iis iongoing iat iIISc iBangalore.

**2.2 Limitations:**

Hydrogen storage could be a downside that has been a spotlight of research project for many years. All those strategies has its benefits and downsides, however all on-board storage technologies ought to meet the necessities like safety, performance, cost, and technical adaptation for the infrastructure, measurability of  tiny and enormous vehicles.  
The variety of strategies are investigated, although, none of those have accomplished the desired performance level to this point. Current strategies for gas storage may be broadly speaking separated into: mechanical storage (storage in a very huge tank of gas or liquid hydrogen) Physisorption (storage in a very solid material) includes, Graphene and different carbon structures,metals and antimonial nano-crystals and composites, metal-organic frameworks, zeolites; gas: storage in solid or liquid material of with chemicals certain hydrogen that's discharged on decomposition, includes, light-weight metal hydrides (alkaline hydrides), boro-hydrides, amines and imides.  
Metal organic frameworks (MOFs) area unit a replacement category of porous materials with density and high area. They're crystalline, infinite networks assembled by linking metal ions with numerous organic linkers through robust bonds. Recently, it had been accomplished that a number of them may be promising candidates for gas storage.

Metal organic frameworks (MOFs) area unit a replacement category of porous materials with rarity and high area.  
They are crystalline, infinite networks assembled by linking metal ions with numerous organic linkers through  
strong bonds. Recently, it absolutely was accomplished that a number of them may be promising candidates for Hstorage. Hydrogen- towards a property energy future: a serious challenge facing our planet nowadays associated with the  
problem of anthropogenetic driven temperature change and therefore the would like of future energy. The technology of element  
energy can contribute considerably to a discount in environmental impact, increased energy security and  
diversity and therefore the creation of latest energy industries . However, the transition from a carbon-based (fossil  
fuel) energy system to a hydrogen-based economy involves vital scientific, technological and  
socioeconomic barriers to the implementation of element because the clean energy technologies of the  
future. International drivers for property energy vision of our future would like to:i) cut back carbonic acid gas emissions and improve air quality. ii) guarantee security of energy offer. ii) produce a brand new industrial and technological energy base, crucial for our economic prosperity.

**2.3 Applications**:

i) The vision of associate degree integrated energy system of the long run would mix giant and tiny fuel cells for domestic  
and suburbanised heat and electricity power generation with native element provide networks that may even be  
used to fuel typical (internal combustion) or fuel-cell vehicles.  
ii) in contrast to coal, gas or oil, element isn't a primary energy supply. Its role a lot of closely to it of electricity as  
an 'energy carrier', that initial is made mistreatment energy from another supply then transported for future use,  
where energy will be used. Element will be kept as a fuel and used in transportation  
and distributed heat and power generation mistreatment fuel cells, combustion engines or turbines, and,  
importantly, an element cell produces solely water and no carbon dioxide.  
iii) element may be used as data-storage medium for electricity generated from intermittent, renewable  
resources like star, wind, wave and recurrent event power. It so provides the answer to 1 of the most important problems  
of property energy, specifically the vexing drawback of irregularity of provide. As long because the element is  
produced from non-fossil-fuel feed stock, it's a genuinely inexperienced fuel. Moreover, regionally made element  
allows

operation and safety, and these will, over potency, verify the success or failure of any of the  
proposed solutions for a district of the H cycle. For sensible applications of H storage, the storage  
material ought to be reversible. H2O is incredibly troublesome to be absolutely off from business H sources.  
For sensible applications, it's not economical to use super-high purity H for transportation as a result of  
the additional value for purifying H. Thus, the H2O sorption characteristics and also the structure stability  
upon H2O sorption ar vital problems for a promising H storage material for sensible  
applications. this can be even additional problematic for MOFs as a result of MOFs decompose simply at elevated  
temperatures, indicating the instability of this kind of fabric .

