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Effects of LnF$_3$ on reversible and cyclic hydrogen sorption behaviors in NaBH$_4$: Electronic nature of Ln versus crystallographic factors

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Effects of LnF$_3$ on reversible and cyclic hydrogen sorption behaviors in NaBH$_4$: Electronic nature of Ln versus crystallographic factors

1. Introduction

Hydrogen is regarded as one of the most promising clean energy resources for replacing fossil fuels. However, the storage of hydrogen is becoming the most crucial problem to the implementation of hydrogen energy. Apart from the classical techniques, such as high pressure storage and cryogenics storage, a well-investigated alternative approach is the chemical hydrogen storage in solid-state form. Complex hydrides, such as metal borohydrides, imides and alanates, are considered as promising solid-state hydrogen storage materials due to their high gravimetric and volumetric hydrogen density. To meet the requirements for proton exchange membrane fuel cells, the hydrogen storage systems must desorb hydrogen at temperatures below 300 °C, and be reversible under moderate conditions. These conditions restrict the flexibility of dehydrogenation enthalpies of the hydrogen storage systems in the range of 30 ~ 60 kJ mol$^{-1}$ H$_2$ estimated for the reversible H$_2$ storage materials. NaBH$_4$, for instance, has a high gravimetric capacity of 10.8 wt%, high volumetric hydrogen density of 113 kg m$^{-3}$ H$_2$, and low cost along with good stability to air exposure, fulfilling some of the basic requirements for onboard hydrogen storage set by the US Department of Energy (DOE). The full dehydrogenation of NaBH$_4$ takes place as:

\[ \text{NaBH}_4 \rightarrow \text{Na} + \text{B} + 2\text{H}_2 \]  

The decomposition enthalpy of NaBH$_4$ is 108 ± 3 kJ mol$^{-1}$ H$_2$, which means that the dehydrogenation of NaBH$_4$ only occurs at about 534 ± 10 °C at 1 bar H$_2$. It is too high to be used for practical applications. Moreover, the reversibility of NaBH$_4$ alone cannot be achieved. To overcome the drawbacks mentioned above, extensive efforts have been devoted to improve the hydrogen sorption thermodynamics, kinetics and reversibility of NaBH$_4$. Recently, Nakamori et al. proposed that the formation enthalpy of metal borohydride M(BH$_4$)$_n$ (M = metal, n depending on valence of the metal) displays an intrinsic correlation with the Pauling electronegativity ($\chi_p$) of the metal cation, showing that the dehydrogenation temperature of the M(BH$_4$)$_n$ decreases with increasing the $\chi_p$ of the metal cation. Such finding opens up a possible way to destabilize NaBH$_4$, that is, the partial substitution of Na$^-$ by other cations having higher $\chi_p$ may be effective for lowering down the hydrogen desorption temperature of NaBH$_4$.

Such a speculation has been realized in cation substitution in NaBH$_4$ through synthesizing double or multi-cation borohydrides, e.g. NaZn$_x$(BH$_4$)$_y$ and NaZn(BH$_4$)$_3$, and the decomposition temperatures of these multi-cation borohydrides are far lower than that of pure NaBH$_4$. Unfortunately, no reversibility can be obtained in those multi-cation borohydrides. Finding out the suitable electronegativity of the added metal cation is essential for exploring hydrogen carriers with appropriate stability and reversibility for practical applications. Another approach is nano-crystallization or nano-confinement.

Incorporating NaBH$_4$ into nanoporous scaffolds to produce nano-

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scale NaBH₄ particles can shorten the hydrogen diffusion lengths and increase the active surface areas, thereby, promotes hydrogen desorption kinetics. However, nano-confinement reduces the hydrogen storage capacity due to the low loading rate. Catalyst doping is an alternative way to tailor the hydrogen sorption properties of NaBH₄. Despite enhancement in hydrogen desorption performance was demonstrated in Ti-based catalysts doped NaBH₄, the recharging was performed under 5.5 MPa at 500 °C, which was still far from requirements for the on-board hydrogen storage. More recently, the concept “destabilization” was proposed and successfully exemplified in the 2LiBH₄-MgH₂ system. Indeed, the addition of MgH₂ as a destabilizing reactant changed the reaction pathway and thereby reduced the overall dehydrogenation enthalpy by 25 kJ mol⁻¹ H₂. More importantly, the reversibility was achieved under moderate conditions. It turns out that the decrease in dehydrogenation enthalpy and the facilitating in rehydrogenation reaction are attributed to the formation of MgB₂ in which the Mg-B bonds are relatively weaker than B-B bonds in boron. Similarly to the role of MgB₂, AlB₂ in recovering LiBH₄ has also been successfully demonstrated.

