

A fleeting glimpse of dual roles of SiB₄ on promoting hydrogen storage performance of LiBH₄

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Abstract

In this work, the positive effect and dual roles of SiB_4 on the dehydrogenation and rehydrogenation performance of LiBH_4 - SiB_4 system were reported. The experiments were carried out through temperature programmed desorption mass spectrometry (TPD-MS), isothermal kinetics measurement, XRD and FTIR. For the hydrogen desorption from LiBH_4 , SiB_4 played a role of a catalyst to kinetically facilitate the structural destabilization of LiBH_4 and its intermediate phase $\text{Li}_2\text{B}_{12}\text{H}_{12}$, and accordingly a dehydrogenation capacity of 2.24 at. H/f.u. LiBH_4 (close to 10.3 wt.% H) was acquired at a relative temperature of 350 °C. For the hydrogen absorption to generate LiBH_4 , SiB_4 was unexpectedly found to act as a reactant to thermodynamically improve the rehydrogenation process by reacting with LiH under moderate conditions of 10 MPa H_2 and 400 °C, and a superior reversible capacity of 2.16 at. H/f.u. LiBH_4 was achieved. These experimental results remind folks to take into account the explicit role(s) of an employed component during the dehydrogenation and rehydrogenation reactions when designing a desirable LiBH_4 -based system.

Keywords: hydrogen; energy storage; complex; catalyst; hydrogenation

1. Introduction

Solid-state hydrogen storage technology has switched on an exceptional way for on-demand large-scale hydrogen application, such as hydrogen energy vehicle, portable equipment[1]. Along with this line, physical manner using MOFs, COFs, carbon, etc., and chemical means employing light-weight materials of Mg-based alloys, chemical hydrides, complex hydrides, etc. are developed to efficiently stored massive hydrogen[2-4]. Unfortunately, the performance of these chemicals and their derivatives are still far from the technical requirements for onboard hydrogen storage system[5, 6]. On the other side, a finite understanding of the fundamental principle lying behind the interaction between materials and hydrogen postpones the accessibility of desirable hydrogen storage materials (HSMs). Hence, folks have paid great efforts to push forward the scientific know-why in order to accelerate the practice progress of HSMs, especially the complex hydrides having extremely high capacity over 10 wt.%[7].

As a typical example called lithium borohydride (LiBH_4), this promising candidate is employed to create novel HSMs with favorable dehydrogenation and/or rehydrogenation performance guided by the fundamental mechanisms as the following.

(i) Synthesizing derivatives via chemically combining counterparts. These LiBH_4 -based derivatives feature high hydrogen capacity and low dehydrogenation temperature with rapid kinetics. Whereas, irreversibility resulting from a difficulty of reconstructing those compounds is necessitated to be overcome primarily hereafter. Enlightening by a theoretical prediction that higher electronegativities x_p of metal cations (M^{n+}) substituting Li^+ cation could result in lower dehydrogenation temperatures[8, 9], various novel substituted compounds with a general formula of $\text{LiM}_x(\text{BH}_4)_y$ came into sight and their flexible structural properties and modifiable dehydrogenation performances were reported[10-14]. For instance, $\text{LiZn}_2(\text{BH}_4)_5$ and $\text{LiAl}(\text{BH}_4)_4$ quickly decomposed at 127 °C and 67 °C, respectively[10, 15]. Anion substitution of H^- by F^- or of $[\text{BH}_4]^-$ by Cl^- was also predicted to have a capability towards adjustable thermodynamic performance[16, 17]. Stemming from a thought that hydridic H^- interacting with protonic H^+ would advance the hydrogen storage performance, ammoniated LiBH_4 ($\text{LiBH}_4 \cdot n\text{NH}_3$), hydrazine assisted LiBH_4 ($\text{LiBH}_4 \cdot n\text{NH}_2\text{NH}_2$) and ammonia borane assisted LiBH_4 ($\text{LiBH}_4 \cdot n\text{NH}_3\text{BH}_3$) were then experimentally demonstrated to be striking HSMs[18-20]. Taking $\text{LiBH}_4 \cdot n\text{NH}_3$ as an example,

when $n=1$, $4/3$ and 2 , 15.3 wt.%, 17.8 wt.% and 14.3 wt.% hydrogen was released from the corresponding derivative at 250 °C, respectively[21].

