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Hydrogen Storage with Novel Nanomaterials

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General Information

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Most parts of the building are covered by three WLAN Hotspots. Configuration settings for access to the WLAN are as follows: - Infrastructure mode ("access point") - No authentication - 128bit WEP encryption with key

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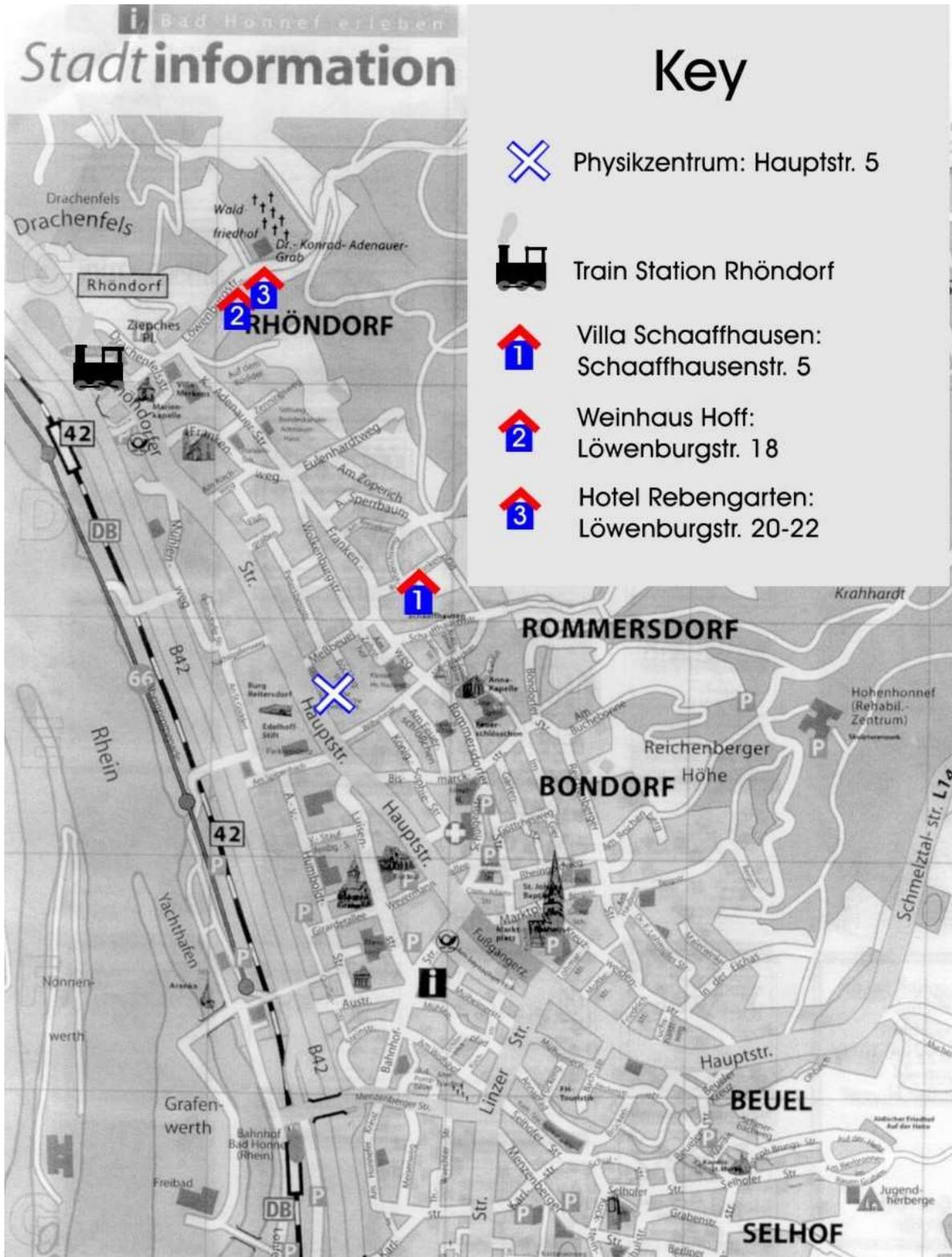
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The locations are marked on the map (See Key).



Locations of Conference Center and hotels.



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Talks

H-Storage in Novel Materials 1

The National Hydrogen Storage Project

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Introduction

The potential energy security and diversity benefits of hydrogen are the basis of the Hydrogen Fuel Initiative launched by President Bush in January 2003. The Hydrogen Fuel Initiative commits government funding for accelerated research, development, and demonstration programs that will enable an industry decision on commercialization of hydrogen by the year 2015. Should industry decide to proceed, a full transition to a U.S. hydrogen economy would require decades. Although the implementation of a hydrogen economy would clearly take time, the key point is that research and development to address the viability of hydrogen needs to occur now.

At the present time, there are three primary technology barriers that must be overcome to enable an industry commercialization decision on hydrogen fuel cell vehicles. First, the cost of safe and efficient hydrogen production and delivery must be lowered to be competitive with gasoline without adverse environmental impacts. Second, fuel cell system costs must be lowered while meeting performance and durability requirements. Finally, on-board hydrogen storage systems must be developed that allow a vehicle range of greater than 300 miles while meeting packaging, cost, and performance requirements.

The barriers associated with hydrogen production, delivery and fuel cells are essentially cost-driven. However, with regard to the on-board hydrogen storage barrier, no approach currently exists that can meet the technical requirements of a greater than 300-mile range, irrespective of the present cost. Therefore, the focus of hydrogen storage research is on performance. New materials and approaches are needed. To accelerate and focus R&D in hydrogen storage, the DOE has initiated the implementation of a National Hydrogen Storage Project.

Storage Issues for Hydrogen-Powered Vehicles

Storing enough hydrogen on vehicles to achieve greater than 300-mile driving range is clearly a significant challenge. On a weight basis, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline). However, on a volume basis the situation is reversed (8 MJ/liter for liquid hydrogen versus 32 MJ/liter for gasoline). On-board hydrogen storage in the range of 5-13 kg is required to encompass the full platform of light duty vehicles. The average fleet on-board storage requirement is approximately 8 kg.

System-Driven Storage Targets

On-board hydrogen storage system targets have been developed through the FreedomCAR Partnership between DOE and the US Council for Automotive Research (USCAR). These targets are system-driven, based on achieving similar performance and cost levels as current gasoline fuel storage systems. The storage system includes the tank, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and any other balance-of-plant components in addition to the first charge of hydrogen and any material such as solid sorbent or liquid used to store the hydrogen. Some of the key targets for the years 2010, and 2015 are shown in Figure 1.

Storage Parameter	Units	2007	2010	2015
Gravimetric energy capacity	kWh/kg (wt. %)	1.5 (4.5)	2.0 (6.0)	3.0 (9.0)
Volumetric energy capacity	kWh/liter (gm H ₂ /liter)	1.2 (36)	1.5 (45)	2.7 (81)
Storage system cost	\$/kWh (\$/kg H ₂ stored)	6 (200)	4 (133)	2 (66)
Cycle life (1/4 tank to full)	cycles	500	1000	1500
Minimum full-flow rate	(g/sec)/kW	0.02	0.02	0.02
Min/Max delivery temp from tank	C	-20/85	-30/85	-40/85
System fill time for 5-kg hydrogen system	min	10	3	2.5
Loss of usable H ₂	(g/hr)/kg H ₂ stored	1	0.1	0.05

Figure 1: *Hydrogen Storage System Targets*

Also shown is an example of near-term targets, such as those outlined for the year 2007. High pressure hydrogen tanks and liquid hydrogen meet some, though clearly not all, of the near term (2007) targets. These 2007 targets are therefore primarily for materials-based systems such as solid-state (e.g. metal hydride) or liquid (e.g. chemical hydride) systems. The focus of the DOE National Hydrogen Storage Project is on materials-based technologies to meet 2010 targets and with potential to eventually meet 2015 targets. Targets in interim years such as those shown in 2007 are meant to help guide research efforts, monitor and compare results, and provide feedback to DOE on technical progress to help refocus research and development as required. Currently, research priorities are on achieving the gravimetric and volumetric capacity targets in Table 1. It is important to note that to achieve system-level capacities of 2 kWh/kg (6 wt.% hydrogen) and 1.5 kWh/L (0.045 kg hydrogen/L) in 2010, the gravimetric and volumetric capacities of the material alone must clearly be higher than the system-level targets.

Hydrogen Storage in Metal-Organic Frameworks

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Increased attention is being focused on metal-organic frameworks as candidates for hydrogen storage materials. This is a result of their many favorable attributes; such as high porosity, reproducible and facile syntheses, amenability to scale-up, and chemical modification for targeting desired properties. A discussion of several strategies aimed at improving hydrogen uptake in these materials is presented. These strategies include the optimization of pore size and adsorption energy by linker modification, impregnation, catenation, and the inclusion of open metal sites and lighter metals.

Nanostructures with High Surface Area for Hydrogen Storage

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The major bottleneck for commercializing fuel-cell vehicles is onboard hydrogen storage. The presently available systems are high pressure tanks or liquefied hydrogen in cryogenic vessels, which both possess severe disadvantages. Storage in light-weight solids could be the solution to this problem. Two principle storage mechanisms exist: i) Adsorption of hydrogen molecules on surfaces, i.e., physisorption. ii) Hydrogen atoms dissolved or forming chemical bonds, i.e., chemisorption. The presentation will focus on physisorption of new nanoscale materials with high specific surface area. In the first part, the presentation will give a critical review of the literature. For many years this area was dominated by announcements of high storage capacities in carbon nanostructures. However, the experimental results on hydrogen storage in carbon nanomaterials scatter over several orders of magnitude and experiments claiming very high values could not independently be reproduced in any laboratory. Therefore, in the light of present-day knowledge it may be said that at moderate pressures and around room temperature, carbon nanostructures cannot store the amount of hydrogen required for automotive applications [1]. The second part will focus on microporous materials which show a high potential for hydrogen storage by physisorption at lower temperatures. Carbon nanomaterials possess high specific surface area, microporosity, and low mass. Apart from these characteristics, materials like activated carbons are cheap and easy to produce. It can be shown for different carbon nanomaterials that the storage capacity depends linearly on the BET specific surface area (SSA) and is independent of the individual nanostructure [2], [3], [4]. Zeolites are aluminosilicates with a very open microporous structure with channels that are large enough to contain gas molecules. Moreover, the presence of electrostatic forces within the channels is a unique characteristic of the zeolites. For zeolites a similar relation between the storage capacity at low temperatures and the SSA is found [5], however, the SSAs obtained for zeolites are typically smaller. In recent years a new class of materials with high specific surface area, the metal-organic frameworks (MOFs), have been developed and studied for gas adsorption [6], [7]. These MOFs consist of metal oxide clusters connected by rigid aromatic linkers giving a three dimensional porous structure and, furthermore, they possess the lowest density of all known crystalline materials. Newest measurements on the hydrogen uptake in MOFs will be discussed, e.g. [8], [9], [10]. Together these results indicate that nanostructures with high SSA and micropore density are very promising materials for hydrogen storage at low temperature which, e.g., may be used for cryogenic storage systems in long-term satellite missions.

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[5] H.W. Langmi et al., *J. Alloys Comp.* 356-357, 710 (2003)

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[7] N.L. Rosi et al., *Science* 300, 1127 (2003)

[8] B. Panella and M. Hirscher, *Adv. Mater.* 17, 538 (2005)

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Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material

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The development of high capacity, hydrogen storage materials that can be recharged under moderate conditions is a key barrier to the realization of a hydrogen economy. Among the field of new materials that are being developed as onboard hydrogen carriers, Ti-doped NaAlH_4 has the best combination of critical hydrogen storage properties. In recognition of this distinction, both United Technologies and GM have launched multi-million dollar projects to develop state-of-the-art, hydrogen storage tanks based on Ti-doped NaAlH_4 for utilization PEM powered vehicles. Efforts to develop Ti-doped NaAlH_4 as a hydrogen storage material arose following Bogdanovic and Schwickardi's report in 1997 that the elimination of hydrogen from solid NaAlH_4 is markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. This was a revolutionary finding in the area of metal hydrides as hydrogen cycling at moderate temperatures was unprecedented behavior for saline hydrides. We subsequently discovered an alternative method of doping of NaAlH_4 that further enhances the kinetics of the reversible dehydrogenation of the hydride and stabilizes its hydrogen cycling capacity. In order, to obtain guiding principles for the design and synthesis of related materials with improved hydrogen storage properties, a growing number of research efforts have sought to elucidate the nature of the Ti species responsible for the enhanced hydrogen cycling kinetics of Ti-doped NaAlH_4 . We have probed the remarkable hydrogen storage properties of this material through kinetic studies; tunneling and scanning electron microscopy; X-ray and neutron diffraction; as well as infrared, electron paramagnetic resonance, nuclear magnetic resonance, X-ray absorption and anelastic spectroscopy. We have found that highly mobile, hydrogen containing point defects are generated in the doped material by an active Ti species. A model of the doped hydride has evolved from these studies in which titanium dopants proximal to the complex aluminum hydride anions generate the point defects that give rise to the enhanced hydrogen cycling kinetics. The details the fundamental studies and our model of the doped hydride will be presented.

