Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 45

Adsorption based Solid State Hydrogen Storage Materials

In the previous class, we have studied the adsorption based material. We started with the fundamentals of such materials, how hydrogen is taken up, how are the isotherms being considered for hydrogen uptake in such materials. And, in this class we will look at what are the different materials which can be used for hydrogen storage which operate on physisorption.

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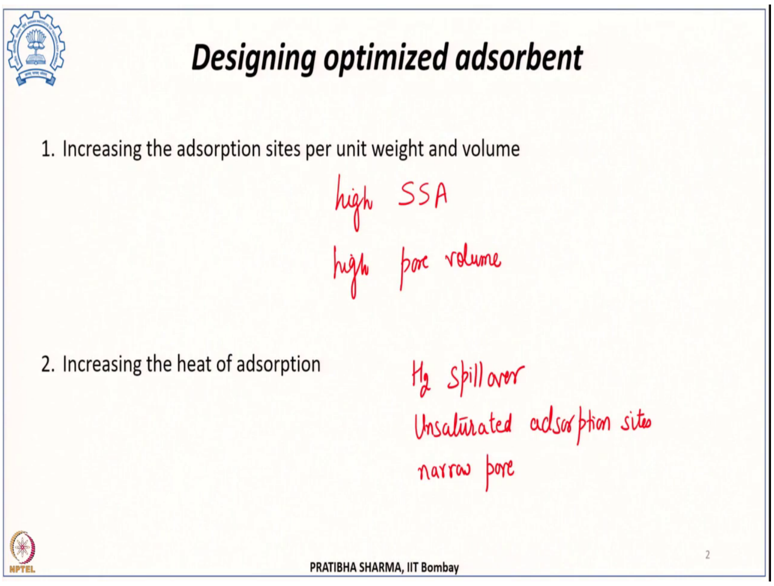

Designing optimized adsorbent

1. Increasing the adsorption sites per unit weight and volume

high SSA
high pore volume

2. Increasing the heat of adsorption

H_2 spillover
Unsaturated adsorption sites
narrow pore

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Now, the important thing is that designing such optimized adsorbent materials is a challenging task. Now, there are two requirements that can be met and that has to be taken care of this is one is like we have to increase the number of adsorption sites per unit weight and per unit volume of the adsorbent. Now, this can be done by either using selecting materials which have high specific surface area and they have a high pore volume.

So, the hydrogen uptake will depend upon the pore dimensions here and the specific surface area. Another, thing that we can do is we can increase the heat of the adsorbent. This can be done through different ways. This can be increased by either introducing hydrogen spillover effect or we can have the unsaturated adsorption sites or we can even look at the adsorption, when it is in a constructing these materials such that they have narrow pores, very small sized pores where the adsorption potential can be increased.

Now, if we see the first effect that is the hydrogen spillover effect. In that case, transition metals like platinum or palladium have been introduced inside the host matrix. But, this has not shown much of promising results. The another thing that can be done is by including unsaturated adsorption sites. And, this can be done by changing the chemical composition of the porous host material by introducing certain other species and these species can be even metal.

But, the problem that was found only partially that was helpful. The reason being the interaction of the hydrogen molecule with the functionalized adsorption sites was not very strong. And, as such this not held much, at the same time the metals which we introduced they were heavy and that in fact, reduced the gravimetric capacity.

So, the other choice could be adsorption of hydrogen into very small or very narrow sized pores. And, in that case the hydrogen molecule can interact with multiple pore walls and that helps in improving on to the adsorption potential. Now, what are the different materials that can be used for adsorption of hydrogen and thereby can be used for solid state hydrogen storage let us see those.