(ii) Establishing destabilization systems through physically mixing with other components. These systems have the main virtues of remarkable reversibility and fast dehydrogenation rate. However, a big obstacle in these systems right now is the high dehydrogenation temperature necessitating further improvement. Pioneering by a strategy called reactive hydride composites (RHCs) having alternative dehydrogenation pathways[22], intensive attention was poured into selecting suitable binary or ternary compounds and employing them to form new LiBH_4 -based destabilization systems. Experimental trials on materials like metal hydrides (e.g. MgH_2 , CaH_2 , YH_3 , LaH_2 , etc.)[23-25], metal halides (e.g. NdF_3 , SrF_2 , TiF_3 , LaCl_3 , CeCl_3 , etc.)[26-29], metal chalcogenides (e.g. Fe_3O_4 , TiO_2 , SiO_2 , CoS , MoS , etc.)[30-33], and chemical/complex hydrides (e.g. LiNH_2 , $\text{Mg}(\text{NH}_2)_2$, NaBH_4 , KBH_4 , $\text{Ca}(\text{BH}_4)_2$, etc.)[34-41] had been reported. In particular, a synergetic effect of destabilization/catalysis or destabilization/nanoconfinement using other effective materials was further employed to promote the hydrogen storage performance of those new systems[42-47]. As an instance, for a graphene-wrapped nanostructured LiBH_4 - MgH_2 system, 8.9 wt.% hydrogen was acquired in 1 hour at 350 °C without degradation within 25 cycles[23], which was dramatically superior to that of 1.8 wt.% hydrogen in 4 hours at 450 °C and 10th cycle for bulk LiBH_4 - MgH_2 system[48].

Although establishing LiBH_4 -based HSMs with favorable performance is admittedly important, exposing the mechanism lying behind the dehydrogenation and rehydrogenation behaviors of those interest systems is also vital to guide the design of novel HSMs. Recently, intensive attention had paid to the catalytic efficiency of boron-based compounds on tuning the hydrogen storage performance of HSMs, such as *h*-BN, NiB, NbB₂, TiB₂, CoNiB, etc[49-52]. In our previous work, an insight into the linear relationship between catalytic efficiency and cation electronegativity of $\text{MgB}_2/\text{TiB}_2/\text{FeB}/\text{SiB}_4$ was reported[53]. However, the real role of SiB_4 was still puzzled by the coexistence of dehydrogenated products of B or intermediate phase $\text{Li}_2\text{B}_{12}\text{H}_{12}$ which can serve as boron sources for the rehydrogenation of the LiBH_4 - SiB_4 system. Accordingly, a revisited system was provided in this work, and dual roles of SiB_4 in dehydrogenation and rehydrogenation processes of LiBH_4 were found. This finding directed to that a more preferable hydrogen storage performance

could be achieved in LiBH_4 -based materials, especially utilizing a component containing higher stoichiometry of B, like SiB_6 or others. To be specific, the higher content of B in the component, the higher preservation the catalyst for dehydrogenation, and the lower depletion the reactant for rehydrogenation. Thus, a superior balance will be achieved via this boron-designed approach to advance an efficient design of LiBH_4 -based HSMs.

2. Experimental section

Commercial LiBH_4 ($\geq 95\%$, Sigma Aldrich), SiB_4 (Sigma Aldrich) and LiH (Chemical Reagent Co., Tianjin) were used directly as raw materials. Later, SiB_4 was milled into a size of less than 500 nm by a ball milling machinery (QM-3SP2, Nanjing Nanda Instrument Plant) under the conditions of a ball-to-powder ratio of 40:1, a rotation speed of 90 rpm and a milling time of 70 hours. LiH was also milled with a ball-to-powder ratio of 40:1, a rotation speed of 1000 rpm and a milling time of 2 hours. Systems of LiBH_4 - SiB_4 with a molar ratio of 1:0.3 and LiH- SiB_4 with a molar ratio of 4:1 were subsequently milled under the conditions of a ball-to-powder ratio of 120:1, a rotation speed of 600 rpm and a milling time of 1 hour. The samples were sealed in a stainless steel vessel with hardened stainless steel balls under 1 bar argon gas protection.