Destabilized Complex Hydrides

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Complex hydrides are regarded as potential candidates for advanced hydrogen storage media, because of their high gravimetric hydrogen densities. However, in order to employ the complex hydrides for solid state hydrogen storage applications, several researches are required to be conducted from the perspective both of kinetics and thermodynamics. Kinetically, the dehydriding and (re-)hydriding reactions of complex hydrides are slow, although Bogdanovic[?] and Schwickardi reported a dramatic improvement by the addition of $\text{Ti}(\text{O}i\text{Bu})_4$ or TiCl_3 to NaAlH_4 [1]. We studied LiNH_2 and LiBH_4 from the perspective of thermodynamics. So far, two effective methods, 'substitution of M elements' and 'preparation of appropriate mixtures' are investigated with the primary aim of destabilization for promoting the dehydriding reactions. In the former method, first principles calculations have been applied to LiNH_2 [2] and LiBH_4 [3] for characterizing the electronic structures. It was clarified that electron are strongly localized around the $[\text{NH}_2]^-$ and $[\text{BH}_4]^-$ anion, which are compensated by Li^+ cation. Based on the characters, it was predicted that the substitution of Li by other elements with larger electronegativity, such as Mg weakens the ionic bonding between Li^+ and $[\text{NH}_2]^-$ or $[\text{BH}_4]^-$ anion. Experimental results on the dehydriding reactions of LiNH_2 and LiBH_4 with/without Mg substitutions indicated that the dehydriding temperatures of the samples become lower with the increasing Mg concentrations [4] [5]; this is in agreement with the prediction. In the latter method, we studied two types of mixtures; one is the mixture of $\text{Mg}(\text{NH}_2)_2$ and LiH , the other is the mixture of LiBH_4 and 2LiNH_2 . A mixture of $\text{Mg}(\text{NH}_2)_2$ with a low decomposition temperature and LiH showing rapid reactions to ammonia was chosen as one of the best compositions for decreasing the dehydriding temperature among mixtures of $\text{M}(\text{NH}_2)_x$ and MH_y [6]. To prevent ammonia release, increasing the LiH ratio in the mixtures is effective, which results in a reduction in the amount of desorbed hydrogen. In the mixture of LiBH_4 and 2LiNH_2 , new pathways with appropriate enthalpy changes were investigated [7],[8]. Moreover, two criteria for selecting complex hydrides that are mixed together for producing new pathways were proposed.

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Toward an Ammonia-Mediated Hydrogen Economy

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Materialization of a hydrogen economy could provide a solution to significant global challenges. In particular, the possibility of improving the efficiency and simultaneously minimizing the environmental impact of energy conversion processes, together with the opportunity to reduce the dependency of fossil fuels, are main drivers for the currently increasing research and development efforts. However, significant technological breakthroughs are necessary for making a hydrogen economy feasible. Particularly, it is necessary to develop appropriate hydrogen storage and transportation technologies. Recently, metal ammine salts were proposed as safe, reversible, high-density and low-cost hydrogen carriers. Here, we discuss how this development could provide a platform for using ammonia as a fuel for the hydrogen economy. We do that by comparing various possible hydrogen carriers with respect to energy and cost efficiency, infrastructure requirements, safety concerns and also environmental impact.

Industry Day

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Hydrogen Storage Technology Commitment to Environmentally Friendly Vehicles

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We, Honda, have been working in three major fields to realize "Hydrogen Energy World". Firstly, since pure hydrogen does not exist in the natural form, we must produce hydrogen economically as an energy resource (Production). Secondly, we have to store those produced hydrogen with safe, in a small size and a lightweight system (Storage). Lastly, we need to develop a system to utilize hydrogen efficiently (Fuel Cell).

We will focus in the hydrogen storage technology aspects from automotive industry, a leader of fuel cell vehicles yet distributed to individual customer.[1] A hydrogen storage system for the fuel cell vehicle requires efficient both of storage and extraction of H_2 with the following fundamental characteristics: (1) High storage capacity (7kg H_2 / 100kg) of the storage system weight. (2) High storage capacity (7kg H_2 / 100L) of the storage system volume. (3) Near the room temperature and/or ambient pressure operation. (3) Quick uptake / extraction, in the matter of seconds. (4) Stability and reusability. We see none of those technologies could satisfy our final target at this moment.

In the first part of our talk, we will introduce some of major activities in the fuel cell vehicle, FCX [2] then we will be looking into technical part. We will state some important aspects for hydrogen storage system from industry in the second part. Then we will show some results from our hydrogen storage materials research at Honda.



Figure 1: See through drawing of Honda FCX (right) and its high-pressure hydrogen storage tank (156.6L, 350 atm) could fueled Honda FC stack up to 430 km (270 miles) driving range (left).

[1]<http://world.honda.com/news/2005/4050629.html>

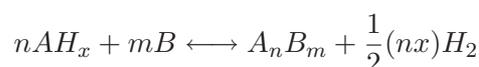
[2]<http://world.honda.com/FuelCell/FCX/>

Behavior and Properties of Metal Hydrides for Reversible Hydrogen Storage

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The chemical and physical properties of so-called conventional metal hydrides (i.e., those phases where hydrogen occupies sites within its host or had not formed covalent complexes) will be described with respect to practical issues for the reversible storage of hydrogen gas. Most attention will be given to the hydrides formed by selected metallic elements (e.g., Li, Mg, V, etc.) and some families of intermetallic alloys and compounds (i.e., AB, AB₂, and AB₅). The range of possible applications for metal hydrides will be reviewed. Hydride destabilization through alloy formation upon dehydrogenation can be used to increase the equilibrium pressures of strongly bound hydrides such as LiH and MgH₂. For two components this process involves the reaction



where AH_x is binary or more complex hydride, B is element that does not form a stable hydride (e.g., Si), and n and m are specified by the stoichiometry of the AB alloy. The impact of the A_nB_m alloy phase diagrams on the hydrogen isotherms will be illustrated for the LiH-Si system.

A brief assessment of the hydrogen diffusion behavior in MH_x phases is given that conveys the extremely wide range of values existing within these materials. In some hydrides (e.g., those formed by the AB₅ and Laves-type AB₂ alloys) hydrogen mobility is sufficiently rapid that diffusion does not normally impede the reaction kinetics during hydrogen absorption and desorption. There are also many other hydrides where the hydrogen diffusion rates do severely impact these kinetics such as seen with the hydride phases formed by the Mg-based alloys. Extended mechanical processing has been done on these alloys to produce nanocrystalline or even amorphous phases in order to reduce effective particle sizes that would help overcome the diffusion limitations occurring in larger particles.

The final topic concerns the intrinsic (i.e., without various contamination effects) degradation, or disproportionation, of ternary hydrides A_nB_mH_x phases either during their formation or as a consequence of temperature/pressure cycling. This latter situation is especially important to most hydrogen storage applications. The most common cause of this disproportionation is from the strong thermodynamic driving force for the formation of very stable binary hydrides such as CaH₂, ZrH₂, or LaH_x. It has been recognized for over 20 years that LaNi₅H_x and most of its related hydrides are only formed due to the severely retarded kinetics preventing phase segregation into mixtures of LaH_x and Ni metal. On the other hand, a few elements (i.e., Al and Sn) have been found to be remarkably effective when partially substituted for Ni in enhancing the stability of the pseudo-ternary hydride phase during thermal and/or electrochemical cycling. A hypothesis will be presented on fundamental degradation processes within the hydrides formed by the LaNi₅ alloys along with a corresponding explanation for why Sn suppresses the resulting degradation effects. Examples of the disproportionation behavior exhibited by hydrides formed by other alloy families (i.e., AB and AB₂) during cycling and heating to elevated temperatures will also be described. It is reasoned that degradation is a general phenomenon where high hydrogen concentrations in metastable hydrides promote accelerated host atom diffusion leading to thermodynamically favored phase segregation along with AH_x formation.

Synthesis, Structure, and Hydrogen Release Characteristics of the Quaternary Light Metal Hydride $\text{Li}_3\text{BN}_2\text{H}_8$

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We have synthesized a light metal quaternary hydride, $\text{Li}_3\text{BN}_2\text{H}_8$, with a theoretical hydrogen capacity of 11.9 wt % [1]. $\text{Li}_3\text{BN}_2\text{H}_8$ is formed by ball milling mixed LiNH_2 and LiBH_4 powders in a 2:1 molar ratio. X-ray diffraction (XRD) results show that the LiNH_2 and LiBH_4 diffraction peaks weaken as the milling time increases, and a new set of peaks emerges. After milling for 40 min the sample is substantially converted to the new phase, and the conversion is complete after 300 min. Continued milling up to 960 min produces no further change. Except for a small quantity of Li_2O impurity, the final XRD pattern is single phase, and all of its XRD peaks index to a body-centered cubic crystal structure with $a = 10.76 \text{ \AA}$. In situ XRD data demonstrate that $\text{Li}_3\text{BN}_2\text{H}_8$ also forms without ball milling by reacting mixed LiNH_2 and LiBH_4 powders at temperatures above about 95°C . Indeed, we have evidence for slow reaction of the mixed powders even when stored at ambient temperature in a glove box. Both synthesis routes produce the same $\text{Li}_3\text{BN}_2\text{H}_8$ phase. $\text{Li}_3\text{BN}_2\text{H}_8$ melts above 190°C , and thermogravimetric and volumetric measurements demonstrate that $\text{Li}_3\text{BN}_2\text{H}_8$ releases 10 wt% H_2 from the liquid when heated above about 250°C . Using simultaneous mass spectrometry residual gas analysis we observe that a small amount of NH_3 (2-3 mole% of the generated gas) is released concurrently. The independent volumetric and gravimetric measurements are in excellent agreement regarding the quantities of H_2 and NH_3 released, and the evolved gases satisfactorily account for all of the available hydrogen content. The dehydrogenated product forms a mixture of solid Li_3BN_2 polymorphs, with the major phase being a new Li_3BN_2 polymorph having a body-centered tetragonal crystal structure. A differential scanning calorimetry measurement shows an endothermic melting peak above 190°C , followed by substantial exothermic heat flow above 250°C associated with hydrogen release and solidification of Li_3BN_2 . The exothermic hydrogen release suggests that the reverse reaction is not thermodynamically favored. Our attempts to directly rehydride the decomposition product by heating under H_2 gas at pressures of up to 8 MPa have so far not achieved significant hydrogen reabsorption. This new material and its derivatives nonetheless represent promising research candidates in the search for practical on-board hydrogen storage materials.

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Hydrogen Storage - Technology Status and Technology Needs

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Adam Opel AG, Bereich "Hydrogen Storage & Technology"*

During an introduction it will be explained why General Motors is investigating hydrogen-propelled vehicles. Additionally, a short history of GM fuel cell vehicles will be provided and the current hydrogen-propelled models will be described. Within the framework of this talk, an overview shall be given on the different possibilities of hydrogen storage. The presentation in particular is to be focused on the implications of an automotive tank system design for the development of novel storage materials. The relationship between system storage values and material storage values will be explained. Challenges, required material properties and perspectives for solid state absorber materials of hydrogen are to be presented.

Nanocrystalline Reactive Light Metal Hydride Composites for Mobile Hydrogen Storage

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Hydrides offer the highest storage capacity by volume, and are one of the most promising alternatives for reversible storage of hydrogen. However, only light metal hydrides can meet the application criteria with respect to weight-related storage capacity, and they have not been considered competitive because of their rather sluggish sorption kinetics. A breakthrough in reaction kinetics was achieved by preparing nanocrystalline hydrides using high energy ball milling and the addition of suitable catalysts. However, a comprehensive understanding of the reaction mechanisms is still lacking. Furthermore, a major problem for technical application of hydrides is the reaction heat for refueling and for discharging hydrogen. Large reaction heats reduce the overall energetic efficiency and necessitate large heat exchangers. Thus, volume and weight related system capacity of metal hydride based storage tanks. In several cases, heat transfer can be rate-limiting for the desired reaction. For combination with a polymer-based fuel cell (Nafion or Polybenzimidazol) operating at temperatures between 80 and 150°C, reaction enthalpies in the range between 25 and 40 kJ/mole-H₂ are favourable. Both, kinetics and thermodynamics issues will be addressed in the presentation. Regarding reaction kinetics, magnesium was chosen as a model system to elucidate the particular advantages of nanocrystalline microstructures and to give tentative rules for good catalyst materials, which may also apply for other hydrides or hydrogen reactions. Therefore, the experimental sorption curves were fitted on the basis of different kinetic models and discussed regarding the respective processes. Reaction kinetics of MgH₂ was determined for different catalyst additions, including transition metal oxides, carbides, nitrides, and chlorides. The results indicate that multiple valencies of the transition metal in the catalyst are required and that high valency states are favourable. In addition, defects in the crystal structure may play an important role as chemisorption sites for hydrogen. As expected, a high affinity of the transition metal to hydrogen further improves reactivity. Among the tested catalysts, best kinetics was obtained for MgH₂ with 0.5 mole% Nb₂O₅. Both, absorption and desorption are possible within 2 minutes and a desorption rate of about 100 kW/kg was obtained. The thermal stability of the nanocrystalline microstructure as well as the respective sorption kinetics of ball-milled MgH₂ with or without catalyst have been investigated after cycling and annealing at technically relevant temperatures between 300°C and 400°C. While kinetics for pure MgH₂ slows down substantially already after few cycles at 300°C, MgH₂ with Nb₂O₅ catalyst still shows fast sorption up to 370°C. At higher temperatures, kinetics for the catalyzed material also breaks down, which is attributed to a deterioration of the catalyst. Continuous coarsening of the microstructure by static annealing leads to an increased fraction of the storage capacity that can only be recharged at slower rate. This is discussed in terms of retarded growth conditions for the MgH₂ phase. With respect to thermodynamics, reactive hydride composites (RHC) were recently proposed to lower the overall reaction enthalpies. This new concept is based on a combination of exothermic and endothermic reactions, which partially compensate the large reaction heat. E.g., LiBH₄ can be combined with MgH₂. Upon hydrogen release, the remaining B and Mg can react to form MgB₂. In this way, the large reaction heat for hydrogen release or absorption may be buffered by the formation or decomposition, respectively, of MgB₂. Indeed, using this method, reversible storage of more than 11 wt.% is feasible. Selected RHC with estimated operation temperatures lower than 150°C will be presented, which are promising for technical application in fuel cell automobiles.

