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Improvement on Hydrogen Storage Properties of Complex Metal Hydride

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1. Introduction

A large challenging of world economic development is to meet the demand of energy consumption while reducing emissions of greenhouse gases and pollutants [1-5]. Hydrogen, as an energy carrier, is widely regarded as a potential cost effective, renewable, and clean energy alternative to petroleum, especially in the transportation sector [1]. Extensive efforts are being made to develop a sustainable hydrogen economy which is involved by hydrogen production, hydrogen storage, and hydrogen fuel cell in the cyclic system of hydrogen combustion [2, 6]. One key component of realizing the hydrogen economy for transportation applications is developing highly efficient hydrogen storage systems.

Table 1 presents the current available hydrogen storage techniques. Although some basic technical means such as pressurized gas and cryogenically liquefied hydrogen in containers can be used at present, hydrogen capacity is not acceptable in practical applications-driving a car up to 300 miles on a single tank, for example. Therefore, storing hydrogen in advanced solid state materials has definite advantage with regard to a low-cost, high gravimetric and volumetric density, efficiently storing and releasing hydrogen under mild thermodynamic conditions. Over the past decades, many advanced materials such as complex metal hydrides [7, 8], metal hydrides [9], metal-organic framework (MOF) [10-12], and modified carbon nanostructures have been explored to develop efficient hydrogen storage techniques [13-19], but none of them can meet all requirements [20].





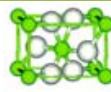
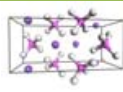
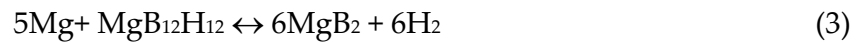
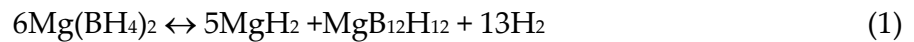
					
Liquid Hydrogen	Compress Hydrogen	MOF	Nanostructure	Metal Hydride	Complex Metal Hydride
-253°C	25 °C	-200 °C	25°C	330°C	>185°C

Table 1. Available hydrogen storage technologies and corresponding operating temperatures.

Complex metal hydrides (for example, NaAlH_4 , LiAlH_4 , LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, LiNH_2) are currently considered as one of the promising hydrogen storage materials mainly because they have a high hydrogen capacity and are facile to tailor structural and compositional to enhance hydrogen storage performance. The typical structure of complex metal hydrides contains cation alkali metal (M^{n+}) and anion hydrides (AlH_4^- , BH_4^- , NH_2^-) with a closed-shell electronic structure. It should be pointed out that this review focuses on Al- and B-based complex metal hydrides. The bonding characteristics of these complex metal hydrides determine that their dehydriding and hydriding are unfavorable either thermodynamically or kinetically under moderate conditions. As a result, a large obstacle to use complex metal hydrides as on-board hydrogen storage materials is a relatively high hydrogen desorption temperature, a low kinetic rate for hydrogen desorption and adsorption, and a poor reversibility. It is very important to develop the effective chemical and physical methods to improve hydrogen storage properties of these materials.

Herein, take $\text{Mg}(\text{BH}_4)_2$ as an example. A possible hydrogen desorption process from $\text{Mg}(\text{BH}_4)_2$ to MgB_2 are depicted by the following equations (1)-(3) [21]:



In fact, hydrogen desorption of $\text{Mg}(\text{BH}_4)_2$ experiences a complicated hydrogen desorption process involving chemical reactions and physical changes such as mass transport and phase separation. Two thermodynamically stable intermediates, $\text{Mg}(\text{B}_{12}\text{H}_{12})$ and MgH_2 , are formed in the first step (Equation (1)) with enthalpy and entropy of $39 \text{ kJ/mol}\cdot\text{H}_2$ [22]. In 2008, a different value of $57 \text{ kJ/mol}\cdot\text{H}_2$ was obtained [23]. The hydrogen desorption reactions of equations (2) and (3) have endothermicity of 75 and $87 \text{ kJ/mol}\cdot\text{H}_2$. Therefore, the equations (2) and (3) only occur at a high temperature, 572 K of equation (2) and 643 K of equation (3) [24]. In addition, a stable intermediate usually leads to a thermodynamic pitfall which trap a large amount of hydrogen cannot be cycled. Very recently, Jensen et al. found that at a high condition ($\sim 400^\circ\text{C}$ and $\sim 950 \text{ bar}$), equations (2)-(3) also can participate hydrogen release/uptake reactions [25]. However, these conditions are unfeasible for practical application.

Promoting the kinetic rates of hydrogen desorption and adsorption of complex metal hydrides play an important role in developing hydrogen storage material. However, because the bonds B–H in BH_4^- and Al–H in AlH_4^- are relatively strong, their dissociations require overcoming a high barrier. Additionally, two processes must be considered to enhance the kinetic rate of hydrogen desorption and adsorption. Firstly, phase transitions coupled with chemical reactions, which sometimes experience a high barrier, slow down the kinetic rate. Secondly, hydrogen diffusion is also important factor to take effect on the kinetic rate of hydrogen desorption and adsorption.