Searching for reactive agents which not only reduce thermodynamic stability but also maintain a high cycling life for NaBH₄ is a great challenge and an essential target. Motivated by this, in our previous work, we have synthesized several reversible hydrogen storage systems via combining NaBH₄ with destabilizing agents on the basis of lanthanide metals, such as La, Nd, Pr and Ho. These systems, though had reversible hydrogen sorption capacities less than 4 wt%, showed fast dehydrogenation rates at low temperatures and excellent rehydrogenation properties under moderate conditions that could not be achieved in pristine NaBH₄. The key feature of the thermodynamically preferred reactions is the formation of metal boride phase, which not only stabilizes the dehydrogenation products, but also allows the regeneration of borohydride taking place under mild conditions. Since lanthanide metals have remarkable self-binding abilities with born, additional with the very similar chemical properties of their trivalent cations due to their similar outer and inner electron configurations, the dehydrogenation of NaBH₄ could be modified by combining it with other lanthanide trifluorides so as to form lanthanide boride compounds upon dehydrogenation and the reversible hydrogen storage systems may be achieved. Moreover, it has been demonstrated recently that lanthanide based additives are effective in decreasing the dehydrogenation temperature of LiBH₄.

Encouraged by the above, 4 new reversible hydrogen storage systems: 3NaBH₄-CeF₃, 3NaBH₄-SmF₃, 3NaBH₄-GdF₃ and 3NaBH₄-YbF₃ were prepared through ball milling in the present work. The aim is to find out the factors governing the thermodynamic and kinetic properties of the 3NaBH₄-LnF₃ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er and Yb) systems. Systematical investigations are carried out via considering the electron configurations and electronegativities of Ln³⁺ cations as well as the crystal structures of Ln-B phases on the hydrogen sorption behaviors of NaBH₄. This study will be a potential indicator for exploring borohydride-based hydrogen storage systems with low operating temperatures, fast de-/rehydrogenation kinetics and good cyclic stability for practical applications.

### 2. Experimental

Commercial NaBH₄ (98%) powders were purchased from Strem Chemicals Inc. All CeF₃ (99.9%), SmF₃ (99.99%), and GdF₃ (99.99%) were obtained from Alfa Aesar. YbF₃ (99.99%) was obtained from Aladdin Chemistry Co. Ltd. All of these materials were used as received states without further purification. The sample storage and handling were manipulated in a Lab 2000 glove box (Etelux Intergas system Co., Ltd.) filled with purified argon and equipped with recirculation system to keep both water and oxygen concentrations below 1 ppm. Samples of 3NaBH₄-CeF₃, 3NaBH₄-SmF₃, 3NaBH₄-GdF₃ and 3NaBH₄-YbF₃ (mole ratio) were prepared by mechanical ball milling under Ar atmosphere for 16 h using a QM-ISP2 planetary ball mill at 456 rpm in a stainless steel vessel. The stainless steel vessel for ball milling was 100 ml, and the weight ratio of the sample to the ball was 1:30.

The hydriding/dehydriding properties were measured in a Sievert type pressure-composition-temperature (PCT) apparatus manufactured by Shanghai Institute of Microsystem and Information Technology. Temperature-programmed-dehydrogenation (TPD) curves were determined by volumetric methods, starting from vacuum with the temperature increased from ambient to about ~ 463 °C at a constant heating rate of 3 °C min⁻¹. The PCT measurements were performed at different temperatures in the hydrogen pressure range of 0.0019 – 4.6 MPa after the sample being completely dehydrogenated. For the hydrogen absorption cycling tests, the sample was directly pressurized with hydrogen at the desired temperature after completely dehydrogenated. Isothermal dehydrogenation cycling tests were performed at 400 °C for 2 h in static vacuum. Approximately ~ 3.0 g of sample was used for PCT measurements, 150 mg for isothermal de-/rehydrogenation kinetic and cycling measurements, and 100 mg for TPD measurements. For an evaluation of the practical hydrogen storage property, the hydrogen-storage capacity of each sample was calculated based on their original total weight including NaBH₄ and LnₓF₃ (Ln = Ce, Sm, Gd, Yb).

Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were carried out using synchronous thermal analyzer (TG/DSC, Netzsch, STA 449 F3 Jupiter). The heating rate was set at 3, 5 and 10 K min⁻¹, respectively, under 1 bar flowing argon atmosphere with the temperature rising from 26 to 500 °C. About 10 mg of sample was used each time.