Hydrogen Storage Properties of Noble Metal Clusters

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In this talk, the difference between nano particle and bulk material in hydrogen storage properties of noble metals (platinum and palladium) is reported. The noble metal nanoparticles were synthesized by polyol method and then coated with PVP (Poly (N-vinyl-2-pyrrolidone)) as a stabilizer [1]. The PVP-coated nanoparticles are suitable for evaluation of hydrogen storage properties, because PVP coating prevents aggregation of nanoparticles, while hydrogen permeates through PVP easily. The P-C-T relations of the PVP-coated nanoparticles/hydrogen system were measured by volumetric apparatus from 323K to 423K. The Pt nanoparticles (average diameter $\sim 3.0\text{nm}$) stored $\text{H/Pt} \sim 0.47$ of hydrogen. The amount of hydrogen uptake of Pt nanoparticles was far more than that of bulk Pt ($\text{H/Pt} < 0.01$). The Langmuir plots from the P-C-T relation of Pt nanoparticles were linear completely. This suggests that Pt nanoparticles chemisorbed hydrogen on the surface just like bulk platinum. The large storage capacity of Pt nanoparticles is probably due to the large specific surface area as against bulk Pt. Pd nanoparticles (average diameter $\sim 2.5\text{nm}$) absorbed $\text{H/Pd} \sim 0.7$ of hydrogen almost equal to that in bulk Pd ($\text{H/Pd} \sim 0.6$). However the limit of solid solubility was extended remarkably and an equilibrium pressure so-called plateau disappeared on the P-C-T relation (Figure 1). The XRD profiles of Pd nanoparticles / hydrogen system suggest that the solid-solution phase may not coexist with hydride phase. The heat of hydrogenation was also calculated from the temperature dependence of the P-C-T relations. The specific heat of hydrogenation of Pd nanoparticles at $\text{H/Pd} = 0.6$ was -22kJ/mol-H_2 , which was less than that of bulk PdH 0.6 formation (-35kJ/mol). This finding may give a clue to reduce heat of hydrogen ab/desorption without decreasing hydrogen storage capacity.

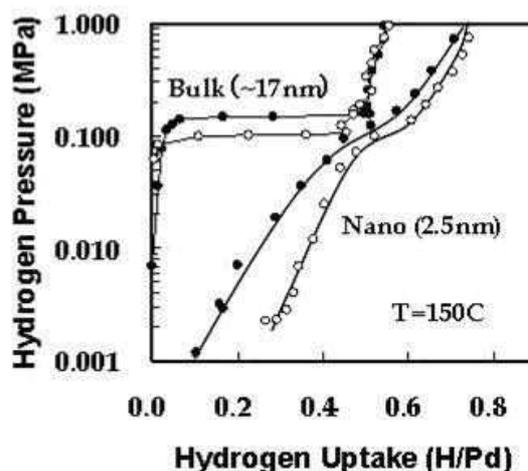


Figure 1: P-C-T curves of nano and bulk palladium. Open (closed) symbols show hydrogen loading (unloading).

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Hydrogen Storage on Carbon Materials

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The use of carbon materials as hydrogen storage systems is paying an important attention by the scientific community. A revision of both experimental and theoretical studies published on the field of hydrogen storage on carbon materials shows a large dispersion in the results. There are studies where the highest values are shown by materials with cylindrical nanoporous [1] (carbon nanotubes). On the other hand, some authors have shown that hydrogen storage is better on slit-shape nanopores [2]. The aim of this work is to evaluate the hydrogen storage capacities of carbon materials with different nano-structure, in order to determinate the optimum nanoporosity (shape and size) for this application. We have used different carbon materials like nanotubes, nanofibers and activated carbons. Thus, we have studied both the effect of the porous texture (volume and pore size distribution) and the porous geometry (slit or cylindrical).

Table 1 reports the porous texture characterization and the amount of H₂ adsorbed at 298 K and 20 MPa on carbon materials with different porosity and pore size distributions. CF is a carbon fiber with a very narrow microporosity (does not adsorb N₂ at 77 K). KUA1 is an activated carbon prepared from anthracite by chemical activation with KOH. This sample has similar values of micropore volumes from N₂[V(N₂)] and CO₂[V(CO₂)], which is characteristic of samples with a narrow micropore size distribution (MPSD) with a mean pore size around 0.5-0.7 nm. AC35 is a physically activated carbon, which shows higher V(N₂) than V(CO₂), this is characteristic of a wide MPSD. Finally, KUA2 is an activated carbon prepared in the same way that KUA1, but it has a very large porosity (SBET = 3355 m² g⁻¹) and a wide MPSD.

Sample	S_{BET} (m ² g ⁻¹)	V(N ₂) (cm ³ g ⁻¹)	V(CO ₂) (cm ³ g ⁻¹)	H ₂ at 20 MPa (wt.%)
CF	0	0	0.18	0.35
KUA1	1058	0.51	0.50	1.26
AC35	1204	0.54	0.40	0.68
KUA2	3355	1.53	0.79	1.62

Figure 1: Porous texture characterization results and the amount of H₂ adsorbed at 298 K and 20 MPa on different carbon materials

The amount of H₂ adsorbed is directly related with the porosity development of the samples, increasing with the narrow micropore volume [V(CO₂)]. A similar trend is observed with the SBET and V(N₂), except for the sample KUA1. This sample presents a much higher hydrogen adsorption capacity than a sample with higher SBET and V(N₂) (sample AC35). These results indicate that the presence of nanopores with a suitable size to hold two layers of adsorbed hydrogen (0.5-0.7 nm) is critical for this application.

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Metal Nitride Nanostructures as Hydrogen Storage Materials

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With the exception of carbon nanostructures, the global R&D effort in hydrogen storage has largely been centred on metals and alloys known for many decades. We have initiated a major search for new hydrogen storage systems, aiming to identify and modify materials with open and porous structures, low densities and controlled morphologies at the nanoscale. Until recently, metal nitrides were relatively unexplored in terms of practical applications as they are predominantly air-sensitive materials necessitating the use of some intricate synthetic methods. However, certain binary and ternary nitrides were recently found to have potential for application in a range of fields including hydrogen storage. We have produced some of these materials as nanostructures with morphological control via synthetic conditions and have shown that these nanomaterials store hydrogen with a significant improvement in rate and cyclability compared with the bulk materials (Figure 1).

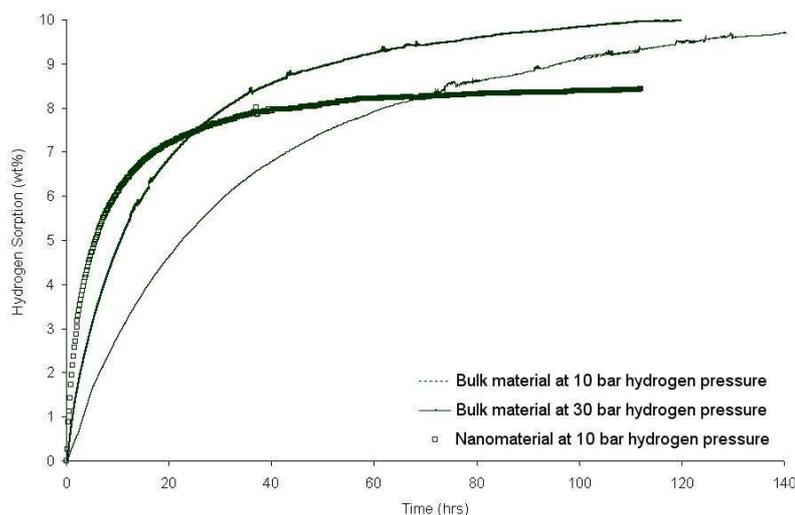


Figure 1: Hydrogen uptake vs. time for bulk and nanostructured metal nitride materials.

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Hydrogen and Clusters

Hydrogen Interaction with Metals

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Hydrogen which is conceptually the simplest atomic system, displays a much more complex behavior in the interaction with metals than most larger atoms. Starting from a molecular source, the first step of the interaction is a dissociation which depends critically on the long range electronic interactions quite far away from the surface. Following dissociation, atomic hydrogen causes extensive and to a certain extent delocalized electronic modifications at the surface. In bulk metals, hydrogen incorporation drastically alters the electronic properties which for some systems change from metallic to insulating, or from highly reflecting for visible light to optically transparent. In this review experiments and theoretical models, highlighting the present level of understanding of these complex interactions will be presented.

Materials for Hydrogen Storage: From Nanostructures to Complex Hydrides

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The limited supply of fossil fuels, its adverse effect on the environment, and growing world-wide demand for energy has necessitated the search for new and clean sources of energy. The possibility of using hydrogen to meet this growing energy need has rekindled interest in the study of safe, efficient, and economical storage of hydrogen. The current methods for storing hydrogen as a compressed gas or liquid are not suitable for practical applications. An alternate method for hydrogen storage involves metal hydrides. Although conventional intermetallic hydrides can store hydrogen reversibly at around room temperature, the relative weight of stored hydrogen in these materials is rather low (1 - 3 wt %) and do not meet the requirements of the transportation industry (≈ 10 wt %). For this the host materials have to consist of light elements such as Li, Be, B, C, Na, Mg, and Al. Unfortunately, the bonding of hydrogen in these materials is rather strong (covalent or ionic) and the thermodynamics and kinetics are poor. Ways must, therefore, be found to weaken the hydrogen bond strength so that light metal complex hydrides can be used as effective hydrogen storage materials.

This talk will discuss the issues and challenges in storing hydrogen in light complex hydrides and discuss the role of nanostructuring and catalysts that can improve the thermodynamics and kinetics of hydrogen. In particular, I will discuss how studies of clusters can help elucidate the fundamental mechanisms for hydrogen storage and how these can be applied in Boron Nitride and Carbon nanocages. I will demonstrate that metallization of these nanostructures is necessary to store hydrogen with large gravimetric density. I will also discuss the properties of a class of materials called alanates which have the chemical composition $[M_n^+(AlH_4)_n]^-$, $M = \text{Li, Na, K, Mg}$ and can store up to 18 wt % hydrogen, although the temperature where hydrogen desorbs is rather high. It was recently discovered that doping of Ti-based catalysts in NaAlH_4 can significantly lower the hydrogen desorption temperature, but why and how Ti accomplishes this task remains a mystery. Using first principles calculations, I will provide a fundamental understanding of the electronic structure and stability of sodium alanates and how it is affected due to Ti doping. The role of Ti based precursors in introducing vacancy like defects and their influence on hydrogen desorption will be highlighted. It is hoped that the understanding gained here can be useful in designing better catalysts as well as hosts for hydrogen storage.

Interaction of Hydrogen with Nanoclusters

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Previous studies have shown that the electronic structures of hydrogen on nanoclusters differ significantly from those on the respective bulk counterparts. As an example, Fig.1 displays the structure of the "magic" cluster Al_{13}H , in which the 13 Al atoms form a symmetric icosahedral frame [1]. Al_{13} can be viewed as a super-halogen atom with 39 electrons, one electron missing for the shell closing at a number of 40 electrons [2]. The electronic properties are changed from metallic-like in Al_{13} to semiconductor-like in Al_{13}H .

Not only the electronic structures but also the reactivities of hydrogen chemisorption on nanoclusters differ significantly from those of the bulk counterparts. The H_2 chemisorption rate as well as those of O_2 and N_2 on metal clusters can vary by several orders of magnitude with each additional metal atom. Due to the superior reactivities regarding hydrogen chemisorption, certain clusters may be suitable candidates for hydrogen storage. The differences in chemisorption between clusters and bulk materials mentioned above open up new pathways for catalysis. Potential applications of size-selected clusters for various catalytic steps including hydrogen adsorption, like, e.g., fuel cells, are unexplored yet.

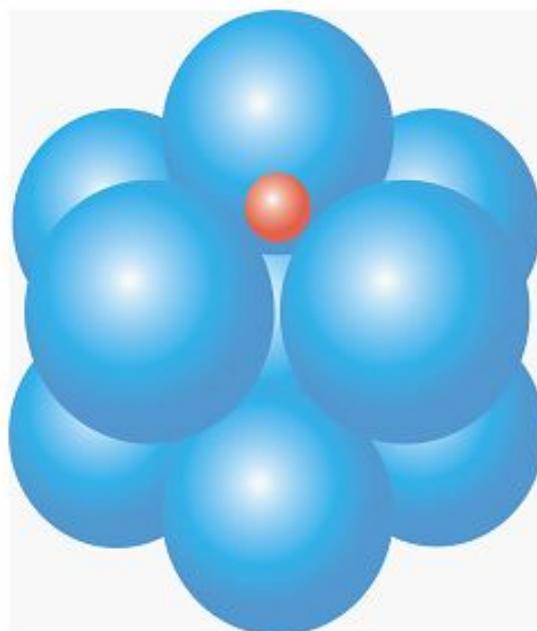


Figure 1: *Calculated structure of Al_{13}H*

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Carbon Nanostructures as Storage Media for Hydrogen

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The potential of Carbon structures to store hydrogen has been discussed in the literature very controversially. Very recently [1] we could show by computer simulations that nanostructured graphitic-like carbon can store molecular hydrogen by physisorption under technically acceptable conditions. The calculations reveal that the DOE target - hydrogen storage capacity of 6.5 weight per cent - can be attained in such structures at a temperature of about -23°C and an external pressure of 10 MPa (100 atmospheres).

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Size Selected Metal Clusters Supported on thin Oxide Films: the Non-Scalable Size Region

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On the basis of specific examples taken from our laboratory, the most important steps in (i) preparing size-selected metal clusters supported on thin oxide films and (ii) investigating their catalytic and chemical properties are presented. The clusters are generated by a high frequency laser vaporization source. After mass selection in ultrahigh vacuum the clusters are softlanded on thin oxide films. Temperature programmed reaction spectroscopy, Fourier-transformation infrared spectroscopy as well as a pulsed beam technique are available for probing the catalytic properties of the clusters. It is demonstrated that the turn over rate for catalytic reactions is strongly dependent on the cluster size [1]. Based on the experimental results for the CO oxidation reaction on small Au clusters in combination with first-principle calculations the role the support material, thin magnesium oxide films, is discussed [2]. It is shown that the interaction of such small metal clusters with the substrate can strongly influence their catalytic properties. By charge transfer from an F-center in the magnesium oxide film to the gold cluster an inactive Au₈ cluster is turned into an active model catalyst. Finally, our first experimental results of an ultrasensitive microcalorimeter are introduced. The device is based on the bending of a micromechanical Si/Au lever [3] and can be used for thermodynamic studies involving supported clusters.