In 1997, Bogdanović et al. demonstrated that a small amount of Ti-compounds doped in NaAlH_4 can enhance the kinetic rates of both hydrogen desorption and adsorption of NaAlH_4 ,

reduce hydrogen desorption temperature from 210 to 120°C and hydrogen adsorption pressure from 350 to 100 bar, as well as have a good reversibility (80% H) [26]. It stimulated the extensive studies in theory [27-41] and experiment [42-54] to improve the kinetic and thermodynamic properties of hydrogen desorption and adsorption of complex metal hydrides in order to develop the practical hydrogen storage material. More importantly, these studies have extended from doping transition metal to chemical and physical methods such as nanoengineering, and cation substitution. These structural and composition tailor are expected to have strong effects on the thermodynamics of the complex hydrides and the kinetics of hydrogen release and uptake from either the bulk crystalline phase or nanosized particles.

In the past years, there are a few reviews to discuss hydrogen storage materials with different points of view. In this chapter, we focus on improvement on hydrogen storage properties of complex metal hydrides, that is, tailoring thermodynamics and kinetic properties of their hydrogen desorption and adsorption by the various techniques. We do not intend to provide a complete review of the literature about this topic, but rather to emphasize tailoring effect on hydrogen storage properties of complex metal hydrides. The research is mainly categorized into three parts: (i) doping transition metal; (ii) nanoengineering techniques; and (iii) cation Substitution. Finally, we present a conclusive remark for developing complex metal hydrides as hydrogen storage materials by means of altering thermodynamic and kinetic properties.

2. Improving hydrogen storage properties

2.1. Doping transition metal

Catalysts have been widely exploited to hydrogen storage materials to improve the kinetic and thermodynamic properties of hydrogen desorption and adsorption in complex metal hydrides and metal hydrides, following the pioneering work of Bogdanović and Schwickardi [26, 55]. They demonstrated that doping the complex metal hydrides NaAlH_4 with a few mol% of Ti lowered the decomposition temperature, improving the kinetics, and, importantly allowed rehydrogenation of the decomposition products. This finding quickly sparks worldwide research activities that aimed at developing catalytically enhanced NaAlH_4 and related complex metal hydrides as practical hydrogen storage medium. Then, a great number of experimental and theoretical studies have been devoted to characterize the structures and effect of Ti in NaAlH_4 . Although many models were proposed to describe (de)hydrogenation of Ti-doped NaAlH_4 , no clear consensus about structures and catalytic mechanism of Ti in NaAlH_4 has been achieved. The only established fact from these studies is a surface-localized species containing a nascent binary phase Ti-Al alloy formed during cyclic dehydrogenating and rehydrogenating processes [28, 43, 51, 56-58].

Many experimental studies about the local structure of Ti-doped NaAlH_4 showed that highly dispersed Ti in the Al surface plays an important role in hydrogen uptake and release processes. As shown in Figure 1, TiAl_3 alloy is the most likely form after dehydrogenating Ti-doped NaAlH_4 [43, 59]. It is consistent with what TiAl_3 is thermodynamically the most stable stability in Ti-Al system. The local structure of active species has Ti-Al and Ti-Ti

bond distance of 2.79 and 3.88 Å, respectively. After mechanical milling, TiCl_3 is reduced to zero-state Ti by interaction with NaAlH_4 . However, TiAl_3 doped in NaAlH_4 were found to be substantially less effective than TiCl_3 . Therefore, the catalytic activity of Ti structure may be summarized as "Ti in the Al surface > TiAl_3 cluster > crystalline TiAl_3 " [50].

In fact, determining accurately the local structures in such a complicated system including a dynamic hydriding/dehydriding processes is extremely challenging to many experimental techniques. In this aspect, DFT-based first-principles methods have shown their advantages. Several theoretical studies have been performed with emphasis on substitution of Ti for Al and Na atoms in Ti-doped NaAlH_4 bulk and surfaces. Substitution of Ti for Al has been shown theoretically to be the preferred location in bulk NaAlH_4 . *Íñiguez et al.* studied the structure, energetics, and dynamics of pure and Ti-doped NaAlH_4 , focusing on the possibility of substitutional Ti doping in the bulk. They found that the doped Ti prefers to substitute for Na and further attract surrounding hydrogen atoms, softening and/or breaking the Al-H bonds. The same group of authors extended their studies to determine the location of Ti. These later results showed that Ti prefers to be on the surface, substituting for Na, and attracting a large number of H atoms to its vicinity. They predicted that a TiAl_n ($n > 1$) structure may be formed on the surface of the sodium alanate [30]. However, *Løvvik et al.* also suggested that substitution of Ti in bulk NaAlH_4 is less favorable than that near surface or defect positions. On the NaAlH_4 (001) surface, DFT calculations by *Yildirim and Íñiguez* showed substitution of Ti for Na is the preferred site [60] whereas *Løvvik and Opalka* found substitution of Ti for Al is more favorable [40]. The difference has been attributed to the different reference states used in energy calculations.