Phase components of samples in ball milled, dehydrogenated and rehydrogenated states were identified by X-ray diffraction (XRD Rigaku D/MAX-2500, VL/PCX, Cu Kα radiation) from 10° to 90° (20) with a step width of 0.02°. To avoid the oxidation during the XRD measurements, sample powders were flattened into a container and covered by a scotch in the Ar filled glove box. Chemical bonding analyses were examined by Fourier transform infrared spectroscopy (FT-IR, Nicolet iS5, Thermo Fisher Scientific Inc. U.S.A.) equipped with a horizontal ATR accessory (Germanium crystal) in an argon-filled glovebox.

### 3. Results and discussions

#### 3.1 Hydrogen release and uptake behaviors

The effects of CeF₃, SmF₃, GdF₃ and YbF₃ on the 1st hydrogen...
desorption behaviors of NaBH₄ in the temperature range 30 ~ 463 °C are evaluated by using TPD (Fig. S1(a)). Evidently, the onset dehydrogenation temperatures of NaBH₄ in CeF₃, SmF₃, GdF₃ and YbF₃ containing composites are measured to be around 150, 212, 112 and 156 °C, and the maximum dehydrogenation rates are obtained at 412, 422, 409 and 440 °C, respectively. To complete the dehydrogenation at 463 °C, about 0.3 h is needed for 3NaBH₄-CeF₃, 3NaBH₄-SmF₃ and 3NaBH₄-YbF₃ composites, while only 0.1 h is required for 3NaBH₄-GdF₃ composite. Finally, 3.49, 3.47, 3.50 and 3.23 wt% of H₂ are released from 3NaBH₄-CeF₃, 3NaBH₄-SmF₃, 3NaBH₄-GdF₃ and 3NaBH₄-YbF₃ composites, respectively, fairly close to their corresponding theoretical values (3.54, 3.58, 3.51 and 3.31 wt%, respectively).

Furthermore, the apparent activation energies (E_a) of the four composites are determined using the Kissinger’s approach, as described below:

\[ \frac{d(\ln \beta)}{d(1/T_m)} = \frac{E_a}{R} \]  

where \( \beta, T_m \) and \( R \) are the heating rate, the absolute temperature for the maximum desorption rate and the gas constant, respectively. In the present work, \( T_m \) is obtained from the non-isothermal dehydrogenation curves conducted by TG/DSC measurements at various heating rates (Fig. 1, data shown in Table S1). The dependence of \( \ln(\beta/T_m^n) \) on \( 1/T_m \) is plotted (Fig. S2(a)), displaying the good linear relationships for all the four composites, and the \( E_a \) value of each composite is calculated (data given in Table S2). In addition, TG curves evidence the close amount of the released hydrogen to their corresponding values determined by TPD (Table S1).

Subsequently, the onset dehydrogenation temperatures - \( T_{on} \), peak temperatures - \( T_p \) and \( E_a \) of 3NaBH₄-LnF₃ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er and Yb) composites as a function of trivalent Ln, are plotted to systematically clarify the effects of the LnF₃ on hydrogen release behaviors in NaBH₄ (Fig. 2, data collected in Table S2). \( T_{on}, T_p \) and \( E_a \) of 3NaBH₄-PrF₃ composite, and \( E_a \) of 3NaBH₄-NdF₃ composite are obtained according to Fig. S1(b) and S2(b, c), respectively. Interestingly, it is found that the \( T_{on}, T_p \) and \( E_a \) of 3NaBH₄-LaF₃ and 3NaBH₄-LnF₃ composites show a gradual decrease from La³⁺ to Nd³⁺, Sm³⁺ to Gd³⁺, and Ho³⁺ to Er³⁺, respectively. Such a phenomenon can be understood considering the so called “Lanthanide Tetrad Effect”, which is originated from the disturbance of coherent periodic filling of the f sub-shell of the electron configuration of trivalent lanthanides in four groups: La³⁺ – Nd³⁺, Sm³⁺ – Gd³⁺, Tb³⁺ – Er³⁺ and Yb³⁺ – Lu³⁺.

Therefore, the effect of LnF₃ on the dehydrogenation performance of NaBH₄ is actually related to the f shell electron configuration of the Ln³⁺ cation.

By integrating the peak areas in DSC profiles, the dehydrogenation enthalpies of 3NaBH₄-LaF₃, 3NaBH₄-CeF₃, 3NaBH₄-SmF₃ and 3NaBH₄-YbF₃ and 3NaBH₄-GdF₃ composites are verified to be 46.3, 47.6, 63.1 and 43.8 kJ mol⁻¹ H₂, respectively, which show reductions of 41.6 ~ 59.4% compared to that of NaBH₄ alone (108 ± 3 kJ mol⁻¹ of H₂) verifying the considerable decrease in dehydrogenation enthalpy of NaBH₄ through the LnF₃ addition.