**2.4 Challenges:**

So as to realize the gas economy, there area unit some obstacles that require to be overcome to  
make gas a viable energy carrier. They're characterised by four main aspects of gas use and a fewof these are self-addressed here

[i) Production:

Since gas has to be created, ideally from water, it  
is necessary to develop production ways that will consume quantity} amount of energy and supply ability  
to produce gas renewably on an oversized scale. ii) Storage: Fuel has to be simply hold on to be used and  
transport, wherever one in all the most needs is that it's promptly accessible, which needs not simply short  
charge/discharge times, however conjointly glorious management of charge/discharge method plus comfortable energy  
and gravimetric/volumetric density. iii) Power generation: Once gas is prepared to be consumed, it is  
necessary to try and do thus within the simplest way: the ability generation system that uses gas has to be each  
efficient and, for mobile application, lightweight weight.  
iv) Safety: gas use and storage comes with some risks (flammability) that necessitate bound  
precautions and safety measures; another facet associated with this is often environmental impact of the gas cycle,  
which depends on the ways wont to manufacture, store and use it.  
Since gas is assumed to be a renewable fuel for the longer term, it's solely applicable that, once we contemplate  
all the challenges related to its production, storage and use, we tend to confine mind that once we contemplate  
proposed systems, potency is just one in all the factors that may confirm the success of those systems. Other  
important aspects area unit cost, durability, stability of the synthesized merchandise. to boot, newer  
mechanisms area unit needed to be fictitious to boost the thermal and chemical stability of synthesized.

**3.BASIC IDEA/CONCEPT**

An effective hydrogen-storage technology that provides a high storage capacity and fast kinetics is a critical factor in the development of a hydrogen fuel for transportation. The successful implementation of the “Hydrogen-Economy” would alleviate greenhouse gas emissions and reduce dependence on fossil fuels. The concept of coordination polymers based on metal ions bridged with each other by organic ligands has been well known since the mid-1960’s, and three-dimensional networks with defined cavities were synthesized for the first time in the late 1980’s. Later the use of carboxylate rigid organic ligands to aggregate metal ion clusters was found to be ideal to form extended frameworks with structural stability and high porosity, which led to the development of a new class of crystal-line materials, the so-called metal–organic frameworks (MOFs). This Review is focused on the use of metal–organic frameworks (MOFs) as new hydrogen storage materials.

**WHAT IS MOF?**

Metal-Organic Framework, abbreviated to MOF, is a Coordination Polymer with an open framework containing potential voids. MOFs are self-assembled metal clusters with organic ligands, are well known for their structure, permanent porosity, and tunable properties and have shown great prospect for various applications.

Simply, metal-organic frameworks are compounds of metal ions and organic molecules that form structured frameworks. These advanced materials can be compared with sponges with unique abilities – being able to take-up, hold and release molecules from their pores. Therefore, metal-organic frameworks (MOFs) are the fastest growing class of materials in chemistry today.

Metal ions + Organic units 🡪 Coordination polymers or MOF materials.

**STRUCTURAL FEATURES:-**

* MOFs are made up of inorganic nodes.
* They have very low density.
* They have large voids.
* Complex unit cell.

**PROPERTIES OF MOFs:-**

The backbone of the compound is constructed from metal ions which act as connectors and organic bridging ligands as linkers

Readily accessible porosity.

The coexistence of inorganic and organic moieties in structure may influence on adsorption properties.

Although most MOFs are electrical insulators, several materials in this class have recently demonstrated excellent electrical conductivity and high charge mobility.

The thermal stability of MOFs is determined by the coordination number and local coordination environment instead of framework topology.

In general MOFs are poor thermal conductors with a thermal conductivity that is similar to concrete.

**3.1 METHODOLOGY**

Metal–organic frameworks (MOFs) are a class of materials that generally work well for hydrogencapacity at low temperatures of roughly 77 K.

At 77 K MOFs can storemore hydrogen than any other crystalline microporousmaterial. The lowtemperature of adsorption and thereversibility of the process are clear indications thatthe process responsible for hydrogen storage in MOFs isphysisorption, i.e. molecular adsorption.

**Adsorption and Absorption:**

Adsorption is the enrichment or depletion of one or more components in an interfacial layer. Absorption occurs when theadsorbates are incorporated into the internal structure of theadsorbent. In absorption, the structure and/or the chemicalnature of the absorbate and absorbent may be modified. Adsorption and absorption refer to the location of the sorbent specieswith respect to the sorbent, that is, surface and bulk, respectively.

**Design and Synthesis of Metal-Organic Frameworks for Hydrogen Storage**

* The types are:
* Carboxylate-Based MOFs.
* Azolate-Based MOFs.
* MOFs with Mixed Ligands.
* MOFs with Metal Complexes as BuildingBlocks that includes MOFs Based on Macrocyclic Complexes and Metal-Cyanide Frameworks.
* Post synthetic Modification that includes Modification of Metal Centers and Modification of Ligand Parts.