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H-Storage in Novel Materials 2

Similarities of Alanates as Potential Hydrogen Storage Materials

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NaAlH_4 is presently the most advanced hydrogen storage material for the temperature range around 100 °C with respect to storage capacity (approaching 5 wt.% over the two stages of dehydrogenation) and kinetics of rehydrogenation (below 10 min). These requirements for mobile applications are only reached if the NaAlH_4 is doped with different catalysts. Titanium compounds are the preferred ones. During the doping process the titanium compound is reduced to the zerovalent state, in which it remains during the de- and rehydrogenation cycle. Besides Ti, some other metals (Sc, Ce) can be used as highly efficient dopants, which come close to or even exceed the efficiency of most titanium compounds as catalysts. Nowadays the preferred process of doping is ball-milling of the alanate with the different catalyst compounds. A doped NaAlH_4 hydrogen storage material with excellent kinetics can be produced through ball-milling of NaH, Al and a catalyst (direct synthesis of doped NaAlH_4) under hydrogen pressure (Fig.1). Depart from NaAlH_4 other light metal aluminium hydrides with high hydrogen content are described. These materials show similar thermal behaviour with a two step decomposition pathway and structural similarity. However, most of these materials are not well described and thermodynamic data are very limited.

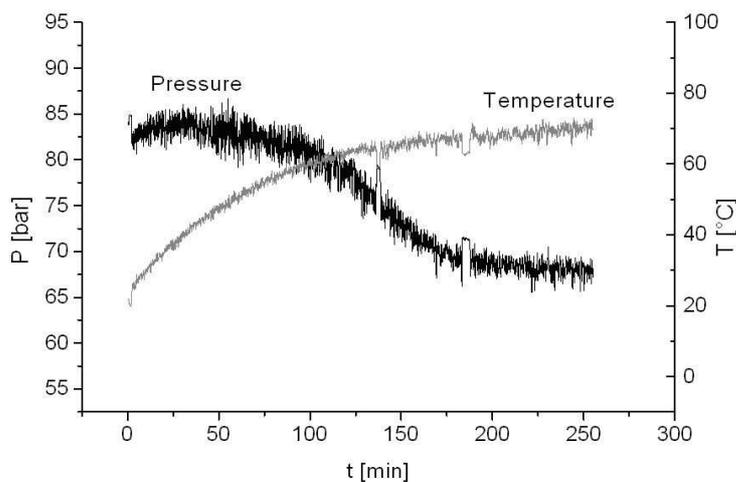


Figure 1: Measurement of pressure and temperature during the ball-milling one-step direct synthesis of Ti-doped NaAlH_4 .

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Interaction of Hydrogen with Defects and their Stabilisation

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The interaction of hydrogen with defects like vacancies, dislocations and grain boundaries is treated in a generalized concept introduced by W. Gibbs for surface adsorption. If hydrogen segregates at the defects, their formation energy is reduced and their concentration will be altered [1]. Thus the microstructure of the absorbing matrix can be changed. Possible consequences with respect to mechanical properties, i.e. embrittlement of alloys and the properties of storage materials will be discussed. For the examples of hydrogen interaction with grain boundaries [2],[3] and dislocations [3] in palladium experimental results allow to calculate the reduction of the line or interfacial energy, respectively. In addition, recent reports on abundant vacancies in metals can be rationalized in a natural way. In all cases the gain in energy caused by hydrogen accumulating at the defects is counted as a decrease of the defect energy. The intriguing question will be discussed whether the defect energy may become zero or whether dislocations and grain boundaries become equilibrium defects, respectively. For the case of surfactant molecules which reduce the surface energy of water this limit has not been reached because precipitation of the molecules as micelles prohibits a further increase of their chemical potentials. For solute atoms in metals and ceramics and their segregation at grain boundaries a similar limit will be analyzed.

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Computational Studies of Hydrogen Storage: Metal Organic Frameworks and Destabilized Metal Hydrides

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Atomistically-detailed computer simulations of hydrogen storage materials can provide useful insights and predictions to help interpret and guide experiments.

We have carried out calculations for physisorption of molecular hydrogen on microporous metal organic framework (MOF) materials, which have recently been identified as potential sorbents for hydrogen storage. The MOF materials are composed of coordinated metal clusters that form vertices linked together with organic struts to form a 3-dimensional porous structure suitable for physisorption of gases. Initial reports of adsorption on MOFs indicated the possibility of very high uptake. We have performed atomistic simulations of hydrogen adsorption in a variety of MOFs and have compared our results with experiments where possible. Good agreement between simulations and experiments were observed in some cases, whereas poor agreement was noted for other cases. We discuss possible reasons for discrepancies between simulations and experiments. We discuss limitations of MOFs for hydrogen storage.

Metal hydrides of period 2 and 3 materials have high volumetric and gravimetric hydrogen storage capacities. However, these materials typically have very high heats of reaction, meaning that high temperatures are required to dissociate the hydrides. Recent experimental work has focused on chemical destabilization of metal hydrides as a means of decreasing the heats of reaction. We have carried out electronic density functional theory (DFT) calculations for various metal hydride systems, calculating the heats of reaction for over 100 different reactions. We have compared our calculations with experimental and tabulated data where available and find reasonable agreement. We have studied the adsorption and dissociation of H₂ on the Mg₂Si(110) surface as a first step in examining the hydrogenation cycle. Our calculations demonstrate the utility of DFT for screening reactions and for identifying promising materials for further computational and experimental studies.

Hydrogen Storage in Isolated Pd NanoParticles[1]

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Palladium is a classic hydride system capable of storing 1 wt% in the bulk. Numerous studies have been made on bulk PdH_x and therefore it is a classic system to observe what is new at the nanoscale. Loosely aggregated nanoparticle storage systems, in general, present several opportunities not available in the bulk phase, i.e., rapid gas diffusion throughout the system, lower energy H-binding at surface and subsurface sites, core-shell geometry (shell can contain catalytic elements enhancing H₂ dissociation kinetics), short proton diffusion distances to saturate the solid phase, etc. Here, we present results of hydriding studies of nano-Pd in platelet and spherical particle form. Typical particle diameters are ~2-5 nm (sphere) and ~2-5 nm thick platelets. In terms of the H-adsorption and desorption isotherms, we observe a loss of the classic wt% plateau with pressure (P) observed in the bulk and identified with the co-existence of the α and β hydride phases. In the nanoparticle system, this wt%-P region of the isotherm has positive slope, indicating that numerous surface and sub-surface sites are contributing to the H-storage. In some cases, we obtain storage in nano-PdH_x larger than found for the bulk in the same apparatus. We have also carried out an in situ x-ray diffraction (XRD) study of the hydriding of small spherical Pd particles coated with nanoporous carbon. These studies were carried out as a function of temperature and pressure. Interesting similarities and differences from the properties of bulk Pd are also observed. The nano-Pd samples exhibit the same face centered cubic structure as the bulk and still undergo the α - to - β phase transition. The XRD studies also show that the samples are highly crystalline with complete transformation of the *alpha* phase to the *beta* phase as the hydrogen concentration is increased. A narrowing of the co-existence region is observed with a critical temperature for the phase boundary of this region lowered by ~140 K in comparison to that of the bulk.

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Hydrogen Release from Ammonia Borane Mediated by a Nanoscaffold of Silica

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Favorable thermodynamics of hydrogen release from the NBH_x ($x=8-2$) compounds, as determined using computational methods of chemistry and solid state physics [1], prompted our experimental studies on ammonia borane (AB), NH_3BH_3 . Differential scanning calorimetry experiments were used to quantify both the thermodynamics and kinetics for the release of hydrogen from neat AB and from AB infused in a nanoporous silica, SBA-15. We demonstrated that the infusion of AB within SBA-15 leads to: a) lowering of the activation barrier for the loss of H_2 , b) modification of the enthalpy of decomposition, and c) suppression of an undesirable release of borazine [2]. The thermodynamic stability of AB relative to its ionic polymorphs, diammoniate of diborane (DADB) and its "umpolung" counterpart, DBDA, has been studied theoretically [3]. We used highly-correlated electronic structure methods for clusters, whereas lattice energies of complex solids were determined using an approximate method of Jenkins et al. [4].

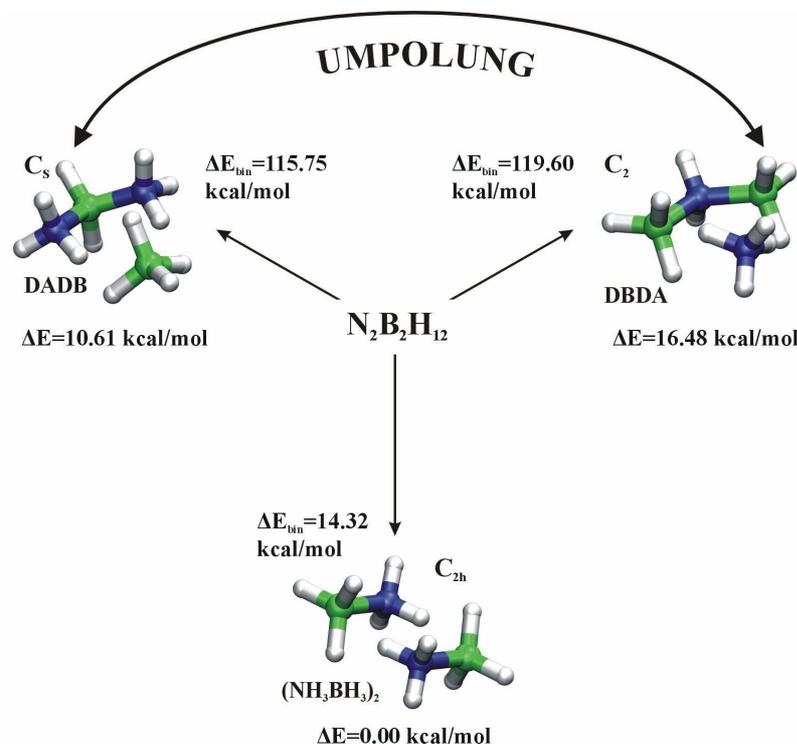


Figure 1: The relative stability of $(\text{AB})_2$, DADB, and DBDA complexes and binding energies determined at the $\text{CCSD(T)}/\text{aug-cc-pVTZ}$ level of theory. Boron atoms in green, nitrogens in blue.

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Carbide-derived Carbons with Tailored Porosity Optimized for Hydrogen Storage

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The poor performance of hydrogen storage materials continues to hinder development of fuel cell-powered automobiles. Nanoscale and nanoporous carbons in particular (activated carbon, exfoliated graphite, fullerenes, nanotubes, nanofibers, and nanohorns) have not fulfilled their initial promise. Here we show that a largely unknown class of porous carbons [1] [2] offers great potential for H₂ storage.

Carbide-derived carbons (CDC) are produced by high temperature halogenation of crystalline binary and ternary carbides. Metals and metalloids are removed as, for example, chlorides, leaving behind a collapsed noncrystalline carbon with up to 80% open pore volume. The first CDC's, circa 1920, (also called mineral carbon) were waste products from the production of high value added chlorides from cheap and abundant carbides and chlorine[3]. The detailed nature of the porosity - average size and size distribution, shape, and total specific surface area (SSA) - can be tuned with high sensitivity by selection of precursor carbide (composition, lattice type) and chlorination temperature[4]. The optimum temperature is bounded from below by thermodynamics and kinetics of chlorination reactions and from above by graphitization which actually decreases SSA and introduces H₂-sorbing surfaces with binding energies too low to be useful.

We recently applied this strategy to identify the best performing CDC for supercapacitor electrodes, in which the highest specific aqueous double layer capacitance correlated with the pore size, volume and SSA of CDC, as determined by precursor material and chlorination temperature[5]. Concerning hydrogen storage, it would appear intuitive that pores of different size and shape contribute differently to hydrogen storage. By correlating pore properties with 77K H₂ isotherms from a wide variety of CDCs, we indeed show that gravimetric hydrogen storage capacity normalized to total pore volume is optimized in materials with primarily micropores (~ 1 nm) rather than mesopores. A narrow size distribution of small pores is desirable for storing hydrogen, while large pores merely degrade the volumetric storage capacity. Useful H₂ capacities should be achievable with CDC's.

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Dehydrogenation of LiBH_4 ; An In-Situ Powder Synchrotron X-ray Diffraction Study

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The complex metal hydride, LiBH_4 , has the highest gravimetric hydrogen content, 18.5 w/w % of all solid hydrides. This value corresponds to higher energy content than gasoline. At room temperatures LiBH_4 exists as an orthorhombic phase that changes to a hexagonal phase at 108°C [1]. The volumetric hydrogen density for these phases, 123.5 g/L and 121.6 g/L, respectively, is much higher than the density of liquid hydrogen, $\rho(\text{H}_2(\text{l})) = 71 \text{ g/L}$. Still, the mechanism for dehydrogenation of LiBH_4 remains not fully understood together with the reported catalytic effect of quartz. In this work we investigate the dehydrogenation of pure LiBH_4 and mixtures of LiBH_4 and SiO_2 .

In situ powder synchrotron X-ray diffraction data were collected at the beamline I711 at MaxLab, Lund and at Brookhaven National Laboratory, NSLS, beamline X7B. The investigated material was pure LiBH_4 and mixtures of LiBH_4 and SiO_2 . Experiments were made with a new sapphire tube sample cell for high pressure/temperature studies using helium or hydrogen atmosphere (up to 35 bar).

A new phase was observed during dehydrogenation of LiBH_4 with existence interval ca. 200 to 310°C. The stability of this phase appear to increase with increasing hydrogen pressure, and it is observed in the range ca. 108 to 310°C, at $p(\text{H}_2) = 33 \text{ bar}$. This phase appear to have slightly higher thermal stability than LiBH_4 , that melts at 275°C. The new phase was indexed with a tetragonal unit cell. The observation of the new tetragonal phase was independent of the chosen sample cell, sapphire (Al_2O_3) or quartz (SiO_2).