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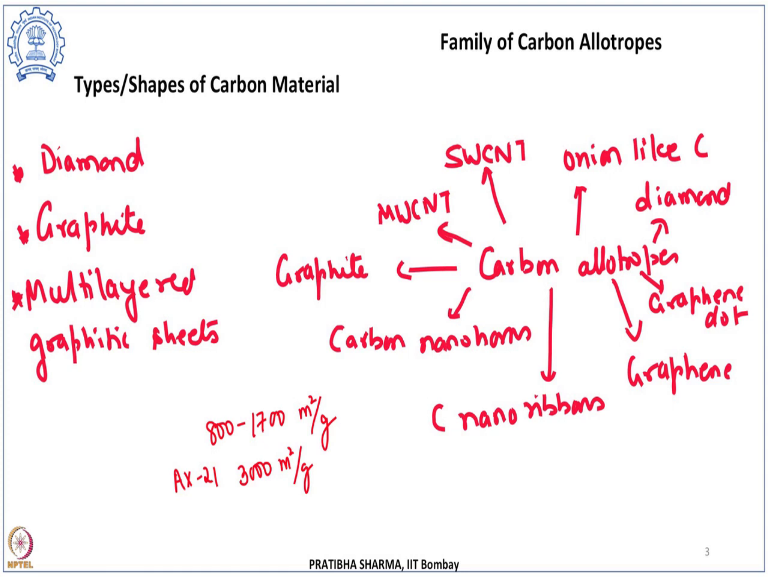

Family of Carbon Allotropes

Types/Shapes of Carbon Material

- Diamond
- Graphite
- Multilayered graphitic sheets

800-1700 m²/g

AX-21 3000 m²/g

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The first one being carbon based materials that we are going to look at. Now, these carbons we know that carbon exist in various allotropic forms. And, they differ these allotropic forms differ in the chemical structures. Now, this allotropic form one of the allotropic form is diamond, another like being graphite, but both of these forms they are nonporous. But, there are several other structures which are highly porous and they have high specific surface areas like the various carbon nano structures.

Now, these carbon nano structures these have structure which is similar to that of benzene like hexagons with carbon being sp2 hybridized. And, these carbon nanostructures they differ in the way these hexagons are being arranged. So, we can divide broadly the different carbon based materials into two classes. One is which have a long range order, like these can be long range order in terms of arranging these hexagons.

And, these are like example being carbon nanotubes or carbon nano fibers and another one could be which have irregular structure like the activated carbon or porous carbon, so amorphous carbon. So, they have highly irregular structure and these activated carbon, porous carbon, they have been found to be very good for hydrogen storage. They have a higher hydrogen uptake capacity. Now, these activated carbons in fact, they have very high specific surface area like the regular activated carbon can have specific surface area of about 800 to 1700 meter square per gram area.

But, the highly porous forms of activated carbon can even have like AX-21, that can even have specific surface area could that could be 3000 meter square per gram. Now, there are different nanostructures of carbon which are ordered one like the single walled carbon nanotubes. Now, these carbon nanotubes are in fact, considered to be like rolled graphene sheets.

And, this is having a single wall, then there can be multiple such walls. So, multi wall carbon nanotubes. Then, there are other carbon structures like onion like carbon or carbon dots, fullrenes, graphene dots. Then, it could be multi-layered graphitic sheets or graphene, carbon nano ribbons, carbon nano horns, carbon nano fibers. So, there are large number of such carbon allotropes which are existing.

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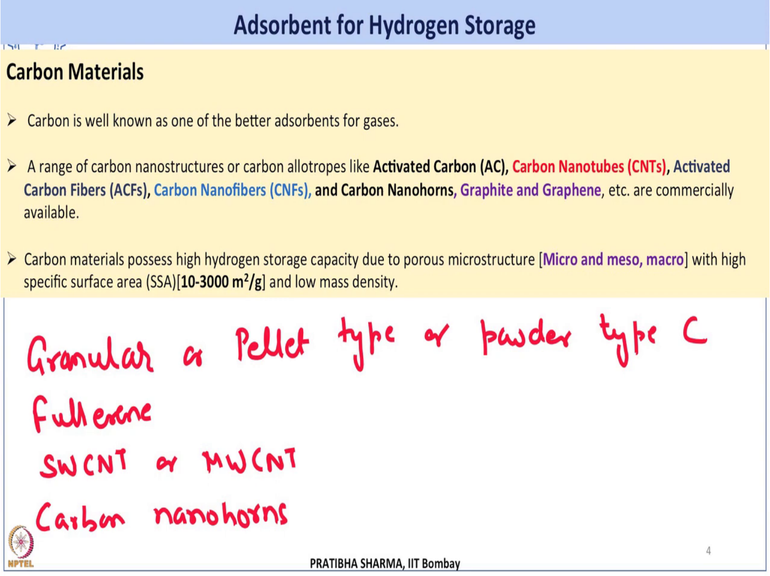