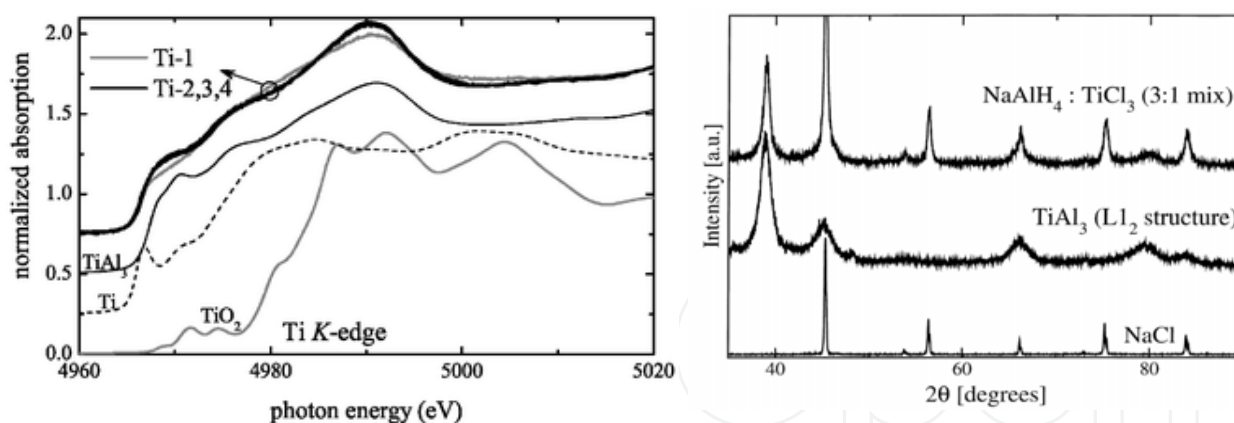


Figure 1. Normalized XANES spectra for Ti-doped NaAlH_4 and the reference compounds (left); X-ray diffraction indicating TiAl_3 production in the NaAlH_4 system when mechanically milled in a 3:1 ratio with TiCl_3 . Reproduced from [43] for (left) by permission of The Royal Society of Chemistry, and from [59] for (right) by permission of Elsevier.

However we approached this problem based on a surface model and found a different structure and mechanism. The $\text{TiAl}_3\text{H}_{12}$ local structure was identified in Ti-doped NaAlH_4 (001) and (100) surfaces [41]. Our calculated results show that the hydrogen desorption energies from many positions of TiAl_3H_x are reduced considerably as compared with that from the corresponding clean, undoped NaAlH_4 surfaces. Furthermore, we showed that the

$\text{TiAl}_3\text{H}_{12}$ complex has an extended effect beyond locally reducing the hydrogen desorption energy. It also facilitates hydrogen desorption at a reduced desorption energy by either transferring the hydrogen to TiAl_3H_x or by reducing the hydrogen desorption energy in neighboring AlH_4^- by linking these AlH_4^- units with the complex structure. Our predicted interstitial TiAl_3H_x structure was supported by a recent combined Ti K-edge EXAFS, Ti K-edge XANES, and XRD study of TiCl_3 -doped NaAlH_4 by Baldé et. al [61]. These authors observed that the interstitial structure accounts for more than 70% of all Ti doped in NaAlH_4 .

Extensive experimental studies have demonstrated that transition metals (TM) can accelerate the kinetic rate of hydrogenation and dehydrogenation reactions in this system. In terms of chemical reactions, TM can weaken Al–H and H–H bonds and thus reduce transition state barriers of hydrogen reactions through electron backdonation interaction from d orbital of TM to σ^* of these bonds [33]. In addition, addition of TM also leads to formation of defect which is also favorable to kinetic improvement of hydrogen diffusion in solid-state materials [31, 62].

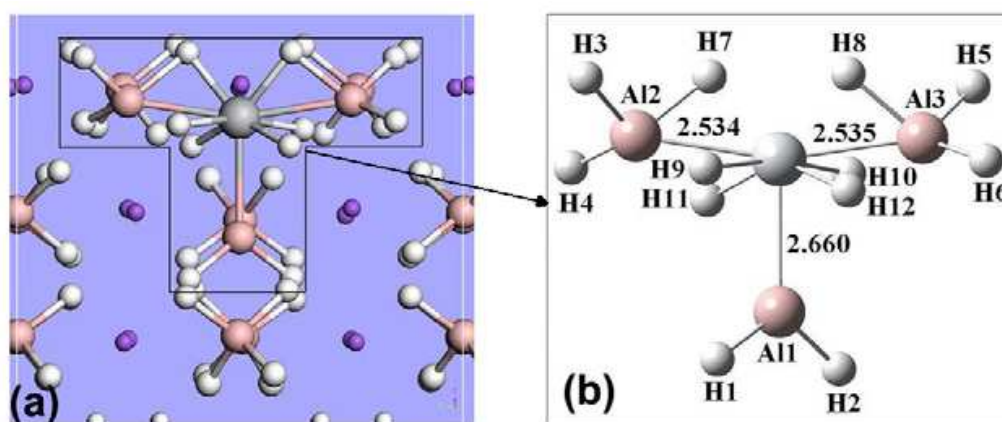


Figure 2. DFT-GGA relaxed structure of Ti-doped $\text{NaAlH}_4(001)$ with Ti in the surface interstitial site. (b) Detailed local structure of the $\text{TiAl}_3\text{H}_{12}$ complex shown in (a). Reprinted from [41].