Mixtures of LiBH_4 and quartz was also investigated. At, $T = 330^\circ\text{C}$, SiO_2 (cristobalite, high) reflections disappear due to a reaction with the melt of LiBH_4 . At low concentrations of SiO_2 the silicate Li_3SiO_3 forms while Li_4SiO_4 forms at higher concentrations. An amorphous boro-silicate glass phases might be formed simultaneously. There is no indications of any boron compounds at temperatures above the melting point of LiBH_4 . The silicates Li_3SiO_3 and Li_4SiO_4 forms as nano-particles, with sizes of 10 and 8 nm, respectively. The formation of lithium silicates contributes presumably to the driving force for the decomposition of LiBH_4 and thereby decreasing the decomposition temperature. This can be an important contribution to a catalytic effect of glass previously observed [2].

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Hydrogen Storage in Molecular Compounds

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At high pressures (P), hydrogen molecules bond to other simple molecules to form crystalline molecular compounds. These compounds can retain an enormous amount of hydrogen; for examples, $Ar(H_2)_2$ holds 9.1 wt% molecular hydrogen, $H_2(H_2O)$ holds 10 wt% molecular hydrogen (20% atomic H), and $(H_2)_4(CH_4)$ holds 33.4 wt% molecular hydrogen (50% atomic H), all significantly above the DOE target. Hydrogen retained by the weak van der Waals force in these solids can be readily released, making them an attractive means for potential hydrogen storage. By varying temperatures (T) and composition (x), the synthesis pressure, which has been the main obstacle for the molecular compounds to be a viable hydrogen storage material, can be greatly reduced.

We explored a low temperature route. In this method, hydrogen is retained and solidified by weak bonding to host molecules under moderate synthesis pressure (P_s) and temperature (T_s). The solid is cooled down to moderately low temperature (T_q), and the pressure is released to P_q , and the hydrogen-containing solid is quenched. The stored hydrogen can be released by warming up toward a temperature (T_a) for final applications. As examples of this new route for hydrogen storage, we report $H_2(H_2O)_2$ clathrate that contains a significant amount of hydrogen and are quenchable to ambient P at moderately low T and $H_2(H_2O)$ filled ice and $(H_2)_4(CH_4)$ molecular ice compound which contain higher amounts of hydrogen and can be quenched to moderate P at low T. Ideally, the bonding to the ice host helps to stabilize molecular hydrogen in the crystalline compounds at moderately low P-T, yet is sufficiently weak for easy release.

New compounds could be expected in the hydrogen-ice system by exploration of the multi-component (including ternary compounds, e.g., $H_2O-CH_4-H_2$) system along different P-T paths. Very large hysteresis and the path-dependent phase relationship at low T open opportunities for metastable growth and stabilization of hydrogen-rich phases. Using large "promoter" molecules (such as THF) can further stabilize the H_2O framework structure at near ambient P-T conditions when the promoter molecules enter some large cages. Hydrogen can then be retained in the unfilled small cages and the partially-filled large cages. This approach will reduce the need of high P and low T, but inevitably will also reduce the amount of stored hydrogen as a portion of the cages is occupied by the promoter molecules. Other avenues for research include exploration of other clathrate (sI, sH) and filled ices, and study of multiple occupation of H_2 in cages of other structures.

In summary, the low-temperature and variable chemical path have greatly reduced the P_s and P_q of clathrate and methane hydrides. The field is at its infancy; only reconnaissance studies of the simplest compounds: water, methane, and octane have been attempted. Explorations of hydrides of other molecules in multi-dimensional space of P-T-x may lead to optimization of molecular hydride as a potential method of hydrogen storage. DAC, although not a production equipment, is a versatile tool for such explorations with in-situ Raman, infrared, x-ray, and neutron probes.



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Nuclear Magnetic Resonance Study of Nanocrystalline Mg-Based Alloys Prepared by Ball Milling in Hydrogen Atmosphere

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The ball milling of Mg with some catalysts (such as transition-metal oxides) strongly improves the kinetics of hydrogen absorption/desorption. The resulting nanocrystalline materials are promising for hydrogen storage applications, their storage capacity being up to 7 wt.% of hydrogen. Nuclear magnetic resonance (NMR) is known as an effective technique for studies of the microscopic properties of condensed matter. It is particularly useful for investigation of hydrogen motion in metal - hydrogen systems [1]. In the present work, we apply the proton NMR to study the behavior of hydrogen in a number of nanocrystalline Mg-based alloys prepared by ball milling in hydrogen atmosphere. The measurements have been made on a number of samples with different catalysts. The samples with V_2O_5 have been chosen for detailed investigations, since this oxide appears to be an excellent catalyst of hydrogen absorption. We have measured the proton spin-lattice relaxation rates R_1 and the proton NMR spectra at the resonance frequencies of 23.8 and 90 MHz over the temperature range 4 - 420 K.

The proton NMR spectra for the samples prepared by milling with steel balls show the strong inhomogeneous broadening due to iron particles appearing in the process of milling. In contrast, for the samples prepared by milling with brass balls, the width of the ^1H NMR line at half-maximum (≈ 50 kHz) is typical of the "rigid-lattice" line width due to the dipole-dipole interaction between proton spins in concentrated hydrides. It should be noted that the width of this spectrum does not show any changes in the temperature range 4 - 420 K. This indicates that H atoms remain to be 'static' on the frequency scale of 10^5 s $^{-1}$. For all the nanocrystalline samples studied, the measured proton spin-lattice relaxation rates are much higher than that in a bulk MgH_2 ($R_1 \approx 5 \times 10^{-3}$ s $^{-1}$ [2]). The most probable source of the R_1 enhancement in the nanocrystalline samples is the increase in the contribution due to interaction between proton spins and paramagnetic centers. This conclusion is supported by the observed frequency dependence of the proton spin-lattice relaxation rate: for all the samples studied the values of R_1 measured at 23.8 MHz are considerably higher than those measured at 90 MHz. The paramagnetic centers are likely to be related to the special structure of the ball-milled material where catalyst atoms may appear in the grain boundaries of nanocrystalline MgH_2 . In fact, after removing hydrogen from the ball-milled material followed by regular hydrogenation (this procedure leads to the growth of the average grain size) the measured R_1 values are found to be considerably lower than those of the original ball-milled samples.

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Vibrational Spectroscopy of Hydrogen Complexes of Cationic Co_n^+ ($n=4-22$) Clusters

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Complexes of small metal clusters with hydrogen are useful model systems for studying the metal - hydrogen interaction that is fundamental e.g. for H_2 storage and catalysis. We studied the binding of hydrogen to cationic cobalt clusters Co_n^+ ($n=4-22$) with Infrared Multiple Photon Dissociation Spectroscopy (IR-MPD) using the intense and tunable IR light emitted by the "Free Electron Laser for Infrared eXperiments" FELIX [1] at the FOM Institute in Nieuwegein, The Netherlands. It has been demonstrated previously that this method can give valuable insights in the binding of ligands to isolated metal clusters [2] and the structure of the metal cluster itself [3].

The reactivity of the Co_n clusters towards H_2 is known to be strongly dependent on the number of Co atoms in the cluster[4]. The character of the hydrogen adsorption sites is however still unknown. We applied IR-MPD spectroscopy in combination with density functional theory (DFT) calculations to obtain structural information on these cluster complexes. We found that the IR spectra of the Co_nH_m^+ clusters show multiple bands in the 1000 - 1400 cm^{-1} spectral range. The number of observed bands is dependent on both cluster size and hydrogen coverage. No bands are observed at higher energy and it is therefore concluded that hydrogen does not bind atop on these cationic Co clusters. A comparison with DFT calculations indicates that the bands correspond to hydrogen adsorbed in two- or three-fold bridged sites.

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Hydrogen Physisorption in Metal-Organic Frameworks

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One promising way for hydrogen storage at low temperature is physical adsorption on nanomaterials. The process, which is due to van der Waal forces between adsorbate and adsorbent, is reversible, fast and very small energy loss is involved in desorption. The best candidates for hydrogen storage based on physical interaction are nanostructured materials with high microporosity and high specific surface area (SSA). In fact, it has been demonstrated both for zeolites [1] and for carbon nanostructures [2],[3],[4] that the hydrogen storage capacity is linearly correlated with their SSA. In recent years a new class of crystalline materials with very low density and high specific surface area, the metal-organic frameworks or coordination polymers, has been developed [5]. These materials consist of metal-oxide groups connected by rigid organic ligands to give a very porous open network. We investigated hydrogen storage in metal-organic frameworks consisting of different central metals and organic ligands. In this work we show that the maximum hydrogen uptake is strongly correlated with the specific surface area of MOFs like for other microporous adsorbents while the heat of adsorption in these crystals is strongly material dependent. These results are very important considering that a great variety of MOFs, have been synthesized, however, not studied concerning their hydrogen uptake. Some of these MOFs possess SSA up to $5000 \frac{m^2}{g}$ [6] and, therefore, could store more than 6 wt% hydrogen at 77 K.

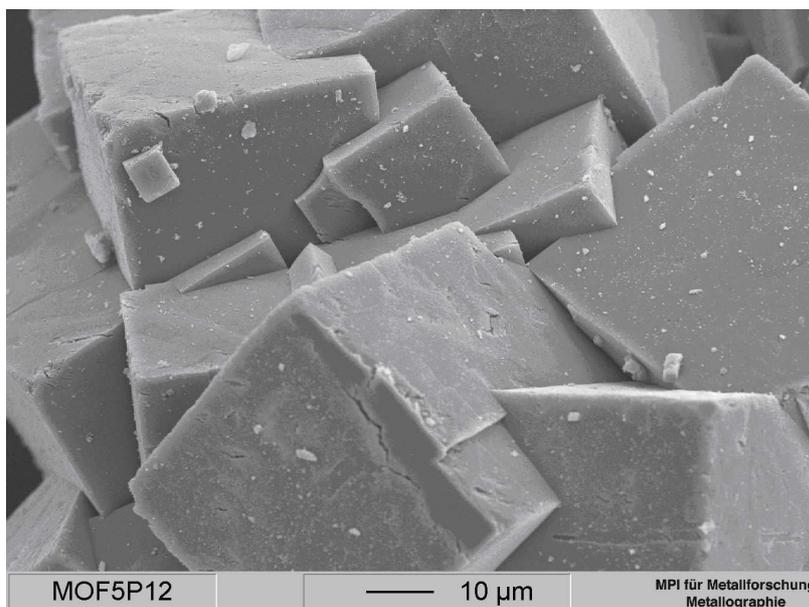


Figure 1: SEM picture of MOF-5 cubic crystals. The samples have been provided by BASF, Ludwigshafen

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A Combinatorial Thin Film Approach to the Search for New Hydrogen Storage Materials

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Due to their high volumetric density, metal-hydrides are attractive for the storage of hydrogen in fuel-cell driven cars. If complex light-weight ternary could be used, also the problem of the weight of these storage materials would be solved. However, for reversible absorption and desorption the required temperatures are too high for use in practical applications. We use a thin film approach to find new ternary hydride storage materials and to understand the role of catalysis in the ab- and (de-)sorption of hydrogen. Co-deposition of metal alloy gradient films gives a fast access to the sorption properties over a wide range of compositions. As all interesting light-weight storage materials investigated so far appear to have an electronic gap, we use optical screening to monitor the sorption properties. This facilitates the search for (complex) metal-hydrides with specific switchable physical properties. The compositional gradient thin films are synthesised by co-sputtering on a 3 inch wafer from three (up to six) off-centred magnetron sources. The (complex) hydride formation during ex-situ hydrogen exposition at well-defined temperatures and hydrogen gas pressures is monitored by the transparency/reflection of the films. Since all complex hydrides found so far have an electronic bandgap their transparency is a good indicator of the amount of absorbed hydrogen. This method is thus applicable to a large class of potential light-weight hydrogen storage materials and electrochromic materials. We studied several Mg-based systems and find that the phases in the as-deposited metallic state are not simply those expected from the phase diagram. In general, the solid solubility range appears to be extended. Secondly, we find that hydrogen absorption can take place close to equilibrium conditions due to the small nanocrystalline grain size obtained by sputter deposition. On the other hand, the small grains preclude the phase identification by X-Rays. Taking the well-known Mg-Ni-H as a model system, we identify the plateau pressure for hydrogen absorption. By fitting the absorption rate against the applied pressure, we find that the enthalpy of formation thus obtained depends subtly on the Mg/Ni ratio. For high Mg contents, on the other hand, the formation enthalpy of MgH_2 is reproduced. As an example of a light-weight storage materials, we studied the Mg-Al-H system. We find that, when loading Mg-Al gradient films, a transparent phase is formed at the $MgAl_2$ composition when exposed to hydrogen gas. The hydrogen is released when the sample is heated to 200°C. This (unfavorable) desorption temperature is reduced to 100 °C by adding a Ti surface layer. In fact, this also shows how powerful this method is to study the role of catalysts.

Hydrogen Adsorption on Graphitic Carbon Particles with High Specific Surface Area

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Recent results of accurate quantum mechanical calculations [1] showed that hydrogen molecules feel minima of the potential energy near the surface of a graphene sheet at a distance of about 0.3nm from the surface. The depth of the minimum is about 5kJ/mol. Thermodynamic calculations show that the storage capacity is expected to change considerably with temperature in the range from 75K to 100K [2]. We measure pressure-temperature curves of hydrogen in a pressure vessel with and without presence of graphitic carbon nanoparticles. The temperature is varied between 300K and 40K at a maximum pressure of 200 bar. The desorption behaviour of different carbon nanopowders is studied at these conditions. For C_{60} fullerenes, the results reproduce recent adsorption data obtained at 77K [3]. We consider also nanometre-scale carbon powder produced by ball-milling of graphite as a cheap and promising material for hydrogen storage [4]. Variation of the milling conditions including milling at low temperatures is shown to be a way to optimise the carbon powder with respect to storage capacity.