Moreover, these results fall in the range of 30 ~ 60 kJ mol⁻¹ H₂ estimated for the reversible storage materials, implying the reversibilities of the four composites which are corroborated by the PC isotherms measurements (Fig. 3). Obviously, in the case of 3NaBH₄-LaF₃, 3NaBH₄-SmF₃, 3NaBH₄-GdF₃ and 3NaBH₄-YbF₃ composites (Fig. 3- up), reversible capacities of 1.52, 1.90 and 1.45 wt% are obtained with sloping absorption/desorption plateaus under 4.5 MPa, respectively. Remarkably, the 3NaBH₄-GdF₃ composite exhibits the highest reversible hydrogen-storage capacity with stable and flat absorption/desorption plateaus (Fig. 3-down), indicating that the 3NaBH₄-GdF₃ composite has the best hydrogen storage kinetics and reversibility among the four composites. Table 1 summarizes the data corresponding to Fig. 3-down. In contrast, regeneration of NaBH₄ from its decomposition products (NaH + B) under 350 bar hydrogen pressure at 400 °C for 24 h was unsuccessful.

3.2 Relationship of de-/rehydrogenation mechanisms and the crystal structures of Ln-B phases

For investigation of the hydrogen sorption mechanisms, the phases in the four composites after ball milling, dehydrogenation and rehydrogenation are characterized by XRD, in tandem with FTIR. For the ball-milled 3NaBH₄-GdF₃ composite, XRD pattern (Fig. 4, line A) proves that no new phases formed after ball

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Fig. 1 DSC curves (heating rate 3, 5 and 10 K min⁻¹) and TG curves (heating rate 3 K min⁻¹) of the 3NaBH₄-CeF₃, 3NaBH₄-SmF₃, 3NaBH₄-GdF₃ and 3NaBH₄-YbF₃ composites under 1 bar argon atmosphere.

Fig. 2 Relations between the onset dehydrogenation temperature- \( T_{on} \) (black square), peak temperature- \( T_p \) (red rhombus), \( E_a \) (blue circle) of 3NaBH₄-LnF₃ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er and Yb) composites and trivalent Ln, respectively.
Fig. 3 PCT curves of the 3NaBH₄-CeF₃, 3NaBH₄-SmF₃; and 3NaBH₄-YbF₃ composites measured at 410 °C, as well as 3NaBH₄-GdF₃ composite measured at 350, 375, 395 and 405 °C.

Table 1 PCT data of 3NaBH₄-GdF₃ composite at different temperatures. Data for pure NaBH₄ are given as a reference.

<table>
<thead>
<tr>
<th>sample</th>
<th>T / °C</th>
<th>Rehyd. P / MPa</th>
<th>Dehyd. P / MPa</th>
<th>Reversible H₂ capacity / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure NaBH₄</td>
<td>684</td>
<td>35 (400 °C)²</td>
<td>0.96</td>
<td>irreversible</td>
</tr>
<tr>
<td>3NaBH₄-GdF₃</td>
<td>350</td>
<td>1.56</td>
<td>0.11</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>375</td>
<td>1.17</td>
<td>0.33</td>
<td>3.38</td>
</tr>
<tr>
<td></td>
<td>395</td>
<td>1.26</td>
<td>0.47</td>
<td>3.36</td>
</tr>
<tr>
<td></td>
<td>405</td>
<td>1.33</td>
<td>0.55</td>
<td>3.11</td>
</tr>
</tbody>
</table>

milling except for NaBH₄ and GdF₃. In contrast, the formations of bimetallic borohydride chlorides or lanthanide borohydrides were observed in the ball milled LiBH₄-LnCl₃ and NaBH₄-LnCl₃ systems.²⁰, ²¹, ²⁴ The characteristic peaks of B-H bonds of NaBH₄ are further revealed in the FTIR spectra (Fig. S3(a)). However, after complete dehydrogenation (Fig. 4, line B), new compounds, NaF, GdB₄ and GdH₂, instead of the original ones appear, indicating that the observed hydrogen desorption corresponds to the dehydrogenation reaction between NaBH₄ and GdF₃. FTIR result further confirms the complete decomposition of NaBH₄ by showing the disappearance of the B-H bonds of NaBH₄ after dehydrogenation (Fig. S3(b)). Based on XRD and FTIR results, the main dehydrogenation reaction pathway of the 3NaBH₄-GdF₃ composite can be therefore described as follows:

\[
12\text{NaBH}_4 + 4\text{GdF}_3 = 12\text{NaF} + 3\text{GdB}_4 + \text{GdH}_2 + 23\text{H}_2(g)
\]  (3).