Few experimental studies on tailoring thermodynamic properties of NaAlH_4 by doping TM were performed. Bogdanović and Schüth performed pressure-concentration isotherms for hydrogen desorption of NaAlH_4 with different doping levels of Ti [63]. They found Ti doping can significantly alter the thermodynamics of the system, which is demonstrated by the change of the dissociation pressure with doping level. Such a thermodynamic change is mainly attributed to Ti-Al alloy formation.

As mentioned previously, our studies for Ti-doped NaAlH_4 found that TiAl_3H_x structure has a significant effect to reducing hydrogen desorption energy [41, 64]. Such a thermodynamic tuning effect can be explained by the closed-shell 18-electron rule of transition metal structures. In addition, Mainardi et al. performed electronic structure calculations and molecular dynamic simulations for kinetics of hydrogen desorption of NaAlH_4 [65]. They found that the rate-determining step for hydrogen desorption was hydrogen evolution from associated AlH_4 species. Ti is predicted to stay on the hydride surface and serves as both the catalytic species in splitting hydrogen from $\text{AlH}_4^-/\text{AlH}_3$ groups as well as the initiator Al nucleation sites in Ti-doped NaAlH_4 system.

In terms of NaAlH_4 , an important issue is to select high efficient catalyst for improving thermodynamic and kinetic properties of hydrogenation and dehydrogenation. Anton and Bogdanović studied the hydrogen desorption kinetics of NaAlH_4 by different transition metals(TM) and found early TMs have a better catalytic effect for hydrogen desorption kinetics than later TMs [66, 67]. In 2008, we performed DFT calculations for hydrogen desorption mechanism of 3d TM-doped NaAlH_4 . Similarly, TMAI_3H_x were determined to the most stable structures [33]. In these structures, the electron transfer between hydrogen and Al groups mediated by the d-orbitals of TMs plays an important role in hydrogen release/uptake from analate-based materials.

Only a few publications focus on the theoretical exploration for the mechanism of Ti-catalyzed hydrogenation process [28, 29, 68]. In fact, Ti-catalyzed hydrogenation process includes hydrogen dissociation and the subsequent formation of any hydrogen-containing mobile species from Ti active sites. In 2005, Chaudhuri et. al performed DFT calculations to investigate the position and catalytic mechanism for hydrogenation of Ti in Al (001) surface structure [29]. Two next-nearest-neighbor Ti atoms located on the top of 2×2 Al(001) surface are more favorable to hydrogen dissociation than others positions such as two nearest-neighbor. In this particular local arrangement, the H–H bond can be automatically broken and the dissociated H atoms are connected with Ti and Al. The analysis of electronic structure showed that the bond-breaking process is enhanced by electron backdonation from Ti-3d orbitals to hydrogen σ^* orbitals. However, Ti was believed to promote formation of AlH_3 or NaH vacancies but not included explicitly in the model. Furthermore, NaH was not treated explicitly as the study focused on dehydrogenation. Therefore, a system directly involving NaH is necessary to account for its role in the cyclic process of using NaAlH_4 as a hydrogen storage medium.

Recently, we studied hydrogen adsorption process of TiAl_3H_x supported on the NaH(001) surface in order to understand hydrogenation mechanism of Ti-doped NaH/Al [69]. Our results support that TiAl_3H_x gains electronic charge from the NaH hydrides. The hydrided TiAl_3H_x cluster on the NaH surface which dissociates the H_2 molecule at the Ti site in contact with the surface. Furthermore, our DFT-based molecular dynamics simulation (Figure 3) demonstrated that TiAl_3H_x clusters are active for H_2 dissociation after acquiring electrons from the hydride of NaH surface.

Another complex hydride similar to NaAlH_4 but having an even higher intrinsic hydrogen capacity is LiAlH_4 . The decomposition of LiAlH_4 is believed to undergo similar steps to NaAlH_4 . The first decomposition step from tetrahedral LiAlH_4 to octahedral Li_3AlH_6 is weakly endothermic [70, 71]. The second decomposition reaction from octahedral Li_3AlH_6 to LiH and Al phase was found to be endothermic with ΔH of 25 kJ/mol· H_2 . Its dehydriding was observed to occur at 228-282 °C, likely due to kinetic limiting steps. Apparently, the decomposition temperature is too high for practical purposes. The decomposition of LiAlH_4 is very slow without a catalyst [72-75].

Balema et al. found that the mixture of 3 mol% TiCl_4 and LiAlH_4 under ball milling can cause LiAlH_4 to rapidly transform into Li_3AlH_6 [72, 73]. In 2010, Langmi et al. found that

TiCl₃ can enhance thermodynamic properties to reduce hydrogen desorption temperature from ~170°C for the first step while melting and 225°C for the second step to 60-75°C below the melting point [76]. These studies indicated that doping TiCl₃ can improve thermodynamic and kinetic properties of (de)hydrogenation processes of LiAlH₄.