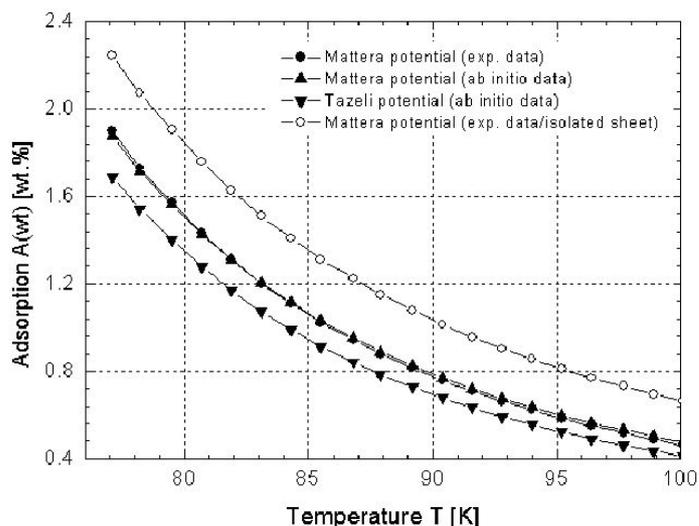


Figure 1: Adsorption of hydrogen on a graphite surface at 0.1 MPa as obtained from thermodynamic calculations. Due to adsorption on both sides of the layer the storage capacity is substantially higher for isolated sheets (open circles) than for the surface on a bulk sample.

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Structural and Magnetic Properties of HoMn_2H_x Hydrides

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Hydrogen causes strong expansion of the unit cell, diverse phase transformations and changes of magnetic properties in function of hydrogen content and temperature in Laves phase compounds. Such behaviour was reported for RMn_2H_x hydrides [R = Y, Tb, Gd, Dy] with $C15$ Laves phase structures [1],[2],[3],[4]. The behaviour of HoMn_2H_x is reported in this work. The increase of the unit cell volume in the function of hydrogen content is not linear as it is for the hydrides with other Rare Earths and can be described by the function proposed by Hirata[5]. Depending on the hydrogen concentration reversible phase transformations in function of temperature are observed. For lower hydrogen concentrations ($0 < x < 1.65$) the spinodal decomposition to hydrogen deficient θ and hydrogen rich r phases was observed. This segregation is very similar to the behaviour of other cubic systems (Y, Tb, Gd, Dy). Additionally r phase shows a structural distortion into the monoclinic system observed in ErMn_2H_x hydrides. For the hydrides with $x = 1.65, 2.5, 3.0$ the reduction of the crystal structure symmetry was observed at low temperatures. Only for $x = 2$ and 3.5 single cubic phases exist in the whole temperature range. The sample with maximal hydrogen concentration $x = 4.3$ prefers rhombohedral system, however at elevated temperatures (> 350 K) the rhombohedral phase is replaced by the cubic one, what is typical behaviour for cubic systems. The results of magnetic measurements reflect the strong influence of hydrogen on magnetic properties. First of all, the presence of hydrogen atoms in HoMn_2H_x compounds leads to magnetic moments induced at Mn atoms. The temperatures of magnetic ordering are strongly increased (~ 205 to 270 K) in comparison with the initial compound (25 K). All the samples do not reach saturation in the maximal field of 55 kOe, what points to a strong antiferromagnetic coupling. For $x = 2$ and $x = 4.3$ the relatively small values of magnetisation at 55 kOe are observed, what is similar to the other RMn_2H_x hydrides with the same hydrogen contents.

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Symmetry Analysis of Structural Transformations in Laves Phase Hydrides

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The intermetallic compounds of Rare Earths and Yttrium with 3-d metal compounds easily absorb hydrogen which enters the interstitial positions. Absorption of hydrogen causes structure distortions and transformations depending on hydrogen content, and for unsaturated hydrides structural phase transformations appear in function of temperature [1], [2], [3]. One of the most intriguing problems which appeared for the unsaturated hydrides is a tendency for ordering of hydrogen atoms. The neutron diffraction studies prove appearance of hydrogen ordered in superstructures (super-lattices) connected with lowering of structure symmetry of the unsaturated hydride [4]. To find the explanation of the observed transformations and hydrogen ordering the symmetry analysis method in the frame of theory of space groups and their representations is applied to structural phase transitions (order-disorder and displacement types) induced by different concentration of hydrogen (deuterium) atoms and temperature for non saturated Laves phase hydrides RMn_2 (R = rare earth & yttrium). There are analysed all possible transformations of the parent face-centred cubic structure, with symmetry space group $Fm\bar{3}m$ leading to the structures of lower symmetry. In such structures of lower symmetry the positions of RE and 3d metal can remain the same, but the hydrogen interstitial positions, for example 96g split into subgroups(super-lattices) with differentiated local symmetries and abundances. If one of such super-lattices is occupied by hydrogen and the other are empty, we receive effect of hydrogen ordering. The cases with displacements of R and 3d metal atoms are also considered. In the present work all transformations allowed by symmetry rules are presented and discussed with the aim to analyse and understand the conditions determining phase transitions and hydrogen ordering in the Laves phase hydrides.

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DFT Study of the Adsorption of Molecular Hydrogen on pure and Lithium-doped Carbon Nanotubes and Graphene

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Experiments of hydrogen adsorption on pure carbon nanotubes and another graphitic materials have shown that the adsorption is very small (2-3 weight % in the most optimistic cases) and it is due to hydrogen physisorption on the surface. Thermodynamic estimations [1] indicate that an adsorption binding energy of 300-400 meV/molecule would be necessary to obtain efficient cyclic adsorption/desorption at room temperature and normal pressures. This binding energy is about 3-4 times larger than typical hydrogen physisorption energies on graphitic materials[1], [2], [3], which explains the low hydrogen adsorption on pure carbon nanotubes and another graphitic materials. On the other hand, some experiments have reported an adsorption of 14-20 wt % in Li- and K-doped carbon nanotubes at ambient pressure and moderate temperatures [4].

We have performed Density Functional calculations of the adsorption of molecular hydrogen on single wall carbon nanotubes. The adsorption is weak and molecular physisorption is favorable with respect to dissociative atomic chemisorption. The chemisorption barrier is about 2.5 eV. Physisorption binding energies are about 100 meV/molecule in the most stable configurations. The physisorption energies on metallic and semiconducting nanotubes are similar. When the nanotube surface is fully covered, with one molecule per graphitic hexagon, the binding energy per molecule decreases for some nanotubes (with respect to the binding energy of an isolated molecule) because of repulsive interactions between neighbour adsorbed molecules. For the same reason, direct adsorption of a single hydrogen layer with coverages of more than one molecule per graphitic hexagon is not possible, even at low temperatures. Adsorption of a second layer is possible, although the molecules of the outer layer are more weakly bound compared to those of the inner layer.

Similar calculations have been performed for pentaheptite nanotubes, generated by rolling up a two-dimensional three-fold coordinated carbon network composed of pentagons and heptagons. The results are similar to those obtained for hexagonal carbon nanotubes: physisorption energies are also about 100 meV/molecule on pentagons, heptagons and other sites of the surface, and the chemisorption barrier is about 2 eV. Finally, we have performed calculations of the physisorption of molecular hydrogen on Li-doped graphene layers and carbon nanotubes. The binding energy of the hydrogen molecule in the Li-doped systems increases by a factor of 2 with respect to the pure undoped ones. These results indicate that Li-doping increases the binding energy of molecular hydrogen to graphitic materials, and will then enhance their hydrogen storage capacity, giving qualitative support to the experimental findings.

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SPD-Nanocrystalline Mg and Mg-Alloys for Hydrogen Storage

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Magnesium and its alloys are very promising materials for hydrogen storage, since they are light and can absorb up to 7.6 wt.% of hydrogen in the form of reversible magnesium hydride (MgH₂)[1]. These features, combined with the low cost and huge abundance of magnesium, represent an excellent potential for commercial applications. However, the very sluggish reaction kinetics even at elevated temperatures have prevented a breakthrough in practical use to date. Two main factors significantly reducing the rate of hydrogenation are (i) the formation of magnesium oxide layers on the surface, which are non-penetrable to hydrogen molecules [2], and (ii) the extremely low hydrogen diffusion rate in magnesium hydride (β phase), which is smaller by at least three orders of magnitude than that in the α phase [3]. However, in the last years a remarkable improvement of desorption kinetics has been achieved by the use of oxide and metallic catalysts[4],

[5], [6] as well as of nanocrystalline magnesium powders[4], [5], [6], [7]. Nevertheless, the powder technique possesses some intrinsic drawbacks: surface contamination, fire hazard, time consumption and health concerns. These disadvantages can be avoided by the use of Severe Plastic Deformation (SPD) methods, which permit direct conversion (i.e. without powders) of bulk conventionally grain-sized metals to nano-crystalline ones [8]. The deformation occurs without changing the original shape of samples, however, it demands appropriate conditions, i.e. changes of deformation path and enhanced hydrostatic pressure. Although in the last decade many different SPD techniques have been developed, the two most well-known and promising ones are Equal Channel Angular Pressing (ECAP) and High Pressure Torsion (HPT) [8]. In order to allow for a comparison between SPD and powder techniques two materials were chosen: (i) pure Mg - since a lot of data of ball milled Mg is available in the literature, e.g. [4], [9], [6],[7] - and (ii) the commercial ZK60 alloy, which has already been tested by ECAP [10]. The absorption and desorption kinetics was determined in a self-constructed Sievert-type apparatus. First results are discussed and compared with the literature. This work was part of the A3-Research Program No. 809401-KA/HN provided by the Austrian Federal Ministry for Traffic, Innovation and Technology, and supported by the FWF Austrian Science Fund under project No. P17095-N02.

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Powder Diffraction Investigations of the Crystal Structure of Li and Mg Amide and Imide

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Li-Mg-N-H systems are promising candidates for high capacity hydrogen storage. For example, a 1:4 mixture of $\text{Mg}(\text{NH}_2)_2$ and LiH decompose reversibly to Mg nitride, Li nitride and hydrogen gas to yield 6.5 wt% H_2 (theoretically 9.1 wt%) [1]. The onset temperature of the decomposition is 150°C.

We have investigated the crystal structures of LiND_2 , Li_2ND , $\text{Mg}(\text{ND}_2)_2$ and MgND by combined powder neutron- and synchrotron radiation X-ray diffraction. The obtained crystal structures for LiND_2 , Li_2ND and $\text{Mg}(\text{ND}_2)_2$ are in good agreement with earlier reports. The previously unknown crystal structure of MgND is presented (hexagonal, space group P6322, $a = 11.583 \text{ \AA}$, $c = 3.672 \text{ \AA}$, $Z = 12$). Similarities and differences between the crystal structures are discussed.

Thermal decomposition has been studied by in-situ diffraction techniques.

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High Amount of Electrosorbed Hydrogen in Nanoporous Carbons at Room Temperature

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Recently, we have demonstrated a noticeable hydrogen uptake in nanoporous carbons at room temperature by electro-decomposition of aqueous electrolytes [1],[2]. In alkaline solution, the reversible redox reaction which takes place can be expressed as:



where $\langle C \rangle$ and $\langle CH_x \rangle$ stand for the nanoporous carbon and for hydrogen inserted in the material during charging and oxidized during discharging, respectively [3]. By contrast, the amount of di-hydrogen adsorbed in porous carbons at room temperature is negligible even when a high pressure is applied [4]. The objective of our work is to understand the peculiarity of the electrochemical process and especially to know more about the specific mechanism which allows a better efficiency of hydrogen trapping. The reversible electrochemical hydrogen storage was studied in a microporous activated carbon cloth using a 3 electrode cell in $6 \text{ mol} \cdot \text{L}^{-1}$ KOH aqueous solution as electrolyte. The carbon samples were charged/discharged by galvanostatic cycling and cyclic voltammetry at different temperatures ranging from 20 to 60°C , and an Arrhenius plot was created in order to evaluate the activation energy. The results obtained show that, as temperature increases, both cathodic and anodic processes are accelerated (Fig. 1) by reducing the kinetic barriers. The most interesting observation from the curves is an increase of the amount of hydrogen reversibly stored with temperature. This result is a direct proof that hydrogen trapped in nanoporous carbons during electrolysis of water is not purely physisorbed, and that it exhibits partially a chemical character. In appropriate conditions, the reversible capacity of nanoporous carbons reaches 1.8 wt% at room temperature, that is quite interesting for energy storage applications by comparison with metallic hydrides.

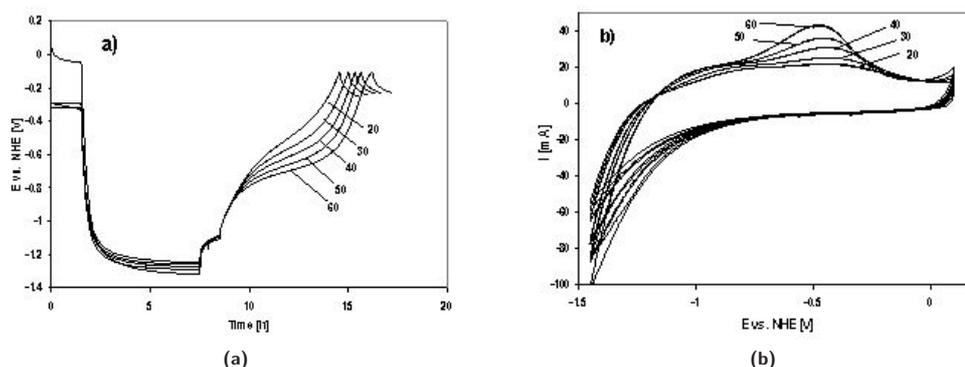


Figure 1: Electrochemical experiments on a microporous carbon cloth at different temperatures; sample mass 20 mg. (a) Galvanostatic cycling with charging/discharging current densities of -150/50 mA/g, respectively. (b) Cyclic voltammetry at a voltage scan rate of 1mV/s.

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Hydrogen Storage in Carbon Nanotubes and Related Materials

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Single-walled carbon nanotubes (SWCNTs), B-C-N compounds (BN, CN and BCN) and so on were comparatively studied to discover novel materials with high hydrogen capacity. Since our purpose is to reach 6.5 wt.% of hydrogen, every possible means has been tried until now. Metal hydrides with ceramic shells [1], lithium alanates compositionally modified by nickel [2] and palladium clusters in zeolites [3] have been studied and cooperative effects between metals and coexisting substances and enhanced hydrogen capacity have been found. Hydrogen sorption by SWCNTs and related materials was investigated here with roles of coexisting metals noticed.