Adsorbent for Hydrogen Storage

Carbon Materials

- Carbon is well known as one of the better adsorbents for gases.
- A range of carbon nanostructures or carbon allotropes like **Activated Carbon (AC)**, **Carbon Nanotubes (CNTs)**, **Activated Carbon Fibers (ACFs)**, **Carbon Nanofibers (CNFs)**, **and Carbon Nanohorns**, **Graphite and Graphene**, etc. are commercially available.
- Carbon materials possess high hydrogen storage capacity due to porous microstructure [**Micro and meso, macro**] with high specific surface area (SSA)[**10-3000 m^2/g**] and low mass density.

Granular or Pellet type or powder type C

Fullerene

SWCNT or MWCNT

Carbon nanohorns

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Now, about 2 decades back a lot of interest was developed in these materials for hydrogen storage. And, this was basically driven by very large capacities being reported in such materials. However, for some of the results, these were found to be non-repetitive. This was because there were certain impurities present, there were certain erroneous results. However, still these carbons based materials, they have a higher storage capacity.

And, in these micro porous carbon based structures, actually the capacity depends upon the specific surface area as well as the pore volume. So, there are different forms of carbon which can be used for hydrogen storage. Like the activated carbons, they give the very good hydrogen storage capacity, other than that there can be carbon nanotubes or activated carbon nano fibers or it could be nanohorns, graphene.

And, these are all commercially available and they have a very porous microstructure. These microstructures can be micro porous or mesoporous or macro porous. And, they have a very high specific surface area that could range from 10 meter square per gram to 3000 meter square per gram. And, at the same time they possess low mass density, that also results into a higher gravimetric capacity. So, this is one of the adsorbent that can be used for hydrogen storage.

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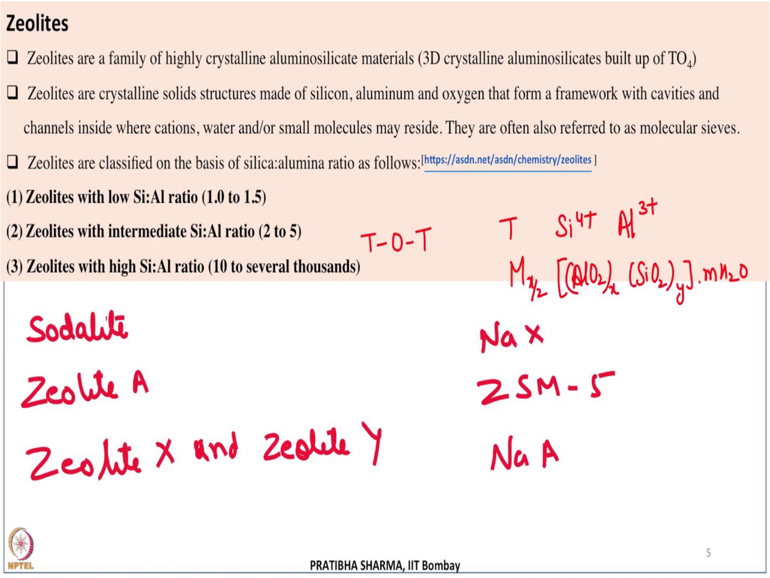

Zeolites

☐ Zeolites are a family of highly crystalline aluminosilicate materials (3D crystalline aluminosilicates built up of TO_4)

☐ Zeolites are crystalline solids structures made of silicon, aluminum and oxygen that form a framework with cavities and channels inside where cations, water and/or small molecules may reside. They are often also referred to as molecular sieves.