XRD, FTIR results combined with calculation by using HSC Chemistry program (Fig. S5)²⁵ evidence the similar dehydrogenation pathways in the 3NaBH₄-LnF₃ (Ln = Ce, Sm and Yb) composites (Fig. S4): during dehydrogenation processes, NaBH₄ reacts with LnF₃ to yield NaF, Ln-B and Ln-H phases. The formations of Ln-B and Ln-H (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er or Yb) were also demonstrated in the dehydrogenated LiBH₄-LnCl₃²⁰,²¹ and NaBH₄-LnCl₃ systems.²⁰,²¹,²⁷

After hydrogen absorption (Fig. 4, line C), the characteristic peaks assigned to NaBH₄ are clearly observed. To clarify this, FTIR investigation was carried out and further confirmed the regeneration of NaBH₄ (Fig. S3(c)). Moreover, the diffraction peaks from NaF, GdB₄ and GdH₂ phases disappear along with the appearance of GdF₃. These results imply that NaF, GdB₄ and GdH₂ take part in the rehydrogenation reaction to yield NaBH₄ and GdF₃ during H₂ uptake process. In addition, NaGdF₄ is also detected in the case of 3NaBH₄-GdF₃ composite. According to XRD and FTIR analyses, the rehydrogenation pathway in 3NaBH₄-GdF₃ composite can be proposed as follows:

\[
12\text{NaF} + 3\text{GdB}_4 + \text{GdH}_2 + 23\text{H}_2(g) = 12\text{NaBH}_4 + 4\text{GdF}_3
\]  (4),

together with a side reaction:

\[
\text{NaF} + \text{GdF}_3 = \text{NaGdF}_4
\]  (5);

A similar rehydrogenation mechanism was reported in the study of 3NaBH₄-NdF₃ system.¹⁵ The analogous H₂ uptake pathways also exist in 3NaBH₄-LnF₃ (Ln = Ce, Sm and Yb) composites, as illustrated in Fig. S3 and S4. More detailed discussions about the de-/-rehydrogenation reactions in 3NaBH₄-LnF₃ (Ln = Ce, Sm and Yb) composites are displayed in the supplementary information.

It is worth noting here that a better hydrogen storage performance, especially the reversibility, is found in NaBH₄-LnF₃ systems than that in corresponding NaBH₄-LnCl₃ ones.²⁴ Such a phenomenon is mainly attributed to the substitution of F⁻ for H² in NaBH₄-LnF₃ systems, which leads to a favorable modification of hydrogen sorption thermodynamics in these systems.²⁶

Besides the lower energy needed to break the bond of Ln-B contributing to the thermodynamic regeneration of NaBH₄, it is interesting to note that the crystal structure of Ln-B phase should be also of great importance facilitating the recombination of NaBH₄ with Ln-B₆ molecular blocks. Ln-B₆ exhibits cubic structure with a space group of Pm₃m (221), while SmB₆, GdB₆ and NdB₆ exhibit cubic structure with the special crystal structure of LaB₆, which presents a tetragonal P4/mmb (127) structure as illustrated in Fig. S6(a)(I) and (II). B appears in the form of B₆ octahedron configuration in either LnB₆ or LnB₄ phases, which offers dangling bond for hydrogen atoms to embed in. Taking LaB₆ for example, it is reported that LaB₆ displays potential in promoting the hydrogen equilibrium due to the catalytic effect from La for hydrogen sorption²⁷ and the special crystal structure of LaB₆. The thermodynamically stable (001) plane of LaB₆ presumably contains lattice imperfections, such as vacancies, which are responsible for the catalytic behaviors.²⁷ The unsaturated dangling bonds in the vacancies might be used for trapping hydrogen atoms, which occurs on the boron atoms at each corner as well as the upper layer of the vacancy. Furthermore, the top layer of the LaB₆ (111) surface is composed of the triangular faces of B₆ octahedron, and in forming the