**Strategies for Improvising Hydrogen storage Capacities in MOFs:**

There are several ways for improving the Hydrogen storage in MOFs some of them could be: Increase in the Pore Volume and Surface area that includes, Elongation of ligands, Catenation and Interpenetration and Mixed ligand system.The other way is Increase in Isosteric Heat of Hydrogen Adsorption which includes Generation of Active Metal sites in Metal-Organic Frameworks and Control of Pore size and Functionalization of MOFs.

**Manufacturing of MOFs:**

MOFs are normally synthesized using hydrothermal or solvothermal methods, in which metal salts and organic ligands are dissolved by water and solvents in a Teflon lined autoclave. The quality and the framework structure of MOFs are usually analyzed using X-ray diffraction method.

The most common metal ions used in the synthesis of MOFs are Zn(II) and Cu(II), but other transition metal ions such as those in the first transition series may be employed as metal building blocks. Various carboxylic acids as well as heterocyclic compounds containing nitrogen donors are used as the organic building blocks for the construction of MOFs.

Synthesis strategies generally include formulation of reactants, crystallization and processing methods to create specific crystallographic structures, to control the crystal size and morphology and to optimize the operation conditions for large-scale production. Good formulations are achieved by judicious selection of metal cations and their counter ions (NO3 −, CO3 2−, SO4 2−, Cl−, CH3CO2 −, etc.), organic ligands and pH values. The solvents (H2O, EtOH, THF, DMF, etc.) used as media for crystallization not only dissolve reactants but also play a role as structure directing agents (SDAs), which influence the properties of the final products. Operation conditions such as temperature, pressure and reaction time are also important for good quality product and yield. The synthesis temperature is generally in the range of 298–493 K. Increase in temperature may lead to different in composition.

In addition to hydrothermal and solvothermal syntheses, new routes have been developed. For example, electrochemical reaction through a loss of copper cathode yielded copper benzene tricarboxylate MOFs (BASF).

MOFs adsorb nonpolar hydrogen molecules to their surface mainly through weak London (dispersion) interactions and electrostatic potentials. This differs from hydrogen storage via metal hydrides in which the hydrogen atoms are dissolved in the solid lattice framework. The dispersion interactions are determined by the polarizability of MOF materials and the distance between H2 and potential surfaces, thus leading to preferential adsorption of hydrogen on the functionalized MOFs with highly developed micropores in which the overlapped potential fields from both sides of pores strengthen the potential interactions.

Typical MOF materials used for hydrogen storage include MOF-5, -74 and -177, HKUST-1, MIL-100 and -101, etc. They have unique crystallographic structures, and have demonstrated exceptional performance for hydrogen storage and adsorption of other gases. The names of the MOFs were favorably given by individual research groups, and there is no identical code assigned for the topological frameworks as the nomenclature for zeolite materials by the International Zeolite Association (IZA) yet.

**3.2.1 Effects of Surface Areas and Pore Sizes on Hydrogen Storage in MOFs:**

Surfaceareaplaysanimportantroleingasadsorptiononsolidmaterials.Asageneralprinciple, themaximum(saturated)adsorbedamountofgasonasolidsurfaceisdependentonitssurfacearea. Thiswaswell-demonstratedbycorrelatingthehydrogen-storage capacity with specific surface area for zeolitesstrictly suitable to microporous materials, such asand carbon materials at a low temperature, such as 77 K.

However, when the pressure of the gas is not high enough toreach its saturated adsorption, the amount of the adsorbed gas ismainly determined by the interaction between the gas and thesolid surface (reflected by adsorption heat). This can explainwhy no correlation exists between hydrogen-storage capacity andthe specific surface area of MOFs at a pressure of 1 bar or below,which is much lower than that required for the saturatedadsorption on the MOFs. In contrast, the saturated hydrogencapacity, which corresponds to the plateau of the adsorptionisotherm at 77 K, correlates almost linearly to the specific surfacearea for the MOFs. Nevertheless, it should be noted thatthere are some exceptions for H2 storage in MOFs. For example, although the BET surface area (5500 m2 g1) of MIL-101b (Cr-based MOF) is higher than that (4746 m2 g1) of MOF-177. (Zn-based MOF), its saturated H2 capacity (6.1 wt.%) is lower thanthat (7.5 wt.%) of MOF-177 at 77 K. These exceptions mightbe a result of inappropriate measurement of surface areas. TheBET equation is applicable to materials with large pores (e.g., mesoporous materials) in the absence of capillary condensation, but is notMOFs.