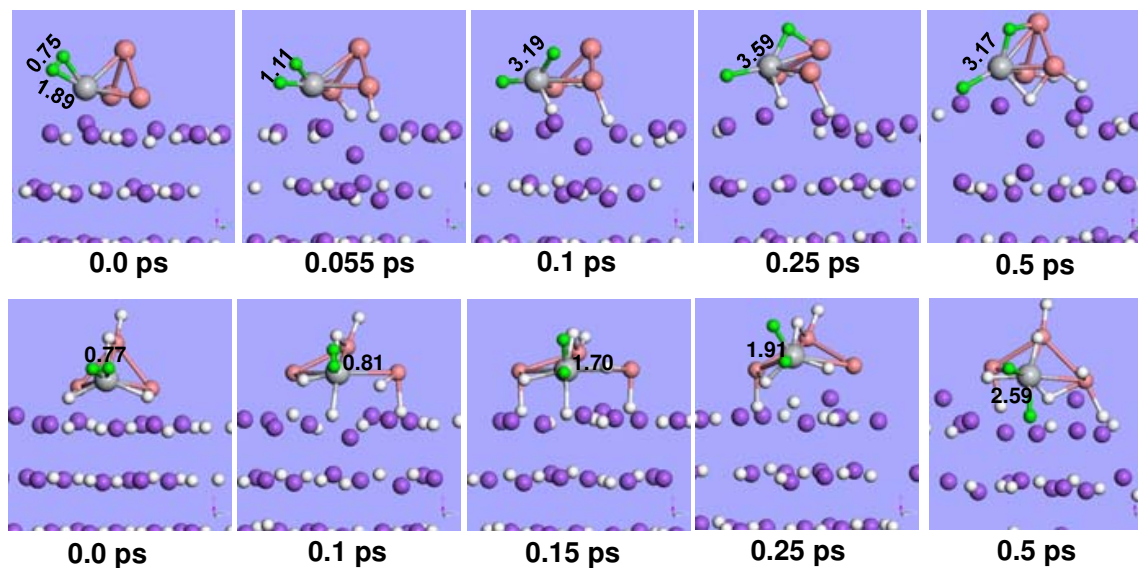


Figure 3. Snapshots from *ab initio* molecular dynamics trajectories for H₂ dissociation on TiAl₃ and TiAl₃H₄ clusters supported on NaH (001) surface. Purple, white, pink, gray, and green balls represent Na, H, Al, and Ti, and dissociating H₂. Reprinted from [69] by American Chemical Society.

Very recently, Liu et al. directly synthesized LiAlH₄ from commercially available LiH and Al powders in the presence of TiCl₃ and Me₂O for the first time [77]. However, without TiCl₃ or adding metallic Ti, LiAlH₄ is not observed in experiment. It suggests that with the presence of TiCl₃, LiAlH₄ can be cycled, making it a reversible hydrogen storage material. However, the catalytic effect of TiCl₃ for enhancing thermodynamic and kinetic properties of LiH+Al+3/2H₂→LiAlH₄ still is not studied so far.

Complex metal borohydrides have attracted extensive attention due to its intrinsically high gravimetric and volumetric hydrogen capacities (for example, LiBH₄, 18.2 wt%, 121 kg/m³). Unfortunately, the B-H bond in pure LiBH₄ material is extremely strong and only liberates 2% hydrogen around the melting point (541-559 K) [1]. Starting from LiBH₄, the partial decomposition to LiH(s)+B(s)+3/2H₂(g) has the standard enthalpy of 100.3 kJ/mol·H₂ [78]. The highly endothermic decomposition reaction indicates hydrogen release from LiBH₄ must occur at elevated temperatures. The experimental results of Züttel et. al showed that a significant hydrogen desorption peak started at 673 K and reached its maximum value around 773 K [79, 80]. In 2007, Au et al. showed that LiBH₄ modified by metal oxides or metal chlorides, such as TiO₂ and TiCl₃, could reduce the dehydrogenation temperature and achieve re-hydrogenation under moderate conditions [81, 82]. Modified LiBH₄ releases 9 wt% H₂, starting as low as 473 K, which is significantly lower than the hydrogen releasing temperature of 673 K for pure LiBH₄. After being dehydrogenated, the modified LiBH₄ can absorb 7~9 wt% H₂ at 873 K and 70 bar, a significant improvement from

923 K and 150 bar for pure LiBH_4 [80]. Very recently, Fang, et al. reported that a mechanically milled $3\text{LiBH}_4/\text{TiF}_3$ mixture released 5-6 wt% hydrogen at temperatures of 343~363 K [83]. Similarly, other dopants have been attempted to reduce the hydrogen desorption temperature of MgH_2 . Clearly, addition of Ti-compounds (TiO_2 , TiCl_3 , and TiF_3) result in a strong improvement for hydrogen desorption and, to a lesser extent, for re-hydrogenation. On the other hand, the improvement brought by these additives to LiBH_4 is not sufficient to make LiBH_4 viable as a practical hydrogen storage media

In 2009, we presented our DFT calculations for structures and hydrogen desorption Ti-doped LiBH_4 surface [84]. Molecular orbital analysis showed that the structural stability could be attributed to the symmetry-adapted orbital overlap between Ti and "inside" B-H bonds. Several surfaces (001) and (010) can desorb hydrogen in molecular form by high spin state (triplet), while surface (100) must first desorb hydrogen atoms, followed by the formation of a hydrogen molecule in the gas phase.