Fig. 4 XRD patterns of the (A) as-prepared; (B) dehydrogenated; (C) rehydrogenated 3NaBH₄-GdF₃ composite.
surface, the inter-octahedral bonds are broken, resulting in three dangling bonds being 55° from normal along three azimuths 120° apart (seen in Fig. S6(b)), whereas on the (100) surface leading to a single boron dangling bond oriented along the surface normal through the middle of a square of four lanthanum atoms. This allows the hydrogen atoms easily access to those active sites on LaB₆. Moreover, as shown in Fig. S6(a)(I) and (II), the LnB₆ (Ln = La, Ce, Pr and Nd) and LnB₄ (Ln = Sm, Gd, Ho, Er and Yb) exhibit the same structure on either (100) or (010) surfaces. Due to the same B₆ octahedron configuration and the analogous chemical properties of lanthanide series, it is believed that LnB₆ and LnB₄ exist similar promoting effect on the rehydrogenation kinetics of NaBH₄. In comparison to the configuration of B atoms in LnB₆ (x = 4 or 6), the crystal structure of NaBH₄ is shown in Fig. S6(a)(III), in which B in the [BH₄]⁻ ligand possesses also the octahedral arrangement. Therefore, the configuration of B in either LnB₆ or LnB₄ phase may offer a possible entrance to facilitate the recombination of [BH₄]⁻ and thereby enhances the hydrogen absorption kinetics. The crystal structures of those well-known metal borides, such as TiB₂, MgB₂, AlB₂ and CaB₆, having promotion effects on the regeneration of borohydrides are also displayed here for comparison. TiB₂, MgB₂ and AlB₂ typically crystallize in the AlB₆-type structure (hexagonal, p6/mmm) (Fig. S6(c)(I)), where the coplanar graphite-like B layers are present alternatively with the close-packed metal sheets. It was suggested that MgB₂ promoted the formation of [BH₄]⁻ ligand and thus enabled the regeneration of NaBH₄. We have studied the reversibility of 2NaBH₄-MgF₂ system. It was found that after complete dehydrogenation at 576 °C, MgB₂ was detected by XRD. However, only 0.6 wt% hydrogen was absorbed during the PCT measurement at 430 °C. In the case of CaB₆ (Fig. S6(c)(II)), though it is also cubic type with B in the form of B₆-octahedrons located at the corners of the cube, Ca atoms are inserted into a network of boron cages and the covalent bonding between B atoms is very strong, thus the spin splitting of the defect level of the B-antisite is too small to offer enough sites for H. Table S3 presents the conditions needed for TiB₂, MgB₂, AlB₂, CaB₆ and Ln-B to regenerate borohydrides. As can be seen, the fastest hydrogen absorption kinetics for the regeneration of NaBH₄ composites were displayed here for comparison. TiB₂, MgB₂ and AlB₂ typically crystallize in the AlB₆-type structure (hexagonal, p6/mmm) (Fig. S6(c)(I)), where the coplanar graphite-like B layers are present alternatively with the close-packed metal sheets. It was suggested that MgB₂ promoted the formation of [BH₄]⁻ ligand and thus enabled the regeneration of NaBH₄. We have studied the reversibility of 2NaBH₄-MgF₂ system. It was found that after complete dehydrogenation at 576 °C, MgB₂ was detected by XRD. However, only 0.6 wt% hydrogen was absorbed during the PCT measurement at 430 °C. In the case of CaB₆ (Fig. S6(c)(II)), though it is also cubic type with B in the form of B₆-octahedrons located at the corners of the cube, Ca atoms are inserted into a network of boron cages and the covalent bonding between B atoms is very strong, thus the spin splitting of the defect level of the B-antisite is too small to offer enough sites for H. Table S3 presents the conditions needed for TiB₂, MgB₂, AlB₂, CaB₆ and Ln-B to regenerate borohydrides. As can be seen, the fastest hydrogen absorption kinetics for the regeneration of borohydrides without any catalyst addition is achieved in systems containing Ln-B phases. These results imply the remarkable contribution of the crystal structure of Ln-B phase to the rehydrogenation kinetics of NaBH₄.

3.3 Relationship between the enthalpy change (ΔH) and the electronegativity (χₚ) of lanthanide trivalent cation

Electronegativity (χₚ) of Ln³⁺ has been considered for further elucidating the significant enhancement of LnF₃ in destabilization and regeneration of NaBH₄, since χₚ of the added metal cation may influence the stability of borohydride. In Fig. 5, the de-/rehydrogenation enthalpies (ΔH_d/ΔH_r) of 3NaBH₄-LnF₃ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er and Yb) composites, as a function of χₚ of Ln³⁺ cation, are plotted (data given in Table S4). The ΔH_d of the 3NaBH₄-GdF₃, 3NaBH₄-ErF₃, and 3NaBH₄-YbF₃ composites were calculated according to Fig. S7, while the ΔH_r of 3NaBH₄-CeF₃, 3NaBH₄-SmF₃ and 3NaBH₄-YbF₃ cannot be obtained by PCT measurements due to the unachievable rehydrogenation equilibrium.