Pore size can affect the interaction between hydrogenmolecules and porous solids, namely materials that containsmall pores with walls of high curvature interact with hydrogenmolecules more strongly than large-pore material. Theideal pore size might be slightly larger than thekinetic diameter of H2 (2.8 A ̊ ) for low-pressureadsorption, because pores with such a smallsize allow the dihydrogen molecule to interactwith multiple portions of the framework ratherthan just one SBU or organic linker, whichincreases the interaction energy between theframework and H2,Furthermore, Panela et al. obtained a linear relationship betweenhydrogen-desorption temperature and poresizes of MOFs, which indicates that a MOFwith smaller pores requires a higher desorptiontemperature than a larger-pore MOF(Fig. 10). This provides solid evidence thatthe smaller the pores, the stronger the adsorption of H2.

**3.2.2 Mechanism of Hydrogen Adsorption on MOFs:**

In order to enhance the ability of hydrogen storage, MOFmaterials would require optimizing the attractive intermolecularinteractions between the hydrogen and the condensed phaseenvironment. In principle, there are two main types of sites forhydrogen adsorption: one associated with inorganic metalclusters and another associated with organic linkers. Severalresearch groups evaluated the interaction of hydrogen moleculeswith the metal oxide sites and organic linker sites. Theneutron powder diffraction along with first-principle calculationsshowed that the metal–oxide cluster was primarily responsible forhydrogen adsorption, while the organic linker played only asecondary role. Furthermore, the neutron-diffractionanalysis at 3.5 K on deuterated MOF-5 revealed four sites foradsorption of hydrogen molecules.95,102] The two sites werefound to be filled first: one at the center of the three ZnO3triangular faces and one on top of the single ZnO3 triangle. Onfurther loading, two additional adsorption sites were occupied:one above the two oxygen ions and one at the top of the hexagonallinkers. The relative binding energies were found to be larger forthe three sites around the clusters than for the one site around theorganic linkers. This was supported by the high-qualitysecond-order Moller–Plessey (MP2) calculations. The MP2calculations showed that the binding energy of H2 on the zincoxide corners using Zn4O(HCO2)6 molecule as a model was6.28 kJ mol1, whereas the binding energies of H2 to theorganic linkers were 4.16–5.42 kJ mol1 depending on the size ofthe linkers.

Properties of the interactions between H2 and MOFs wereevaluated. Bordia et al. reported that the adsorptive properties ofMOF-5 were mainly a result of the weak electrostatic forcesassociated with O13Zn4 clusters and the dispersive interactionswith the internal wall structure. Recently, below et al. employed Monte Carlo simulations to model hydrogen sorptionin soc-MOF, [In3O(C16N2O8H6)1.5]NO3. Unlike most otherMOFs that have been investigated for hydrogen storage, soc-MOFhad a highly ionic framework and many relatively small channels (around 1 nm in diameter). The simulations demonstratedthat, for a high hydrogen capacity, MOFs should have relativelysmall pores and interconnected pores with a high surface area tocreate strong MOF–H2 interactions and, thus, indirectly H2–H2attractions. To promote these interactions, the MOF also needs tobe locally polar with large charge separations on its surfacesufficiently far apart to allow hydrogen molecules to be sensitiveto the dipolar interface. Microscopically, hydrogen interacts with the MOF by three principle attractive potential energy contribution: Van der Waals, charge–quadrupole, and induction. The polarization interactions strongly influence the structure of theadsorbed hydrogen in the region of the metal ions and lead to twodistinct populations of dipolar hydrogen. The cooperativeinteractions may also play an important role. Lee et al. revealedthat hydrogen adsorption occurred by a cooperative mechanismin which the adsorptions on metal sites initiated the propagationof the adsorption across the whole framework. Thesimultaneous adsorption of two hydrogen molecules was morefavorable than individual adsorption of two hydrogen molecules, which indicated that adsorbed hydrogen molecules have a remarkable interaction. Furthermore, the DFT-PBE calculations revealed an important role of the orbital interactions between a transition metal (TM) in MOFs and H2 for hydrogenadsorption.

