



# HYDROGEN STORAGE IN NANO-MATERIALS

B.Viswanathan  
National Centre for Catalysis Research,  
Indian Institute of Technology, Madras, Chennai

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## 1 Abstract

Nano-materials appears to be a new state of matter even though it may for all practical purposes can be considered as part of solid state. However, it has been realized for some time now that his state may have its own equation of state and also the thermodynamics and surface properties of these materials can be different from those observed with bulk solid state materials. In this state unusual mechanical, electrical, electronic, optical, magnetic, dielectric and surface properties have been reported. The high surface/volume ratio of these materials has significant implications with respect to energy storage. Both the high surface area and the opportunity for nanomaterial consolidation are key attributes of this new state class of materials for hydrogen storage devices. Nanostructured systems including carbon nanotubes, nano-magnesium based hydrides, complex hydride/carbon nanocomposites, boron nitride nanotubes, sulphide nano-tubes of titanium and molybdenum, alanates, polymer nanocomposites, and metal organic frameworks are considered to be potential candidates for storing large quantities of hydrogen. Recent investigations have shown that nanoscale materials may offer advantages if certain physical and chemical effects related to the nanoscale can be used efficiently. The present write up focuses on the application of nanostructured materials for storing atomic or molecular hydrogen. The synergistic effects of nanocrystallinity and nanocatalyst doping on the metal or complex hydrides for improving the thermodynamics and hydrogen reaction kinetics are considered. In addition, various carbonaceous nanomaterials and novel sorbent systems (e.g. carbon nanotubes, fullerenes, nanofibers, polyaniline

nanospheres and metal organic frameworks etc.) and their hydrogen storage characteristics are considered.

## **2 Introduction**

Hydrogen as the future generation fuel has been realized for some time now for various reasons including its high combustion value and also the possibility of generating the fuel from renewable sources like water through photo-electrochemical or photo-catalytic routes. Various issues with respect to hydrogen economy have been considered in literature [1,2]. The essential criteria that have to be considered for selection of materials for hydrogen storage include : (1) light weight (2) cost and availability (3) high volumetric and gravimetric density of hydrogen (4) fast hydrogen sorption kinetics (5) easy and quick regenerability of the materials and reversibility (6) low temperature operation and favourable thermodynamics of the process (7) long term cyclability and also durability. All these characteristics for an appropriate hydrogen storage material place considerable restrictions on the choice of materials for hydrogen storage application. Among the various possibilities that have been considered and evaluated, nanomaterials like nanotubes, nanofibres, nanohorns, nanospheres and nanoparticles have been examined for the hydrogen storage capacity to fulfill the specifications of DOE[3]. In spite of these consistent and persistent efforts, these materials are yet to satisfy the required characteristics like storage capacity of around 6 weight percent, favourable and tuning thermodynamics around 30-55 KJ/mol of hydrogen and temperature of operation around 373 K with about 1000s of cycles of operation.

## **3 Nano Materials - Potentials and Possibilities**

In addition to the unique surface properties of nano materials, dimensionality is one of the specific features of nano materials. One dimensional nano rods and nanotubes are particularly interesting since they can store hydrogen. However the possibility nano horns and other three dimensional architectures also open up wide scope for this application. Nano-scale processing have been used in a generic way to enhance the performance of known hydrides and also to develop entirely new systems. Exploitation of these techniques is still in its early days, and one may expect in the next few years to see a continued refinement even in of metal hydrides, with more and more materials being