☐ Zeolites are classified on the basis of silica:alumina ratio as follows:[https://asdn.net/asdn/chemistry/zeolites]

(1) Zeolites with low Si:Al ratio (1.0 to 1.5)

(2) Zeolites with intermediate Si:Al ratio (2 to 5)

(3) Zeolites with high Si:Al ratio (10 to several thousands)

T-O-T

T Si^{4+} Al^{3+}

$M_{x/2}[(AlO_2)_x(SiO_2)_y].mH_2O$

Sodalite

Zeolite A

Zeolite X and Zeolite Y

Na X

ZSM-5

Na A

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Now, the other possible sorbent could be zeolites. Now, these zeolites are in fact, 3D crystalline alumino-silicate structures. These are built up of TO_4 type of tetrahedron structures with corner sharing. Now, this T here stands for Si^{4+} or Al^{3+}. Now, in them the general chemical formula for these type of zeolites can be written as, where the capital M is the non-framework metal cation or exchange metal cation.

Now, in this type of zeolite structures the bond which is T-O-T bond, this is highly flexible. And, this flexibility of this bond that allows these tetrahedrons to get linked in a variety of ways to form a large number of network topologies. So, there are large number of such zeolite structures which are existing. At the same time, this flexibility of T-O-T bond that also makes the framework flexible. And, the framework can adopt for various changes in the temperature or pressure or chemical surroundings.

Now, the electro neutrality of such structures, because if let us say Si^{4+} is being replaced by Al^{3+}, then the electro-neutrality of this structure will be maintained by introducing a non-framework exchanged metal cation. Now, this non-framework exchange metal cation, this choice will depend upon what is the accommodating pore volume. At the same time, it will also depend upon what is the charge on this metal cation.

Now, when we introduce this charge metal cation into the framework structure, it introduces an electrostatic force. And, that electrostatic force that increases the polarizations effect of the various adsorption sites. And in fact, the channels or the pores which are there in such frameworks, their polarization increases and that electrostatic force that depends upon what is the charge on the cation.

So, that electrostatic force increases when the charge on the cation increases and it decreases with the pore volume. So, these type of zeolites in fact, these are some of these zeolites are naturally occurring. However, most of these zeolites are synthetically synthesized in laboratory. In this type of materials, the hydrogen uptake primarily depends upon what is the specific surface area, what is the type of the metal cation which is being used, what is the concentration of these metal cations.

So, there are different classes of such zeolites. Like these can be classified on the basis of what is the silica to alumina ratio. Like this can be with low silica to alumina ratio, where the ratio Si:Al could be between 1 to 1.5. These zeolites can be with intermediate Si:Al ratio, where in this ratio is 2 to 5 or it can be with high Si:Al ratio so, from 10 to several thousands.

So, there are different types of zeolite structures, like the three X type of zeolites, wherein the cation could be different. It could be sodium or it could be potassium. Then, there are like sodium A type of another type of like these sodalite type of cages then you are getting. So, there are lot many zeolite structures which are being synthesized and these have been studied for hydrogen uptake.

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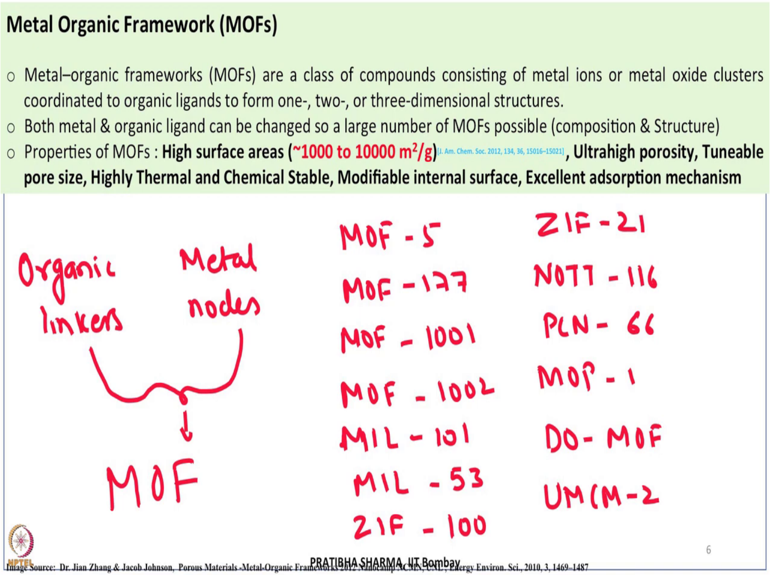