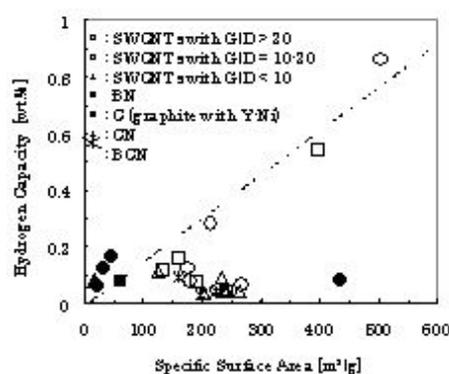


Figure 1: Variation of hydrogen capacity at 295 K and 100 kPa with specific surface area.

Maximum hydrogen concentration in SWCNTs fabricated by arc discharge of graphite with Y and Ni was 0.9 wt.% at 295 K under 100 kPa [4]. That was compared with other values for various SWCNTs and related materials in Figure 1. Hydrogen capacity of SWCNTs with G/D ratios less than 10 was small irrespectively of surface area. A necessary condition to sorb significant amounts of hydrogen would be high G/D ratios evaluated by Raman spectrometry, that is, the intensity ratios of graphitic G band peaks to distorted D band peaks must exceed 10. Some SWCNTs with high G/D ratios showed poor sorption and the data points downwards deviated from the dotted line. X-ray photoelectron spectroscopy showed poor presence of Y on such SWCNTs. Substantial presence of Y on the surface would thus be a second necessary condition to have high hydrogen capacity. Those data points for B-C-N compounds, which were free from metals, showed decreasing capacity with surface area larger than 150 m²/g. It is likely that crosslinking that led to high surface area would reduce the hydrogen capacity. Complete planes typical of high G/D ratios having high surface area without three dimensional crosslinking would behave as hydrogen absorbers cooperated with highly dispersed metals. The speculated cooperation has been evidenced for Zr-carbonaceous composites elsewhere [5].

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Simulation of Hydrogen Interaction with Si Nanoclusters

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Semi-empirical calculations of hydrogen interaction with Si(100) surfaces clusters are presented in this work. The hydrogen is an elementary adsorbate and at the same time plays the important technological role. Our calculations were carried out with the help of semi-empirical MNDO method (modified neglect of differential overlap) for Si_47 and Si_63 clusters, which are modeling the ordered Si(100)-(2x1) surfaces with the dihydride phase. Hydrogen can act as a corrosive factor by removing some surface Si atoms and forming volatile silanes Si_nH_m . As for this possibility there are different opinions: some authors consider such a mechanism rather probable [1],[2], other based on their experimental data almost exclude it [3]. So, it is of great interest to simulate corrosive affect of hydrogen on ordered and disordered (defect) Si(100) surfaces. Atomic hydrogen interaction with dihydride phase on Si(100) surface can result in: repulse of H-atoms from surface; desorption of molecular hydrogen; hydrogen adsorption with threehydride surface phase formation; diffusion of hydrogen atoms into subsurface layers of semiconductor. We have simulated each of these possible processes. Energy barriers of adsorption (with threehydride or silane formation), desorption, hydrogen diffusion are estimated; surface geometry and electron characteristics for each state are described.

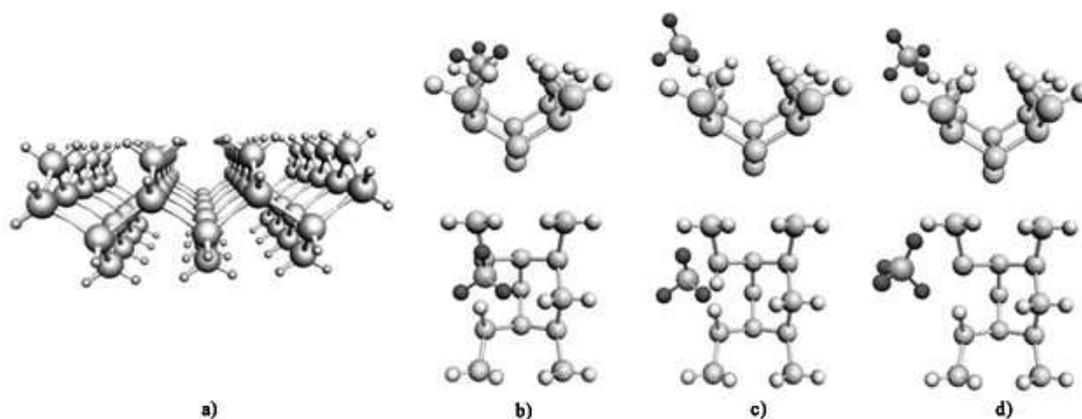


Figure 1: Results of hydrogen adsorption on Si(100)-(2x1) surface: a) cluster Si_63 modelling Si(100) surface with the dihydride phase; b) a part of a cluster modelling Si(100) surface with the threehydride phase; c, d) examples of hydrogen corrosive affect with volatile silanes SiH_3 or SiH_4 forming.

The influence of surface defects on the processes of "hydrogen - cluster" interaction and the possible reaction mechanisms are discussed. Comparative analysis of results of simulation for clusters of different size is carried out.

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Synthesis and Characterization of Li-based Alanates by High-Pressure Techniques

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Solid-state storage is a safe alternative for on-board hydrogen storage in mobile applications such as emission-free vehicles or portable electronic devices. The application of high hydrogen pressure techniques such as high-pressure reactive ball milling and high-pressure differential scanning calorimetry (DSC) is advantageous when synthesizing novel hydrides for hydrogen storage under non-equilibrium conditions and characterizing their complex thermodynamic properties. We have developed a novel synthesis technique, which involves high-energy ball milling in an especially designed vial, allowing in-situ monitoring of temperature and, more importantly, of hydrogen pressure in the pressure range of 1-150 bar. This technique has been proven useful in terms of promoting nanocrystallinity, hydride formation and monitoring and controlling decomposition reactions during milling as well as for direct synthesis of novel and catalyzed compounds [1]. In this study, $LiAlH_4$ and $LiAlH_4$ modified by adding MgH_2 and $TiCl_3$ were investigated. Similar compositions were prepared starting by Li_3AlH_6 , synthesized with milling of $LiAlH_4+2LiH$. Structural characterization was performed by x-ray diffraction (XRD), the thermal stability was studied by high-pressure DSC using a dedicated apparatus inside a glove box to minimize contamination, able to work in a range pressure 1-150 bar in a "dynamic mode", i.e. keeping the hydrogen pressure constant over the entire temperature range. Milling of pure $LiAlH_4$ induces a partial decomposition of the hydride into Li_3AlH_6 . DSC performed on the as-received commercial powder and the sample milled for 8 hours at H_2 pressures of 3, 10 and 50 bar respectively, shows a complex sequence of decomposition reactions. Several exothermic and endothermic transitions were observed during heating: at $\sim 150^\circ C$ the solid state decomposition of $LiAlH_4$ into Li_3AlH_6 starts, $\sim 160^\circ C$ melting of $LiAlH_4$, decomposition of liquid $LiAlH_4$ into Li_3AlH_6 and at $220^\circ C$ decomposition of Li_3AlH_6 into LiH. DSC performed under isothermal conditions ($150^\circ C$) showed that it is possible to achieve a complete solid-state decomposition of $LiAlH_4$ into Li_3AlH_6 , i.e. without the normally observed melting reaction. In the case of the samples doped with MgH_2 and $TiCl_3$, milling under argon induces a complete decomposition of $LiAlH_4$ into nanocrystalline LiH, MgH_2 , LiCl and Al as monitored directly by the increase of pressure during milling, which is consistent with XRD analysis. Similar trials performed under high hydrogen pressure (80 bar) showed the possibility to control the decomposition reaction to some extent. Indeed a lower increase of pressure was observed during milling and afterwards the Li_3AlH_6 phase is clearly visible in the XRD pattern. Finally, the reversibility of hydrogen sorption in these newly synthesized hydrides will be discussed.

[1]Submitted to Journal of Alloys and Compounds

Reactivities and Binding Energies of CO to Gold and Mixed Silver-Gold Cluster Cations: Radiative Association Kinetics and DFT Calculations

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The interaction of small molecules with metal clusters is of seminal interest for an understanding of their chemical activity. We present a combined experimental and computational study of gold and small silver/gold-alloy cluster cations reacting with carbon monoxide in the Penning trap of an FT-ICR mass spectrometer. From the experimentally determined absolute rate constants the binding energies of CO to the clusters is determined by applying a radiative association kinetics model. The results for Au_n^+ ($n < 66$) show a general trend of decreasing binding energy with cluster size.[1] For the small clusters ($n=4-8, 20$) the values are in good agreement with the computed energetics based on DFT ab-initio calculations and in line with geometric structures found recently by ion-mobility experiments [2].

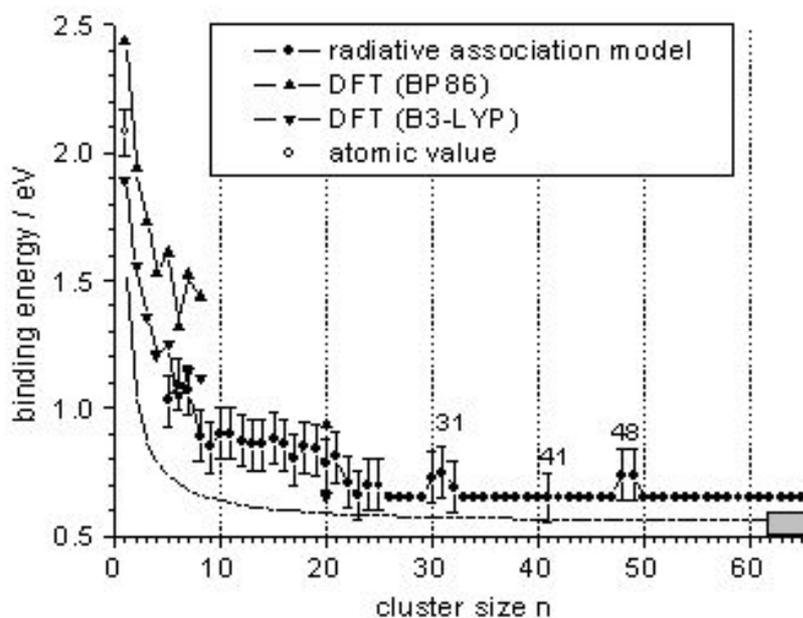


Figure 1: Experimentally determined and computed binding energies for CO to gold cluster cations Au_n^+ .

Results obtained analogously for silver-gold alloy cluster cations $Ag_nAu_m^+$ ($n+m = 4, 5$, and 6) with CO show a lowering of the reactivity with increasing silver content n in the cluster. Binding energies derived [3] are again in very good agreement with DFT predictions [4].

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An Ab Initio Investigation of the Electronic and Structural Properties of Crystalline and Nanostructured Pure and M-doped MgH₂ (M = Sc, Ti, V, Ni and Al).

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MgH₂ has attracted a considerable amount of attention for being a promising hydrogen storage material due to its light weight, low manufacturing cost and high hydrogen storage capacity (7.6 wt%). But its slow hydrogen absorption/desorption kinetics and high dissociation temperature (nearly 300°C) limit its practical applications for hydrogen storage. To overcome these limitations, much of the effort has been paid mainly by making nanocrystalline Mg and/or by adding alloying elements. In this work, we provide a theoretical investigation of the electronic and structural properties of pure and M-doped MgH₂ (with M=Sc, Ti, V, Ni, Al). We have performed calculations for both the crystalline state and ≈ 1.0 nm particles. The self-consistent total energy calculations are performed within the framework of density functional theory using the VASP package for crystals and TURBO-MOLE package for clusters. One of the aims of this study is to see if the alloying elements can weaken Mg-H bonds in their vicinity and/or can act as catalytic centers for the formation of H₂. We also like to understand the improvement in thermodynamics with the use of nanoparticles compared to the bulk material.

BNH Compounds - Promising Hydrogen Sources?

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Different BNH-compounds have a high hydrogen content per mass unit (up to 20% of hydrogen) and unusual hydrogen exchange properties at the decomposition and formation reactions, respectively. They could be therefore interesting and suitable materials for the use as a hydrogen source or for storage. The compounds are isosteric to well known aliphatic or cyclic hydrocarbons. Since the hydrogen should be given in both states (hydridic and protic) in the BNH-compounds, we observe at the decomposition and formation completely other properties compared with the corresponding CH-compounds. Similar statements are follow from the comparison of the thermophysical properties of the BNH-compounds with the comparable results for other interesting hydrogen storage materials, e.g. of complex hydrides (alkali alanates or boranates) or of lithium- and magnesiumamides, respectively. . The thermal decomposition of solid aliphatic and of cyclic BNH-compounds and with it the evolution of hydrogen was studied by use of different types of calorimetric investigations, combined with gravimetric, volumetric and spectroscopic measurements. The sequence of the thermal events seems to be strongly controlled kinetically. Dependent on the investigated compound we observed a well defined exothermic decomposition steps between 90 °C and 200°C [1],[2],[3],[4]. The hydrogen evolution from solutions of the BNH-compounds in different solvents was realized near room temperature in presence of a catalyst. Interesting parameters of the reactions in solution are determined by calorimetric process monitoring The influence of high hydrogen pressure (up to 5kbar) on the decomposition of different BNH solids and solutions was studied.

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First-Principles Study of $\text{LiNH}_2\text{-MgH}_2$ as a Potential Hydrogen Storage Material

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LiNH_2 possesses high capacity for hydrogen storage [1], but its large hydride formation enthalpy leads to operating temperatures and pressures that lie outside the practicable range for vehicular applications. Partial substitution of Li by Mg can destabilize the system and thus improve the hydrogen de-sorption characteristics, as it has been shown in recent experimental studies[2]. We present and discuss results from our density functional theory investigations of the $\text{LiNH}_2\text{-MgH}_2$ system. The main aim of this study is to understand the bonding characteristics, the Mg-induced destabilization mechanism, and the thermodynamics of hydrogen de-sorption from an electronic structure viewpoint.