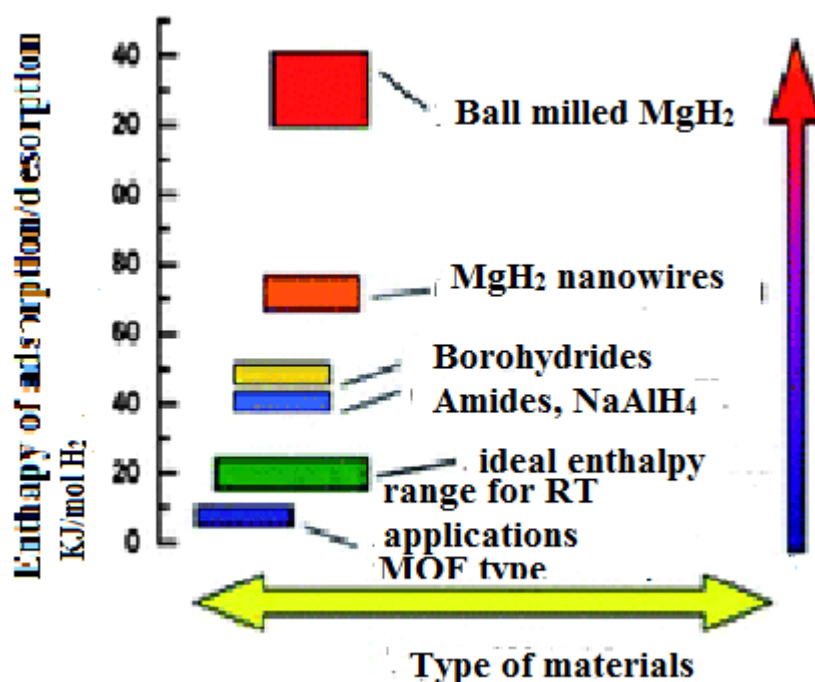


Figure 1: Relationship between type of materials and enthalpy of adsorption/desorption in  $\text{KJ}\cdot\text{mol}^{-1} \text{H}_2$

developed to meet specific performance criteria. Furthermore, the underlying process ball milling is already used in industrial production, implying that upscaling the process to large volume should not present any insuperable obstacles.

Solid state hydrogen storage has always been appealing though the other possibilities exist and have also been demonstrated. This is because new routes for the synthesis of new solid state materials with tailored and also patterned solids like meso porous solids, templated materials, metal organic frameworks and functionalized materials like poly aniline where functional amino groups can hook on hydrogen can be designed and synthesized for examination and exploitation as hydrogen storage materials.

In the following presentation, the role of nano state is considered in several subtopics.

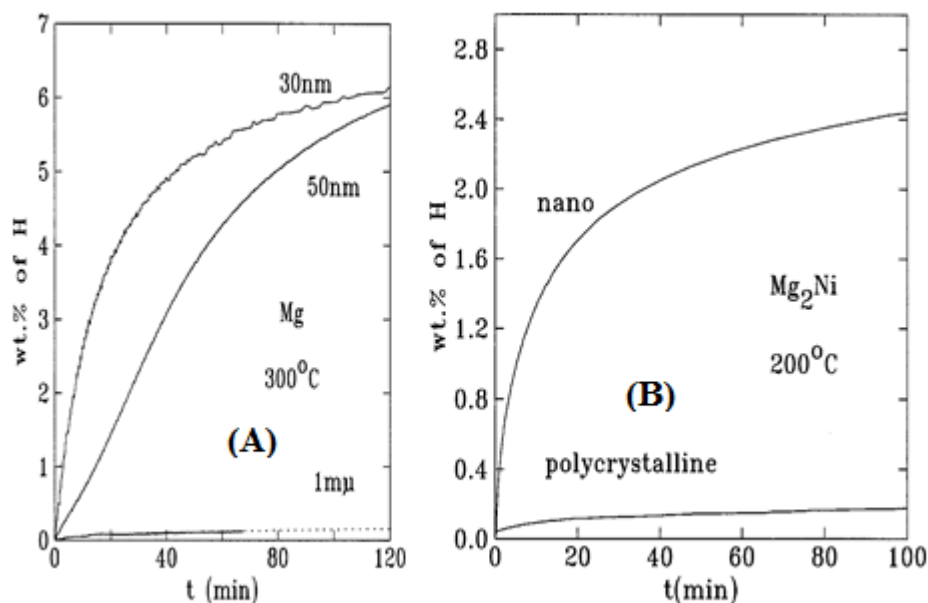


Figure 2: (A) Effect of grain size on hydrogen absorption of ball-milled Mg powder at 573 K no activation; (B) Rate of hydrogen absorption on polycrystalline and nanocrystalline Mg<sub>2</sub>Ni at 473 K Reproduced from Ref.8

## 4 The role of nano scale structure on hydrogen sorption

Nano structures materials are generally defined that type of material which has at least one of the dimensions in nanometer scale only. The issue that is not yet definite is the detailed mechanism of hydrogen diffusion in nano materials. However, there are unequivocal proof that the materials in nanostate is capable of sorbing higher quantity of hydrogen as compared to the conventional material. Let us demonstrate with one specific example. In Fig.2a the capacity for hydrogen absorption on 50 and 30 nm at 573 K on Mg sample is shown. It is seen the sorption capacity on 30 nm sample is higher than that in 50 nm sample and also the equilibration time is also considerably reduced. To demonstrate this effect unambiguously, the kinetic of hydrogen absorption on Mg<sub>2</sub>Ni at 473 K is shown wherein it is obvious that the rate is several orders of magnitude higher on nano state as compared to the bulk polycrystalline state. The points of relevance are:

(1) Poly crystalline samples required prior activation while in nano state the

same material absorbed hydrogen in the first cycle itself.

(2) Higher quantities of hydrogen is sorbed as compared to that on polycrystalline samples. This observation has been consistently recorded in the literature [4-8].