$\text{Mg}(\text{BH}_4)_2$ is considered as another promising hydrogen storage materials and it releases approximately 14.9 wt% of hydrogen when heated up to 870K [22, 23, 85-93]. As discussed in Introduction, the dehydrogen process is found to go through multiple steps with formation of some stable intermediates such as $\text{MgB}_{12}\text{H}_{12}$ and MgH_2 [21]. Therefore, it is very necessary to tune thermodynamic and kinetic properties of hydrogenation and dehydrogenation of $\text{Mg}(\text{BH}_4)_2$. The addition of TiCl_3 into $\text{Mg}(\text{BH}_4)_2$ was demonstrated to be effective on tuning thermodynamic properties [86]. Hydrogen desorption temperature is reduced to from 870 K to 361 K. However, Ti species gradually convert to Ti_2O_3 and TiB_2 during cycling experiments of hydrogen desorption/adsorption [94], though the catalytic mechanism is still not clear.

2.2. Nanoengineering techniques

Due to size effect and morphology, nanoparticles often display some different physical and chemical properties compared to bulk particles and are applied for instance in catalysis, chemical sensors, or optics [95-98]. A small size of particle can decrease hydrogen diffusion lengths and increase surface interaction with H_2 . More importantly, thermodynamics of hydrogen desorption/adsorption of complex metal hydrides usually can be adjusted by controlling particle size [34, 99-103]. Particle size of complex metal hydrides can be usually reduced to ~200 nm by ball milling technique, for NaAlH_4 preferably in the presence of TM-based catalysts [57, 104, 105]. Obtaining smaller certain sizes of particles of complex metal hydrides is still challenging. Moreover, with the method of ball milling, the particle size is very difficult to control in an exact value and the size distribution is broad.

In the recent years, a new technique, nanoscaffold, has been extensively used to produce a different size of nanoparticles of complex metal hydrides. However, it should be pointed out that development of controlling nanosize of particle by nanoscaffold technique is really dependent on preparation of porous nanomaterials. Additionally, it is understood that a nanoscaffold technique unavoidably results in a low hydrogen capacity of complex metal hydrides.

By this technique, Baldé et al. synthesized a nanofiber-supported NaAlH_4 with discrete particle size ranges of 1-10 μm , 19-30nm, and 2-10nm [99]. The experimental measurement on temperature programmed desorption of H_2 for NaAlH_4 nanoparticles was presented in Figure 4. The hydrogen desorption temperatures are decreased from 186°C of 1-10 μm to 70°C of 2-10nm. More importantly, the activation barriers of hydrogen desorption also change from 116 to 58 kJ/mol correspondingly. It suggests that size reduction of nanoparticle can tailor thermodynamic and kinetic properties of hydrogen desorption/adsorption process of NaAlH_4 . In addition, they also reported that decreasing particle sizes also lowered the pressures needed for hydrogen uptake. In 2010, Gao et al. confined NaAlH_4 into 2-3 nm nanoporous carbon [102]. They observed that H_2 release temperature and rehydrogenation conditions were significantly improved. More importantly, the total reaction is changed to a single step reaction without Na_3AlH_6 formed. The similar studies also exhibited nanosize effect on tuning thermodynamic and kinetic properties for complex metal hydrides.

In 2011, Majzoub et al. presented first-principles calculations for phase diagram of small cluster of Na-Al-H system [34]. They found that decreasing cluster size not only reduces hydrogen desorption temperature but also change reaction path from $\text{NaAlH}_4 \rightarrow \text{Na}_3\text{AlH}_6 + \text{Al} + \text{H}_2 \rightarrow \text{NaH} + \text{Al} + \text{H}_2$ in bulk structure to $\text{NaAlH}_4 \rightarrow \text{NaH} + \text{Al} + \text{H}_2$ in a small size of nanoparticles. It should be attributed to the instability of Na_3AlH_6 nanoparticle with a small size. All these studies indicate that controlling nanostructure size provides a practical avenue to tailor thermodynamic and kinetic properties of (de)hydrogenation of complex metal hydrides.