Metal Organic Framework (MOFs)

- Metal–organic frameworks (MOFs) are a class of compounds consisting of metal ions or metal oxide clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures.
- Both metal & organic ligand can be changed so a large number of MOFs possible (composition & Structure)
- Properties of MOFs : **High surface areas (~1000 to 10000 m^2/g)**[J. Am. Chem. Soc. 2012, 134, 36, 15016–15021], **Ultrahigh porosity, Tuneable pore size, Highly Thermal and Chemical Stable, Modifiable internal surface, Excellent adsorption mechanism**

Organic linkers
Metal nodes
MOF

MOF - 5
MOF - 177
MOF - 1001
MOF - 1002
MIL - 101
MIL - 53
ZIF - 100

ZIF - 21
NOTT - 116
PCN - 66
MOP - 1
DO - MOF
UMCM - 2

Image Source: Dr. Jian Zhang & Jacob Johnson, Porous Materials -Metal-Organic Frameworks 2012 Nanocamp NCMN, UNL; Energy Environ. Sci., 2010, 3, 1469–1487

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The another class of material which could be used for hydrogen storage, these are the adsorbent based materials, these are metal organic frameworks. Now, these metal organic frameworks these are in fact, the class of compounds which consists of a metal ion. It could be metal ion or metal oxide cluster or inorganic cluster which is having high dimensionality. And, this can be coordinated with organic ligand and that forms either one, two or three-dimensional structures.

Now, we can change this metal, at the same time we can change this organic ligand. So, this combination of this metal and the organic linker, that makes the framework. Now, we can change this metal, we can change this organic linker and that can give us a wide variety of possibilities. So, a large number of metal organic frameworks they exist and they vary depending upon what is the composition, what is the structure.

Like there are the well-known metal organic frameworks like MOF5 or MOF177, then there are ZIF, ZIF100 or ZIF 21, MIL 53, MIL 101. And, there are many other metal organic frameworks which are having high specific surface areas. So, they can have surface areas as high as even predicted ones like more than 10000-meter square per gram they can have. So, they have specific surface areas like 1000 ranging to 10000-meter square per gram.

They have ultra high porosity, at the same time the pore sizes can be tuned depending upon the choices. They have high thermal and chemical stability and we can modify their internal structure. They have very good adsorption capacity with these metal organic frameworks. However, the challenge remains are to have homogeneous material and that too synthesized on a larger scale; so, having large scale MOF being synthesized that is the major bottleneck.

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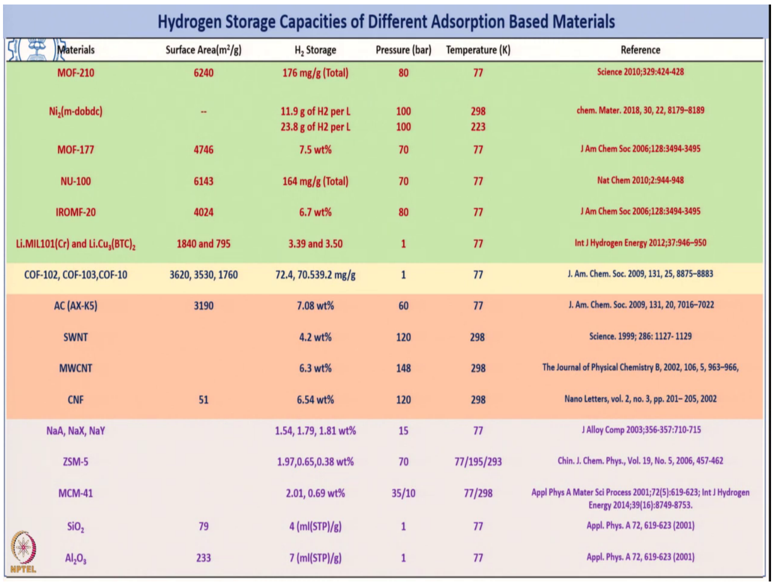