These studies indicated that a carefully monitored homogeneous nano structured material is required and hence other techniques other than ball milling like vapour condensation or sputtering have to be resorted to for generating homogeneous nano structured materials without much imperfections. These materials showed remarkable recovery to the nano structure after hydrogenation-dehydrogenation cycles though they may or may not retain the nano structure in the hydrogenated state.

## **5 Nano-scale catalysis for improved hydrogen sorption**

It is well known that the presence of small quantity of catalysts only affects the kinetics of the process. However, this effect is perceptible only when the catalyst particles are well dispersed in the system. In this case the catalyst and sorbing material are all in nano scale and could be in intimate contact. In Fig 3, a demonstrative example is shown wherein  $\text{LaNi}_5$  system showed remarkably higher sorption of hydrogen when the nano crystalline alloy is mixed with catalyst. The choice of the catalyst possibly depends on the basic hydrogen sorbing system. Various different methodologies have been adopted like introduction of hetero atoms in carbon material whose function can be considered to be to dissociate hydrogen molecule and also facilitate the sorption kinetics[9-10]. The results shown in Fig.4. demonstrate the validity of these postulates. The points of relevance are:

1. The actual mechanism of action is yet to be fully understood and also the choice and selection of catalyst materials for the sorbing system have to be delineated.
2. Efficient dispersion methodologies have to be developed for the catalyst.
3. One has to be able to recognise the role of catalyst and distinguish it from the conventional role of active component. The later systems have to be identified as composite materials.

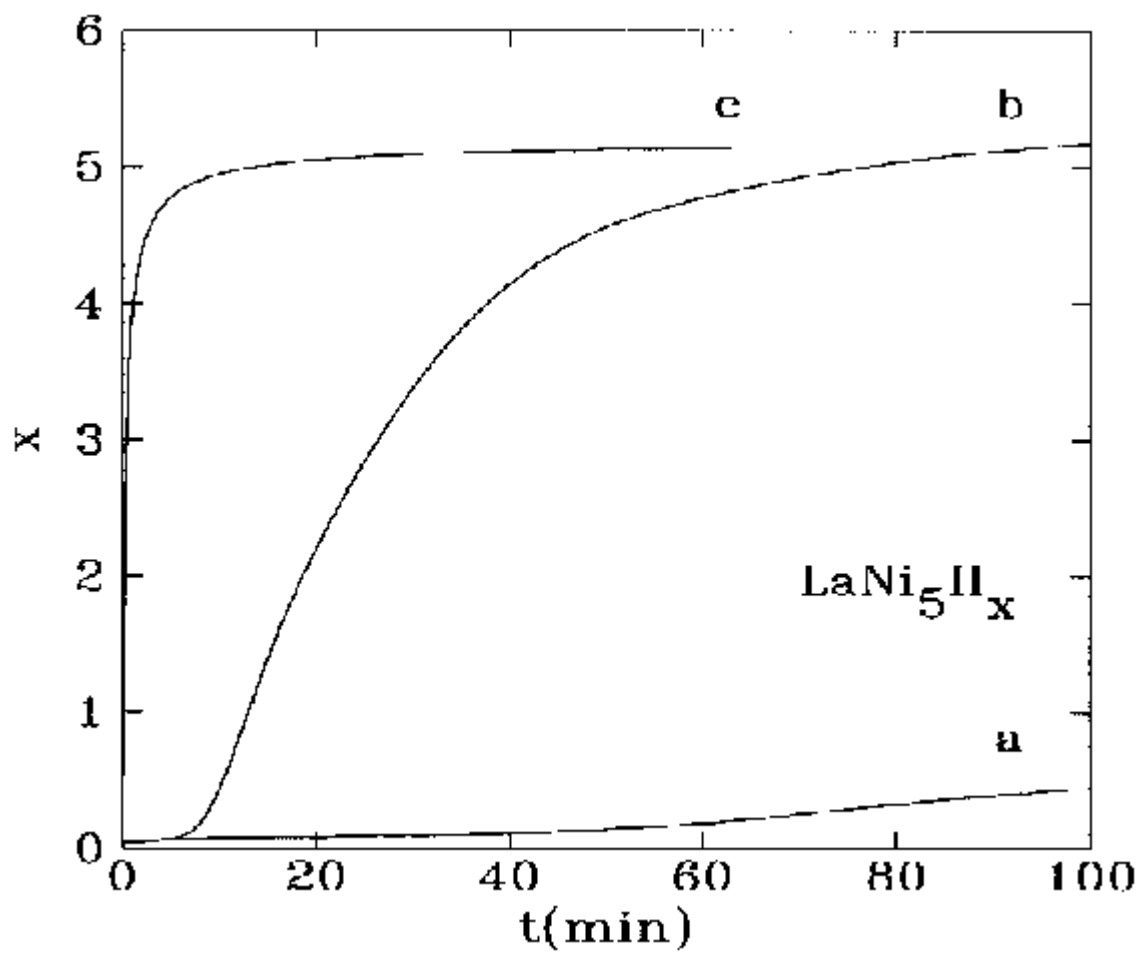


Figure 3: Rate of hydrogen absorption by  $\text{LaNi}_5$  (a) Polycrystalline (b) nanocrystalline, and (c) nanocrystalline with catalyst