The diffusion of H2 in MOFs was first investigated bySkoulidas and Sholl. They employed equilibrium molecular dynamics to probe the self- and transport-diffusivities of H2 inMOF-5 at room temperature. This work was followed by thestudies of Yang and Zhongand Liu et al. Yang and Zhongperformed a systematic molecular simulation to evaluate theself-diffusivities of H2 in MOF-5, IR-MOF-8, and IRMOF-18 at77 K. They found that the self-diffusivities of H2 in theseMOFs are the same order of magnitude as diffusion of H2 insome zeolites. However, from the neutron scattering measurements, Salles et al. found that the diffusivity of hydrogen at low loading is about 100 times higher in MIL-47(V) and MIL-53(Cr)frameworks than in zeolites. Furthermore, MIL-47(V)exhibited a significantly higher diffusivity than MIL-53(Cr)because of the presence of m2-OH groups in MIL-53(Cr). Them2-OH groups could act as attractive sites and steric barriers forH2, which results in a resistance to H2 diffusion. Furthermore, inH2 and D2 adsorption and desorption kinetics experiments, Chenet al. observed quantum effects on hydrogen diffusion in a mixedzinc/copper MOF Zn3(BDC)3[Cu (PYEN)] (DMF)5 (H2O)5,namely, 1D diffusion in very narrow porosity in the b-axisdirection was a slow process. These results indicate that thenature of the skeleton of the MOFs strongly affects H2 diffusion.

|  |  |  |  |
| --- | --- | --- | --- |
| **MATERIALS** | **Apparent surface**  **area [b] [m^2/g]** | **Heat of**  **adsorption**  **[kJ mol^-1]** | **H2 uptake [i]**  **[wt%]** |
| Zn4O(BDC)3, MOF-5 or IRMOF-1 | 2000  3362, 2900 [c]  2296 [c]  3100 [c] | 3.8/4.8 [f] | 4.5  1.32  4.7  5.1 |
| Zn4O(C8H3BrO4)3, IRMOF-2 | 2544, 1722 [c] | / | 1.2 |
| Zn4O(C8H5NO4)3, IRMOF-3 | 3563  3062, 2446 [c] | / | 1.4 |
| Zn4O(C14H8O4)3, IRMOF-9 | 2631,1904 [c] | / | 4.8 (31) |
| Zn4O(C18H8O4)3, IRMOF-13 | 2100,1551 [c] | / | 0.89 |
| Zn4O(NDC)3, IRMOF-8 | 3263,2476 [c] | / | 1.50 |
| Zn4O(HPDC)3, IRMOF-11 | 1911,2340 | 6.1 [f] | 1.62 |
| Zn4O(TMBDC)3, IRMOF -18 | 1501 | 9.1 [f] | 3.5 (27)  0.89 |
| Zn4O(TTDC)3, IRMOF-20 | 4346,3409 [c] | / | 2.1 |
| [Mn(NDC)]n | 191 | / | 0.57 |
| Mn(HCO2)2 | 297 [d] | / | 0.9 |
| Mn3(BDT)3 | 290 [c] | -6.3 to -8.4 [f] | 0.97 |
| Mn2(BDT)Cl2 | 530 [c] | -6.0 to -8.8 [f] | 0.89 |
| Cu2(BPTC), MOF-505 | 2247 [c] | / | 0.82 |
| Cu2(TPTC) | 2932 [c] | / | 2.48 |
| Cu2(QPTC) | 1958 | / | 2.99 |
| Cu3(BTC)2, HKUST-1 | 1239 [c] | -4.5/-6.8 [f] | 2.18 |

**Table: Summary of hydrogen adsorptionon MOFs at ambient temperature**

**3.2.3 Techniques for Hydrogen CapacityMeasurements:**

It is important to accurately determine the H2 capacity during H2adsorption and desorption. One of the conventional methods isthermogravimetry, which determines the H2 capacity by theweight change. The major disadvantage of thermogravimetry isthat any H2O impurity can lead to a significant error. Thishappens because the weight of a H2O molecule is equal to theweight of nine H2 molecules. Even though the concentration ofthe H2O impurity in H2 is as low as several ppm, the sample isusually kept in a H2 flow for a certain time to determine theweight change. As a result, the sample can adsorb a significantamount of H2O, particularly in small samples and duringprolonged measurements. For example, 0.5 wt.% of H2Oadsorbed can be thought as 4.5 wt.% of H2 capacity. In contrast, the volumetric method determines the pressure change of H2during adsorption (or desorption) in a closed chamber. As aresult, the adsorption of H2O can lead to a much lower error inthe hydrogen capacity in the volumetric method. For this reason, most hydrogen capacities discussed above were obtained byusing volumetric method. Furthermore, these hydrogen capacities were calculated on thematerial basis. However, for a practical hydrogen-storage system, hydrogen capacities should be calculated on the system basis,including storage materials and tank.