Hydrogen Storage Capacities of Different Adsorption Based Materials

Materials	Surface Area(m²/g)	H_2 Storage	Pressure (bar)	Temperature (K)	Reference
MOF-210	6240	176 mg/g (Total)	80	77	Science 2010;329:424-428
Ni_2(m-dobdc)	--	11.9 g of H2 per L 23.8 g of H2 per L	100 100	298 223	chem. Mater. 2018, 30, 22, 8179–8189
MOF-177	4746	7.5 wt%	70	77	J Am Chem Soc 2006;128:3494-3495
NU-100	6143	164 mg/g (Total)	70	77	Nat Chem 2010;2:944-948
IROMF-20	4024	6.7 wt%	80	77	J Am Chem Soc 2006;128:3494-3495
Li.MIL101(Cr) and Li.Cu_3(BTC)$_2$	1840 and 795	3.39 and 3.50	1	77	Int J Hydrogen Energy 2012;37:946–950
COF-102, COF-103,COF-10	3620, 3530, 1760	72.4, 70.539.2 mg/g	1	77	J. Am. Chem. Soc. 2009, 131, 25, 8875–8883
AC (AX-K5)	3190	7.08 wt%	60	77	J. Am. Chem. Soc. 2009, 131, 20, 7016–7022
SWNT		4.2 wt%	120	298	Science. 1999; 286: 1127- 1129
MWCNT		6.3 wt%	148	298	The Journal of Physical Chemistry B, 2002, 106, 5, 963–966,
CNF	51	6.54 wt%	120	298	Nano Letters, vol. 2, no. 3, pp. 201– 205, 2002
NaA, NaX, NaY		1.54, 1.79, 1.81 wt%	15	77	J Alloy Comp 2003;356-357:710-715
ZSM-5		1.97,0.65,0.38 wt%	70	77/195/293	Chin. J. Chem. Phys., Vol. 19, No. 5, 2006, 457-462
MCM-41		2.01, 0.69 wt%	35/10	77/298	Appl Phys A Mater Sci Process 2001;72(5):619-623; Int J Hydrogen Energy 2014;39(16):8749-8753.
SiO_2	79	4 (ml(STP)/g)	1	77	Appl. Phys. A 72, 619-623 (2001)
Al_2O_3	233	7 (ml(STP)/g)	1	77	Appl. Phys. A 72, 619-623 (2001)

Now, if we see some of the representative examples of these materials, that we have studied then like the for the MOFs, the materials like MOF-210, that has a specific surface area of 6240, can store about 176 milligrams of hydrogen per gram of the material, at a pressure of 80 bar and 77 K. So, we have studied in the earlier class that since the bond in these adsorption based materials is a weak van der Waals bond.

As such to have appreciable amount of hydrogen being stored, we have to cool these down to 77 K. At room temperature the capacities are very low. It could be MOF-177 with a specific surface area of 4746 and has shown to give even 7.5 weight percent at a pressure of 70 bar and 77 kelvin temperature.

NU-100, 6143 meter square per gram of specific surface area, hydrogen storage 164 milligrams per gram of the material at 70 bar pressure and 77 K. IROMF-20 that is having a surface area of 4024 meter square per gram, can give a capacity of 6.7 weight percent and this is at 80 bar and 77 K temperature.

Similarly, there are many more MOFs which have been studied and reported in literature. Similarly, there are Covalent Organic Frameworks: COF-102, COF-103, COF-10 with surface areas of 3620 or 3530, 1760 respectively and they have been reported to store 72.4 or 70.53 milligrams per gram of the material at a pressure of 1 bar and 77 K.

Similarly, the different carbon based nanostructures like the activated carbon, a typical example that is being considered here is AX-K5 with a surface area of 3190. And, it has been reported to store 7.08 weight percent at 60 bar pressure and 77 K temperature. Single volt carbon nanotubes, 4.2 weight percent at a pressure of 120 bar and 298 K. Multi volt carbon nano tube nanotube, 6.3 weight percent at 148 bar and 298 K. Carbon nanofibers with a very small specific surface area, it has been reported 6.54 weight percent, 120 bar and 298 K.

In case of zeolites like NaA, NaX or NaY, they have reported to have a smaller capacity of 1.5 to 1.8 weight percent at 50 bar pressure and 77 K. The reason for the low capacity being observed in zeolite is many of the cages they are not accessible to the hydrogen molecule. And, as such they are not considered as they are not available for hydrogen uptake.