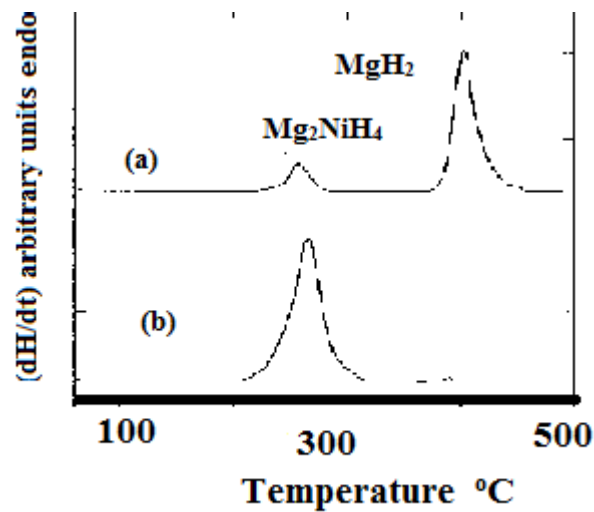


Figure 4: Thermal desorption of a mixture of hydrides (65 weight percent  $\text{MgH}_2$  and 35 weight percent of  $\text{Mg}_2\text{NiH}_4$ ) at 10 degree per minute (a) untreated (b) after ball milling of the hydrogenated mixture

## 6 Nanocomposites

As stated before, nano composites are systems where more than one active component is simultaneously present. To demonstrate this effect one example is shown in Fig.4. In is seen from this figure, it is seen that the desorption temperature is considerably reduced in the composite system  $\text{Mg}_2\text{NiH}_4$  and  $\text{MgH}_2$  composite system when it was subjected to ball milling.

The points of relevance for this class of nano materials for hydrogen sorption are: (1)The nature of mutual synergistic effect is still intriguing and has yet to elucidated.

(2)It has been usually assumed that the desorption kinetic behaviour of the composite system will be more like that the characteristic of the low temperature component. It is possible to build a cascade of components with maximization of the sorption capacity or improving the kinetics of the process or reducing the temperature of operation.

## 7 Functional Nano-composites

The meaning of functional nano composites exhibits special function other than catalysis or sorption capacity and the function improves the main prop-



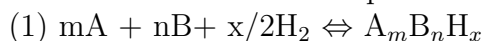
erty of the composite. It can be the second component can facilitate the thermal conductivity of the system, or facilitating the solid state reaction of the active component or alter the hydrogenation thermodynamics in such a way that the system can operate at lower temperature. This aspect has not yet been fully exploited. In fact our understanding of this effect is minimal at this stage and needs careful further intense investigation.

## 8 Nanosale Reactions

There are two possibilities. In one case a normally non miscible two components can become miscible in the presence of hydrogen and thus generating a useful hydrogen absorption system.

A second variation is a metallic hydride and a non absorbing system can give rise to an system as result of hydrogen desorption from the first hydride.

These two cases can be expressed in terms of simple reactions.



Other variations of these reaction sequences are possible in nanofunctional systems for the generation of hydrides.

## 9 Perspective Aspects

There are still a number of issues that have to be answered before nano systems and nano science can be exploited for formulating energy (hydrogen) storage systems. Some of them are listed below:

1. Even though the enhancement of hydrogen absorption in the nano state is established unequivocally, the extent of enhancement and if it will reach the level specified by DOE can be realized are still questions to be answered.
2. The factors like surface to volume ratio and also residual surface tension forces are favourable for higher hydrogen absorption, the precise manner of operation and how to optimize these residual forces are not yet clearly delineated.
3. Hydrogen absorption itself is intriguing since it is the smallest atom, the storage is due to simple trapping by van der Waals forces or due to formation of specific bonds.
4. The optimum size of the nano materials and also the extent of dispersion of nano catalysts have to be established with respect to individual species.
5. In the case of carbon nano materials the hydrogen storage may have many

other implications as stated previously since dimensionality and also possibility of carbon nano tubes, nano rods, nano cones all of them can present various **active sites** and thus show enhanced hydrogen absorption. These aspects have to be established unequivocally. 6. Various levels of theory have been employed at the level of DFT to understand and rationalize the hydrogen absorption in variety of materials and these will also be intensified to formulate and design new materials. It is possible there are other untrodden avenues for exploiting nano state for hydrogen storage.

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