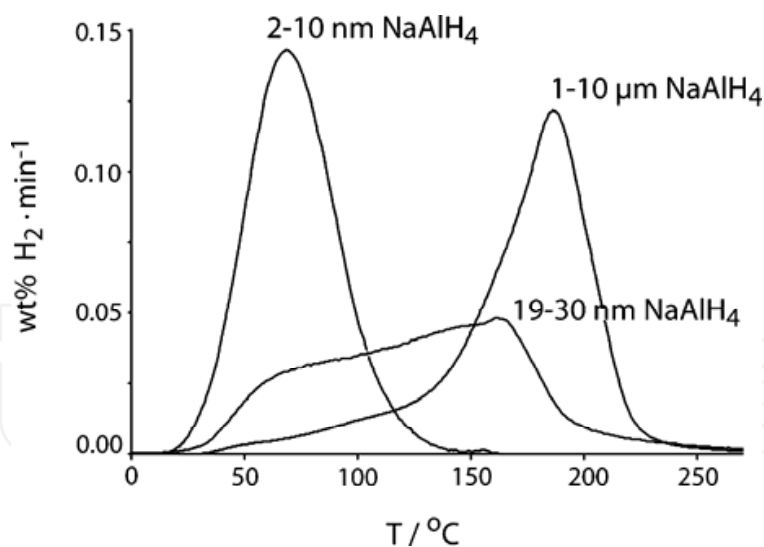


Figure 4. Temperature programmed desorption profile of H_2 for NaAlH_4 supported on carbon nanofiber. Reproduced from [99] by permission of American Chemical Society (copyright 2008).

Similarly, decreasing particle size by nanoscaffold technique has also been extended to LiBH_4 . Vajo and Wang filled LiBH_4 into carbon aerogel and AC carbon to form different nanoparticles [106-108]. They found hydrogen desorption temperature was reduced and kinetic rate was significantly enhanced. Unfortunately, nanosize effect of hydrogen desorption and adsorption of LiBH_4 is still not reported so far.

In sum, a small size of nanoparticle of complex metal hydrides can directly result in the change of thermodynamic and kinetic properties for hydrogen adsorption/desorption processes. However, there are two very important questions on nanosize effect of particles of complex metal hydrides. One is to determine the correlation of tuning thermodynamic and kinetic properties with particle size. The other is to establish the hydrogen desorption/adsorption mechanism of complex metal hydrides in a different nanosize.

Except for size effect, nanoengineering also involves the composition of complex metal hydride and nanostructures. Berseth et al. performed joint experimental and theoretical studies for hydrogen uptake and release of NaAlH_4 attached on carbon nanostructures such as C_{60} , graphene, and nanotubes [15]. Figure 5 displayed the correlation of hydrogen desorption energies of NaAlH_4 with electron affinities of carbon nanostructures. It suggests that the stability of NaAlH_4 originates with the charge transfer from Na to the AlH_4 moiety, resulting in an ionic bond between Na^+ and AlH_4^- and a covalent bond between Al and H. Interaction of NaAlH_4 with an electronegative substrate such as carbon fullerene or nanotube affects the ability of Na to donate its charge to AlH_4 , consequently weakening the Al–H bond and causing hydrogen to desorb at lower temperatures as well as facilitating the absorption of H_2 to reverse the dehydrogenation reaction.

Similarly, Wellons et al. showed that the addition of carbon nanostructure C_{60} to LiBH_4 has a remarkable catalytic effect, enhancing the uptake and release of hydrogen [109]. A fullerene- LiBH_4 composite demonstrates catalytic properties with not only lowered hydrogen desorption temperatures but also regenerative rehydrogenation at a relatively low temperature of 350°C . This catalytic effect is probably attributed to C_{60} interfering with the charge transfer from Li to the BH_4 moiety, resulting in a minimized ionic bond between Li^+ and BH_4^- , and a weakened B–H covalent bond. Interaction of LiBH_4 with an electronegative substrate such as carbon fullerene affects the ability of Li to donate its charge to BH_4 , consequently weakening the B–H bond and causing hydrogen to desorb at lower temperatures as well as facilitating the absorption of H_2 .

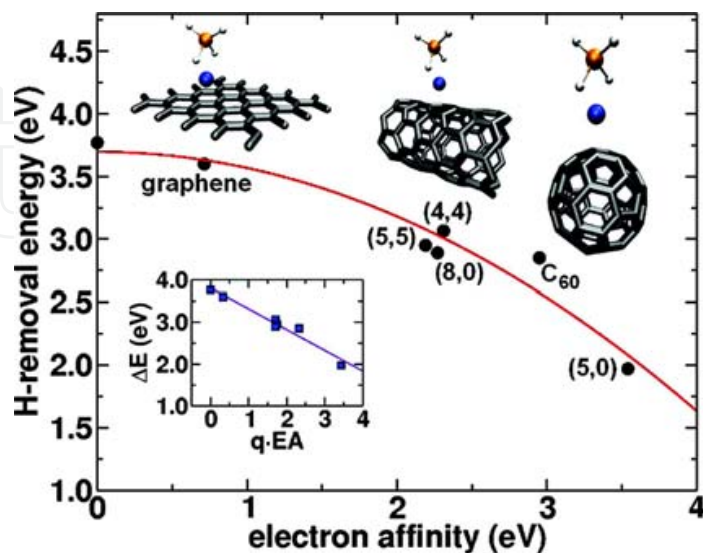


Figure 5. Correlation of the carbon substrate electron affinity and the hydrogen removal energy. Reprinted from [15] by permission of American Chemical Society (copyright 2009).

2.3. Cation substitution

In terms of complex metal hydrides, their stability really depends upon electronic affinity of metal atom. The lower the electronic affinity of metal is, the less stable hydride is. It can further be explained by transferred electron amount from metal atom to hydride. Løvvik, Jensen, Ormio, and Miwa et al. proposed that the metal element with a large electronic affinity can be used to substitute the original metal in order to destabilize reactants, making the enthalpy of the hydrogen release reaction favorable [110-117].