![Fig. 5](image-url) Relationships between the dehydrogenation (up)/rehydrogenation (down) enthalpies (ΔH_d/ΔH_r) and the electronegativities (χₚ) of Ln³⁺ cations.

Fig. 5-up displays a W-type relationship between ΔH_d of 3NaBH₄-LnF₃ and χₚ of Ln³⁺, which is somewhat analogous to the relationship between Ln³⁺ and their electron configurations existing in a W-type tetrad effect. It is worth noting that a V-type relationship between the ΔH_r of 3NaBH₄-LnF₃ and χₚ of Ln³⁺ is found which results from the changes of Ln oxidation states in the dehydrogenated products, and can be described using two lines with the intersection point at Nd³⁺(Fig. 5-down). The first group of elements (I) includes La³⁺, Pr³⁺ and Nd³⁺, and the second one (II) includes Sm³⁺, Gd³⁺, Ho³⁺ and Er³⁺. The linear relations can be written as the following expressions: ΔH_r = 314.04 χₚ – 448.45 (14), for the first group (I); ΔH_r = -295.13 χₚ + 394.15 (15), for the second group (II), in the unit of kJ mol⁻¹ H₂.

This expectation and thus that NaBH₄ based composites with the added metal cations containing χₚ approximately lying in the range 1.23 ~ 1.54 are thermodynamically preferred. In addition, it implies that the added cation plays a crucial role in improving the rehydrogenation property of NaBH₄. This result is not only valuable for Ln cations, but also for other metal cations. For instance, in the studies of LiBH₄-MgH₂/Al/TiF₃/YH₃, NaH-MgB₂, and NaH-TiF₃/YF₃/NiCl₂ systems, the regeneration of LiBH₄/NaBH₄ has been successfully achieved, since the χₚ values of Mg³⁺, Al³⁺, Y³⁺, Ti³⁺ and Ni²⁺ are all lying in 1.23 ~ 1.54. It should be pointed out that the stability of Ln oxidation state is another factor affecting the rehydrogenation performance of NaBH₄. For example, La³⁺, Gd³⁺ and Lu³⁺ have stable electron configurations: La³⁺ (f⁵), Gd³⁺ (f⁷) and Lu³⁺ (f⁷). The nearby Ln³⁺ around these three ions are inclined to change their states according to the environments. Clearly, the better H₂-absorption performances are obtained in La³⁺ and Gd³⁺ added composites compared to other NaBH₄ based composites with Ln having anomalous oxidation states (e.g. Ce³⁺). Therefore, the cation electronegativity as well as its stability can be considered as guiding factors for reasonably design and synthesize of a novel complex hydride-based hydrogen storage system with good reversibility, superior kinetic and thermodynamic properties. The W-type and V-type relationships between de-/rehydrogenation enthalpies and Ln³⁺ are also found (Fig. S8), in consistent with...
the result obtained from Fig. 5, since $\chi_{\text{f}}$ value of Ln cation is the reflection of its 4f electron properties.

3.4 Re-/dehydrogenation cycling behaviors of the 3NaBH$_4$-GdF$_3$ composite

The cycling property of 3NaBH$_4$-GdF$_3$ composite is investigated, since it possesses the best overall rehydrogenation performance among all the studied 3NaBH$_4$-LnF$_3$ composites of which hydrogen storage properties are represented in Table S5 for comparison. Fig. 6 shows the rehydrogenation curves of 3NaBH$_4$-GdF$_3$ composite at 400 °C under 4 MPa hydrogen pressure over 4 cycles. As can be seen, the $H_2$-absorption curves are essentially unchanged, demonstrating the excellent cyclic stability of the 3NaBH$_4$-GdF$_3$ composite. Also, the rehydrogenation kinetics is much more pronounced. Only 4 min is required to reach about 2.40 wt% storage capacity (7.38 wt% in NaBH$_4$) under 3 MPa $H_2$ pressure. However, capacity degradation increases uniformly with pressure at a constant temperature (Fig. S9(b)). Under 4 MPa in the 29th cycle, the rehydrogenation rate under 1 MPa (26% in 3 h) can be still attained within 3 h. While, the rehydrogenation rate under 1 MPa for the same rehydrogenation time of 2 h, 35% can be still attained within 3 h. This implies that the 3NaBH$_4$-GdF$_3$ composite is a promising reversible hydrogen storage system over other previously known borohydride-based systems. Table 2 summaries the cycling properties of some borohydride-based hydrogen storage systems for comparison.