Like the other materials are ZSM-5 with a storage capacity, it has been reported in different literature, the amounts 1.97 or 0.65, 0.38 weight percent at 70 bar pressure and at different temperatures like 77 K or 195 K it was 0.65 at 293 K, it was 0.38. Because, we know that these store hydrogens at a lower temperature and at higher temperature or close to room temperature, the capacity of such materials decreases.

MCM-41 at 35 bar and 77 K has reported to have a capacity of 2.01 weight percent, while at 10 bar pressure and 298 K, it had a capacity of 0.69 weight percent. Silica or alumina, they also have been reported to have certain smaller capacities at 1 bar and 77 K.

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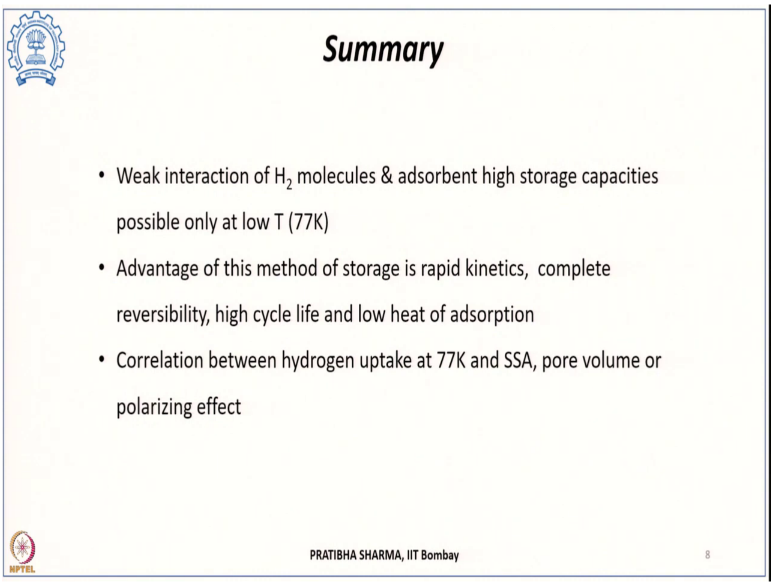

Summary

- Weak interaction of H_2 molecules & adsorbent high storage capacities possible only at low T (77K)
- Advantage of this method of storage is rapid kinetics, complete reversibility, high cycle life and low heat of adsorption
- Correlation between hydrogen uptake at 77K and SSA, pore volume or polarizing effect

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So, to summarize this part, we have seen the different adsorption based materials which can be used for hydrogen storage. And, we know that in them the hydrogen is stored by forming weak bonds and there is a weak interaction, that exists between the adsorbate which is hydrogen molecule and the adsorbent. And, that results into appreciable storage capacity only at low temperature like 77 K; at room temperatures the capacities are lower.

However, the biggest advantage of such materials which are based on adsorption process is that they have a rapid kinetics. Because, since the bond which is formed a weak van der Waals was born and not a strong chemical bond, unlike in case of chemisorption. So, the kinetics is very by slight change in temperature, we can get back that hydrogen or we can store that hydrogen.

At the same time, there is no electronic structure change; there is no diffusion of the hydrogen that takes place into the interstitial sites. As such there is no distortion, structural imperfections or distortions or electronic distribution change. So, as such the reversibility is ensured because, there the bond formed is very weak; at the same time, it is not resulting into severe distortions into the structure. It is not diffusing into the bulk of the material.

At the same time because, of the same reasons the cycle life of such materials is higher. And, since the bond formed is weak so, the heat of adsorption is lower and that is important when we design a hydrogen storage system. So, the heat that will be released will be lower and as such the thermal management will be less severe in such storing such materials.

There is a correlation that we have seen is with the specific surface area of the hydrogen uptake at 77 K. It also depends upon the amount of hydrogen being taken up by these materials that also depends upon the pore volume. And, also like we have seen in case of zeolite, metal organic frameworks and zeolite; if there is a polarizing effect, then that also affects the hydrogen uptake in such materials.

Thank you.