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Fast Dynamics, Gas Adsorption and Bundle Motion in Carbon Nanotubes

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Carbon nanotubes are promising materials in the fields of electronics, mechanical actuators, gas sensing devices and confinement of gases and liquids in 1 and 2 dimensions. In this study the anelastic properties of bucky papers made of HiPco single wall carbon nanotubes were investigated for the first time in the temperature range from 4 to 700 K. The low temperature elastic energy loss curve displays two peaks, A around 20 K and B around 150 K. The intensity, IA, of Peak A strongly depends on the hydrogen content of the samples. In intentionally hydrogenated samples IA is almost zero, but after subsequent thermal treatments which partially remove hydrogen, IA progressively increases. We propose that the relaxation is due to hydrogen, and IA increases with decrease of cH as more free sites are made available for the H jumps. The fact that the species giving rise to peak A is very mobile, performing about 1000 jumps/s at 25 K, suggests that hydrogen is in the atomic form. The classical Debye or Fuoss-Kirkwood models cannot reproduce the lineshape of peak A, indicating that the motion of H is governed by a quantum tunneling. The intensity of Peak B increases after exposition to a H₂ atmosphere at 80 K; therefore, we propose that the peak is due to molecular hydrogen adsorbed on the surface of the bucky paper and the dissipation is caused by the magnetoelastic coupling between the orthohydrogen molecules and the 2D hexagonal lattice of carbon nanotubes. On cooling, a strong decrease of the elastic modulus between 80 and 50 K can be observed; this inflection is retraced on heating, and persists also on measuring after a thermal treatment at 700 K without opening the experimental cell. A possibility is that this process is due to liquefaction/solidification of air encapsulated within the nanotubes. In addition, the elastic energy dissipation of HiPco SWNT's measured on heating above room temperature displays three maxima, at about 350 K, 500 K and 530 K, labelled as Peaks C, D, and E, respectively. Peak D is accompanied by a marked modulus variation. After a thermal treatment in vacuum for 19 hours at 600 K: i) Peak C disappears, and this process is attributed to the desorption of air adsorbed on the nanotubes after ambient exposition. Experiments with selected gases composing air indicate that Peak C is due to water vapour adsorbed on the bucky paper; ii) Peak D permanently disappears, and with it the modulus drop; therefore it is concluded that the process may be due to the surfactant fusion, which takes place around the peak temperature; iii) Peak E, which shows thermally activated features, persists after subsequent treatments at high temperature, but its intensity progressively decreases; its behaviour is typical of a glassy dynamics, and it has been attributed to the motion of the bundles.

Hydrogen Motion During Chemical Reactions in Catalyzed Alanates and Formulation of a Model. An Anelastic Spectroscopy Study

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The formation of a new species during the decomposition reactions in Ti-doped and undoped sodium alanates was observed for the first time by anelastic relaxation spectroscopy. This species gives rise to a thermally activated relaxation peak around 70 K at 1 kHz, with an activation energy of 0,126 eV and a pre-exponential factor of 7×10^{-14} s, which is typical of point-defect relaxation. The complex has a fast dynamics and, according to the deuterium isotope effect found, involves hydrogen. Various possible sources of the process have been considered, taking into account the products of decomposition. After excluding even the involvement of catalytic Ti, the most likely cause of the observed process is a hexahydride stoichiometry defect of type AlH_x ($x < 6$) missing one or more H atoms, thus giving rise to local vacancy dynamics. The results show that not all the hydrogen released during the high temperature decomposition reactions evolves out of the samples as gas, but part of it remains in the lattice and distributes itself between the Ti trapping sites and the free interstitial sites. The hydrogen diffusion for equilibrium redistribution, and a spontaneous partial reverse reaction take place at high temperature, whereas H caging at the Ti and at the bond traps occurs when temperature is lowered. Our data demonstrate that the AlH_{6-x} bond is a deeper trap for H than Ti. A novel model to explain the decomposition has been formulated, where the catalytic action of Ti has been identified in the modification of the site- and saddle point-energies of H in the bond, resulting in a lowering of the activation energy for breaking the bond.

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Hydrogen Storage in Magnesium Clusters - A Quantum Chemical Study

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Magnesium hydride is cheap and contains 7.7 wt% hydrogen, making it an attractive hydrogen storage materials. The problem of the sluggish kinetics for reversible (de)hydriding has mostly been solved during the last decade by introducing small amounts of transition metal elements, and reducing the crystal grain size to 20-50 nm by ball milling. Unfortunately, despite the improvement in the kinetics, thermodynamics still dictate that bulk β -MgH₂ only decomposes above ca.300 °C (at 1 bar), which is a major impediment for practical application. It is well known that fundamental properties of materials can change dramatically when material dimensions shift into the nanometer regime. We investigated the influence of the size of the magnesium particles/domains, going much below the 20-50 nm range normally achieved by ball-milling. Density functional theory (DFT) calculations were performed on nanometer-sized Mg and MgH₂ clusters. Figure 1 shows calculated desorption energies as a function of the cluster size.

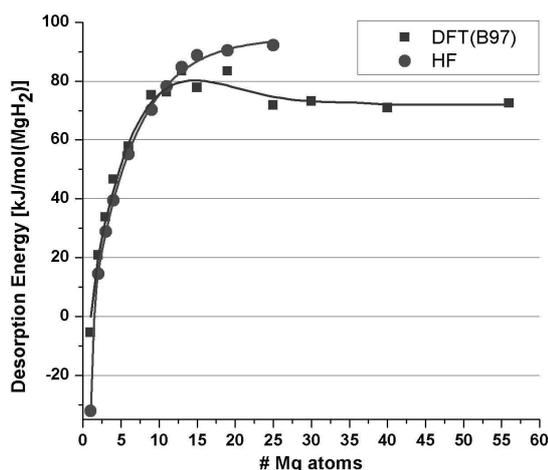


Figure 1: Calculated desorption energies for MgH₂ clusters with both the HF and DFT method (B97 functional). The energies are normalized per mole H₂ released.

Our calculations clearly show (using different functionals and comparing with Hartree-Fock calculations) that the desorption enthalpy of MgH₂, and hence the dehydriding temperature, can be significantly reduced for particles sizes of the order of 1-2 nm. At the moment, high desorption temperatures are a major impediment; hence the projected shift towards more favourable operation temperatures is crucial for the application of Mg as a reversible hydrogen storage material. It is experimentally very demanding to obtain such small particles, and/or to stabilise crystal grains of such a small size. We now focus on novel experimental routes to prepare such spatially confined magnesium clusters.

Storage of Molecular Hydrogen in Carbon Nanostructures by Physisorption

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Recently, we have shown that molecular hydrogen shows a considerable interaction energy with polyaromatic hydrocarbons (PAHs) and graphene[1]. At ambient conditions, and even at temperatures of liquid N₂, the energetics of the system is determined by the interaction free energy. We developed a basic quantum-mechanical approach to calculate this quantity correctly, and showed that the H₂ storage capacity of graphite-based nanostructures is determined by the interlayer distance, with a maximum of about 0.6 nm (Fig. 1), if all necessary contributions to the system free energy are considered properly[2].

In this contribution we design and explore several promising carbon nanostructures for H₂ storage. Both, the stability of the nanostructures themselves and their capacity to store H₂ is addressed in this work. The structures are designed in such way that graphene with interlayer distances of 0.6-1nm is created by the inclusion of spacer molecules, and by functionalization of the graphene layers. Also other carbon nanostructures which have been discussed as potential H₂ storage media, as single- and multiwalled carbon nanotubes and graphite foam, are included in this study.

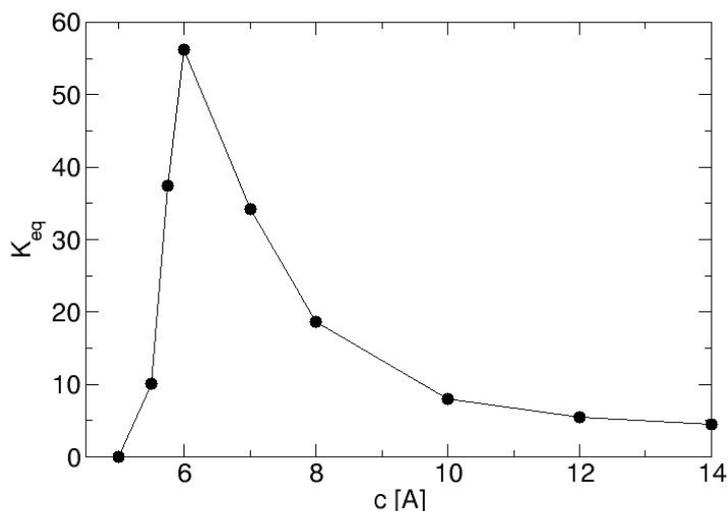


Figure 1: Equilibrium constant of molecular hydrogen K_{eq} in dependence of the graphite interlayer distance c .

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[2]S. Patchkovskii, J. S. Tse, S. N. Yurchenko, L. Zhechkov, T. Heine, G. Seifert, Proc. Natl. Acad. Sci. USA, 102, 10439 (2005)

Proton NMR Studies on MBH₄ (M= Li, Na, K) and pure/doped NaAlH₄

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Complex chemical-hydrides as MBH₄ (M= Li, Na and K) and NaAlH₄ are considered to be promising hydrogen storage materials. The structural and dynamical properties of these compounds can be studied by proton NMR. After turning the nuclear magnetization by a 90° RF pulse, the so called "Free induction decay" (FID) transient response is obtained. In most chemical hydrides, the FIDs decay quite rapidly due to the strong internal dipolar interactions. Unfortunately, the FIDs can only be recorded after a dead time $\tau_D = 10\mu s$ due to intrinsic experimental restrictions. Spectra of the systems are obtained by Fourier transformation of the measured FIDs. A peculiar double peak has been found in all these spectra, if τ_D is not small compared to the length of the FID. The spectra of the samples MBH₄ (M= Li, Na and K) show a doublet with a splitting of approximately 25 kHz. In the case of NaAlH₄ there is also this double peak plus a sharp line in the center. NaAlH₄ releases the hydrogen in 2 steps, the first giving Na₃AlH₆ as a sub-product. By the use of catalysts, the temperature of hydrogen release is reduced and the process of dehydrogenation is reversible. [1]. At room temperature and above the spectra of Na₃AlH₆ consist only of a single line. Making use of the different spectra we could perform in situ measurements of the decomposition of NaAlH₄. Figure 1 shows the changes in the spectra of TiCl₃ doped NaAlH₄ measured at 330 K. After approximately 200 h the material is completely transformed into Na₃AlH₆.

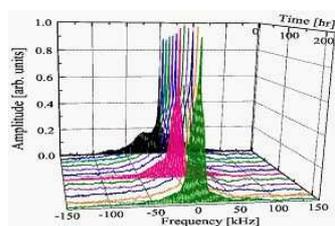


Figure 1: Proton NMR Spectra at 330 K showing the transformation from Ti-doped NaAlH₄ (black spectrum) to Na₃AlH₆ (spectrum in the front) as a function of time

(a)

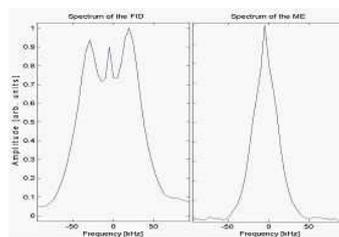


Figure 2: Spectra of NaAlH₄ obtained by Fourier transformation of (a) the FID and (b) the ME.

(b)

In order to measure the FID without any dead time, we applied the Magic Echo (ME) pulse sequence. The spectra thus obtained consist for all sample of a single line. (See e.g. Figure 2) The hydrogen dynamics in the different compounds is investigated by measurements of the spin-lattice relaxation times T_1 . All the chemical hydrides studied here reveal a double exponential recovery of the magnetization, indicating two fractions of hydrogen atoms with different dynamics. In the case of NaAlH₄, the T_1 values indicate an increase of the hydrogen dynamics in the samples with catalysts such as Ti- nanoclusters and TiCl₃. This is consistent with the fact that in the doped samples the decomposition of the hydrogen takes places at lower temperatures [2]. In the case of MBH₄ the relaxation times are shorter than those measured in the NaAlH₄ without catalyst. This may indicate a higher hydrogen dynamics than in MBH₄, even though the relaxation may also be affected by impurities in the MBH₄ samples.

[1]M. Bogdanovic, et al. J. Alloys Comp. 253-254, 1 (1997)

[2]F Majer, G., et al. J. Alloy Comp. (2005) in press

In-Situ XRD and DSC Studies on the Decomposition of Alkali and Alkaline Earth Aluminates

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The dissociation behavior of the systems LiAlH_4 , KAlH_4 , $\text{Mg}(\text{AlH}_4)_2$, $\text{Ca}(\text{AlH}_4)_2$, $\text{LiMg}(\text{AlH}_4)_3$ and $\text{Na}_2\text{LiAlH}_6$ was subject of in-situ X-ray and DSC investigations. For thermodynamic calculations, it is necessary to determine the reaction pathway and the crystalline phases formed during thermolysis correctly. A wrong assignment of DSC data can result in an incorrect mechanism later on used for thermodynamic studies. In-situ X-ray diffraction experiments are a powerful tool for the correct interpretation of observed thermal effects. Nowadays, laboratory instruments provide data of a very high quality allowing a precise analysis of kinetic experiments. The samples were analyzed on a transmission diffractometer from room temperature up to 400°C under protective Ar atmosphere. The use of a 40° 2θ position sensitive detector enabled a very fast data collection time of 60 sec per temperature step. Significant differences of the reaction pathways for the alkali and the alkaline earth aluminum hydrides during thermolysis were determined. The thermal stabilities of the particular compounds and the crystalline phases occurring during thermolysis do not only depend on the chemical composition of the aluminates but also on the presence of different by-phases.



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