**3.2.4 Final Outlook:**

MOFs exhibit excellent performance for hydrogen adsorption at77K. However, it is still a challenge for MOFs to store hydrogen atambient temperature. This is because the interaction betweenmolecular hydrogen and MOFs is relatively weak. Bhatia andMyers obtained the thermodynamic requirement for anadsorbent capable of storing hydrogen at ambient temperature, which is a heat of adsorption of hydrogen equal to15.1 kJ mol1. This value is optimal with respect to theaffinity of hydrogen, which is strong enough to store a largeamount of hydrogen gas at the charging pressure (about 30 bar) but weak enough to release most of that hydrogen at the dischargepressure (about 1.5 bar). Furthermore, Frost et al. reported similarrequirements for hydrogen adsorption heat with a considerationabout the effect of free volume. These requirements can beused as criteria to search and design MOFs for hydrogen storageat ambient temperature. However, so far, there is no material toreach those criteria by molecular hydrogen adsorption.Searching suitable metals and modifying organic linkers are still important approaches to explore MOFs. DFT-PBE calculations have demonstrated that the binding energies to hydrogen molecules were 21.9, 34.6, and 46.5 kJ mol1 for Sc, Ti, and V inMOFs, respectively. This provides a helpful guide forexperimental researchers to design and synthesize effectiveMOFs that will have a larger heat of hydrogen adsorption than15.1 kJ mol1.Doping MOFs by Li or other electropositive metals should beanother promising strategy to increase hydrogen capacity atambient temperature, because it was theoretically predicted thatthe reversible hydrogen capacity of Li-doped MOFs at ambienttemperature and 150 bar can reach 6 wt.%.So far, promising results at ambient temperature wereobtained with a Pt/AC catalyst-promoted IRMOF-8 material,which displayed 4 wt% hydrogen uptake at 100 bar with aprediction of 6 wt.% at 150 barThis indicates that dopingMOFs by catalysts is an effective approach to increase hydrogencapacity at ambient temperature. This occurred because hydrogenadsorption on metal-catalyst-promoted MOFs took place byatomic hydrogen instead of molecular hydrogen, which resultsin a high adsorption heat (above 20 kJ mol1 ). Although MOF-5has almost double the surface area of IRMOF-8, its hydrogenuptake was lower than that of IRMOF-8 when they werecombined with a Pt/AC catalyst. This indicates that thehydrogen uptake by atomic hydrogen adsorption at ambienttemperature is strongly dependent on the organic linkers ofMOFs. For this reason, it can be expected that higher hydrogenuptakes can be obtained by applying Pt/AC catalysts to otherMOFs. Furthermore, it is also worthwhile to explore othercatalysts for combination with MOFs.

**Originality and findings:**

Hydrogen storage is a key enabling technology for the advancement of hydrogen and fuel cell technologies in applications including stationary power, portable power, and transportation. Hydrogen has the highest energy per mass of any fuel; however, its low ambient temperature density results in a low energy per unit volume, therefore requiring the development of advanced storage methods that have potential for higher energy density.

* Moving large amounts of hydrogen around doesn’t necessarily need a hydrogen storage material or chemical carrier. The alternative is to liquefy it, as is already done in huge scale to ship natural gas
* Hydrogen’s simple appeal as a fuel is that when burned, or consumed in a fuel cell to generate electricity, the only emission is water vapour.

**CHALLENGES:**

High density hydrogen storage is a challenge for stationary and portable applications and remains a significant challenge for transportation applications. Presently available storage options typically require large-volume systems that store hydrogen in gaseous form. This is less of an issue for stationary applications, where the footprint of compressed gas tanks may be less critical.

However, fuel-cell-powered vehicles require enough hydrogen to provide a driving range of more than 300 miles with the ability to quickly and easily refuel the vehicle. While some light-duty hydrogen fuel cell electric vehicles (FCEVs) that are capable of this range have emerged onto the market, these vehicles will rely on compressed gas onboard storage using large-volume, high-pressure composite vessels. The required large storage volumes may have less impact for larger vehicles, but providing sufficient hydrogen storage across all light-duty platforms remains a challenge. The importance of the 300-mile-range goal can be appreciated by looking at the sales distribution by range chart on this page, which shows that most vehicles sold today are capable of exceeding this minimum.

On a mass basis, hydrogen has nearly three times the energy content of gasoline—120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline. On a volume basis, however, the situation is reversed; liquid hydrogen has a density of 8 MJ/L whereas gasoline has a density of 32 MJ/L, as shown in the figure comparing energy densities of fuels based on lower heating values. Onboard hydrogen storage capacities of 5–13 kg hydrogen will be required to meet the driving range for the full range of light-duty vehicle platforms.

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