Table 2 Cyclic performances of some borohydride-based hydrogen storage systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Rehy. Temperature / °C</th>
<th>Rehy. Pressure / MPa</th>
<th>Rehy. Time / h</th>
<th>Cycle number</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBH$_4$-MgH$_2$</td>
<td>425</td>
<td>14</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>LiBH$_4$-TiF$_3$</td>
<td>350</td>
<td>10</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>2LiBH$_4$-MgH$_2$</td>
<td>430</td>
<td>8</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>0.1NiCl$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LiF-MgB$_2$</td>
<td>390</td>
<td>6</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>LiBH$_4$-CaF$_2$</td>
<td>~ 500</td>
<td>6</td>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>LiBH$_4$-C</td>
<td>400</td>
<td>10</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>NaBH$_4$/C</td>
<td>325</td>
<td>6</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>2NaH + MgB$_2$</td>
<td>400</td>
<td>35</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>NaBH$_4$-GdF$_3$</td>
<td>180 ~ 400</td>
<td>1 ~ 4</td>
<td>1.6 ~ 10</td>
<td>51</td>
</tr>
</tbody>
</table>

The dependence of rehydrogenation kinetics on pressure and temperature was further analyzed by increasing number of cycles. Clearly, the rehydrogenation rate under 1 MPa (26% in 3 h), 2 MPa (27th, 31st, 51st), 3 MPa (28th, 30th) and 4 MPa (29th) initial pressure increases uniformly with pressure at a constant temperature (Fig. S9(b)). Under 4 MPa in the 29th cycle, the capacity of 3.44 wt% $H_2$ can be still attained within 3 h. While, with increasing the temperature under a constant pressure, the rehydrogenation rate exhibits a gradual increase in the low pressure region and an abrupt increase in the high temperature region (Fig. S9(c)). Rehydrogenation curves under synchronous low-pressure-temperature conditions: 182 °C + 1 MPa, 244 °C + 2 MPa and 400 °C + 4 MPa are also plotted (Fig. S9(d)). It is worth noting that capacities of ~ 0.65 and 1.40 wt% are reached...
under 1 MPa at 182 °C (44th), 2 MPa at 244 °C (42nd), respectively, further demonstrating the remarkable reversible sorption performance of 3NaBH$_4$-GdF$_3$ composite, which are not achieved in other light metal borohydride-based binary hydrogen storage composites.

4. Conclusions

In this work, we have systematically investigated the effects of LnF$_3$ (Ln = La, Ce, Pr, Nd, Sm, Gd, Ho, Er and Yb) on the hydrogen sorption behaviors in NaBH$_4$ by introducing 4 new Ln fluorides - CeF$_3$, SmF$_3$, GdF$_3$ and YbF$_3$ - into NaBH$_4$. The mechanisms associated with thermodynamic and kinetic modifications in NaBH$_4$ with respect to the LnF$_3$ addition were correlated with the electronic nature of Ln trivalent cations (i.e. electronegativity, electron configurations) and the crystal structures of Ln-B phases. The results reveal that all the studied LnF$_3$ additives enable the reversible hydrogen sorption in NaBH$_4$ but in different extent. The hydrogen de-/absorption behaviors of the 3NaBH$_4$-LnF$_3$ composites are related to the electron configurations of Ln$^{3+}$ cations. The relationship between rehydrogenation enthalpies of 3NaBH$_4$-LnF$_3$ and the electronegativities of the added Ln$^{3+}$ shows 2 linear correlations with an intersection point at Nd$^{3+}$. Our results reveal that the 3NaBH$_4$-LnF$_3$ composite with electronegativity of Ln cation lying in the range 1.23 ~ 1.54 is thermodynamically favorable for reversible hydrogen storage. In addition, the unique crystal structure of Ln-B and the geometrical configurations of B in Ln-B crystals facilitate the kinetic recombination of NaBH$_4$. Hydrogen de-/absorption results reveal the best overall promoting effects of GdF$_3$ on the hydrogen sorption properties of NaBH$_4$ among all the studied LnF$_3$. In particular, the 3NaBH$_4$-GdF$_3$ composite possesses high cyclic stability over 51 cycles with fast kinetics, and can be rehydrogenated even under 1 MPa H$_2$ at 182 °C after 44 cycles.

Acknowledgements

Prof. Zou would like to thank the support from the Science and Technology Committee of Shanghai under No. 14JC1491600 and Pujiang’ project (No. 11PJ1406000). This work is partly supported by Research Fund for the Doctoral Program of Higher Education of China (No. 20100073120007) and from the Shanghai Education Commission (No. 12ZZ017).

References