The two cations mixed in one hydride are expected to function synergistically to maintain reasonable stability, and at the same time provide a favorable decomposition enthalpy. Sorby et al. performed an experimental study about dual cation aluminium hydride, $K_2Na(AlH_4)_3$ [118]. Because K has a smaller electron affinity, $K_2Na(AlH_4)_3$ was measured to have a higher hydrogen desorption temperature up to 285°C, which is well consistent with theoretical predict.

Extensive DFT calculations showed that bialkali hexahydrides, such as K_2LiAlH_6 , K_2NaAlH_6 , KNa_2AlH_6 , and $LiNa_2AlH_6$, are stable compared to the pure alanates [110, 111]. In fact, $LiNa_2AlH_6$ has been synthesized experimentally [112, 113]. Mixed aluminohydrides such as $LiMg(AlH_4)_3$ and $LiMgAlH_6$ have also been predicted based on DFT studies and have been synthesized and characterized experimentally [119, 120]. Although their overall hydrogen storage performance was not fully examined, some of these compounds exhibit favorable decomposition temperatures.

Many theoretical and experimental studies on cation modification have been performed to improve thermodynamics and kinetics for borohydrides. Au et al. synthesized a series of bimetallic $M_1M_2(BH_4)_n$ ($M_1, M_2=Li, Mg, \text{ and } Ti$) and experimentally measured their hydrogen desorption temperature and hydrogen capacity [121]. They found that dehydrogenation temperature was reduced considerably and the dehydrogenated bimetallic borohydrides reabsorbed some of hydrogen released, but the full rehydrogenation is still very difficult. In 2010, Fang et al. studied formation of decomposition of dual-cation $LiCa(BH_4)_3$ using X-ray diffraction and thermogravimetry/differential scanning calorimetry/mass spectroscopy techniques [122]. It was found that $LiCa(BH_4)_3$ exhibits improved (de)hydrogenation properties relative to the component phases. In 2011, Jiang et al studied synthesis and hydrogen storage properties of Li-Ca-B-H hydride [123]. They found that the first dehydrogenation temperature is about 70°C, much lower than the pristine $LiBH_4$ and $Ca(BH_4)_2$. All these studies indicate that dual-cation borohydrides have a better thermodynamic property for hydrogen desorption than the single cation borohydride. Therefore, dehydrogenation temperature is significantly improved relative to the single phase.

In addition, some experimental studies on multivalent cation borohydrides such as Al, Sc, and Ti were carried out to reduce hydrogen desorption temperature [115, 117, 124-132]. However, theoretical studies on dehydrogenation mechanism including intermediates and products are desired for further improvement. However, extensive DFT computations have been performed to assess a large number of possible destabilized metal hydrides [133-137]. By assessing the enthalpies of all possible reactions, more than 300 destabilization reactions were predicted to have favorable reaction enthalpies [133]. Wolverton et al. proposed several guidelines to destabilize thermodynamically the metal hydrides in order to design

novel hydrogen storage materials [138]. Basically, the enthalpy of the proposed destabilized reaction must be less than the decomposition enthalpies of the individual reactant phases. In addition, if the proposed reaction involves a reactant that can absorb hydrogen, the formation enthalpy of the corresponding hydride cannot be greater in magnitude than the enthalpy of the destabilized reaction.

Vajo et al. examined this strategy by altering the thermodynamics and kinetics of (de)hydrogenation of several metal hydrides [139]. The equilibrium hydrogen pressure and reaction enthalpies can be changed with additives that form new alloys or compound phases upon dehydriding. The formation of new phases lowers the energy of dehydridated state and efficiently destabilizes the component hydrides. A series of experimental explorations have been performed to destabilize the reaction products of LiBH_4 and successfully reduce the dehydriding temperatures [139-141].

3. Conclusive remarks

Complex metal hydrides with a high hydrogen capacity have been considered as potential candidates for on-board hydrogen storage materials. However, the high hydrogen desorption temperature and sluggish kinetics prevent them from being applied in practice. It is attributed to unfavorable thermodynamic and kinetic properties of (de)hydrogenation. Over a past decade, a number of efforts have been devoted to improve hydrogen storage properties by altering thermodynamic and kinetic properties of (de)hydrogenation. Doping transition metal in complex metal hydrides can be regarded as a very effective means to tailor thermodynamics and promote kinetics. However, the catalytic mechanism of TM doped in hydrides remains unconfirmed because (de)hydrogenation includes complicated physical and chemical processes. TM may exhibit different structures and catalytic mechanisms in each step. Nanoengineering has extensively been applied to improve thermodynamic and kinetic properties of hydrogen storage materials by means of reducing particle size or mixing with nanostructures. However, some catalytic effect is restricted from some properties such as certain size, as well as chemical and physical properties of nanostructures. Cation substitution to form dual-cation hydride is generally used as a technique to alter thermodynamic property. Although this modification is effective to destabilize reactant, the modified crystal structure does not maintain during reversible processes of (de)hydrogenation.

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