The gaseous species released from the sample were detected by temperature programmed desorption mass spectrometry (TPD-MS, Hiden Qic20) in which the heating range was from 50 °C to 700 °C at a rate of 4 °C/min with an argon purge rate of 60 mL/min. The dehydrogenation kinetics was measured by a Sievert-type apparatus (PCTPro 2000, Setaram) at 350 °C under static vacuum. Rehydrogenation of LiBH_4 - SiB_4 and LiH- SiB_4 systems was executed by the same apparatus at the conditions of a hydrogen pressure of 10 MPa and a temperature of 250 °C or 400 °C. The phase analysis was performed by an X-ray diffraction measurement (XRD, Philips X'Pert X-ray diffractometer) with Cu $K\alpha$ radiation and tube parameters of $V=40$ kV, $I=40$ mA. The samples were covered with a 3M film prior to measurement, and its background signal was subtracted in each

XRD pattern. The bond vibration of the phases was detected by a Fourier transform-infrared spectrometer (FTIR, Vector 33; Bruker), and the signals were recorded from 32 scans between 4000 cm^{-1} and 400 cm^{-1} with a 4 cm^{-1} resolution. The background signal was subtracted from the sample spectra. Before testing, the samples were mixed with anhydrous KBr to form pressed pellets. A glove-box filled with highly pure Ar gas (99.999%) was used to handle the samples, and the H_2O and O_2 level in this box were kept below 3 ppm to avoid the contamination of LiBH_4 especially.

3. Results and Discussion

3.1 Catalytic role of SiB_4 on dehydrogenation of LiBH_4

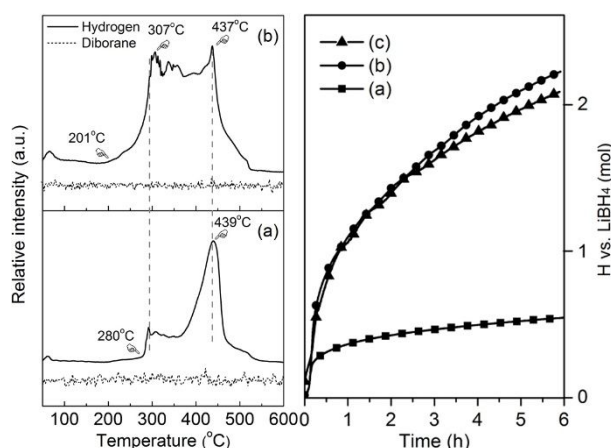


Figure 1 TPD-MS (left) and isothermal kinetics at 350 °C (right) of LiBH_4 (a), $\text{LiBH}_4\text{-SiB}_4$ system of 1st dehydrogenation (b) and 2nd dehydrogenation (c). Dehydrogenation of LiBH_4 was greatly promoted with the assistance of SiB_4 indicating by the faster kinetics.

Figure 1 exhibits the dehydrogenation behavior of $\text{LiBH}_4\text{-SiB}_4$ system together with LiBH_4 for comparison. As revealed by the TPD-MS results, LiBH_4 started to release hydrogen at its molten point of 280 °C and sluggishly reached a dehydrogenation peak at 439 °C similarly with the reported result[9]. When introducing SiB_4 into LiBH_4 , the dehydrogenation was initiated at 201 °C and a broadened plateau between 307 °C and 437 °C was clearly observed. This result states that the dehydrogenation of LiBH_4 took place at its solid state which should be ascribed to the enhancing interaction between SiB_4 and LiBH_4 . It is important that the volcano-like dehydrogenation behavior reveals its faster kinetics indicating by a sharper slope of the profile in contrast to that of pure LiBH_4 . It is also noticeable that this enhanced kinetics happened only at a point near the melting point of

LiBH₄, and therefore it demonstrates that the molten state of LiBH₄ crucially intensifies the dehydrogenation process with the assistance of SiB₄. Whether SiB₄ was used or not, the dehydrogenation of both two systems ended at around 550 °C and pure hydrogen without by-product of diborane (B₂H₆) was acquired.

As for the isothermal dehydrogenation behavior, LiBH₄ displayed a slow dehydrogenation kinetics and released only about 0.50 at. H/f.u. LiBH₄ (close to 2.7 wt.% H) within 6 hours. Whereas, a faster dehydrogenation kinetics and a higher capacity of 2.24 at. H/f.u. LiBH₄ (close to 10.3 wt.% H) with an ever-growing trend were achieved in the LiBH₄-SiB₄ system. This result certainly declares again that SiB₄ had a positive influence on promoting the dehydrogenation of LiBH₄. Significantly, the LiBH₄-SiB₄ system had a superior reversible capacity of 2.16 at. H/f.u. LiBH₄ (close to 9.9 wt.% H) when it was rehydrogenated at a moderate condition of 10 MPa and 400 °C H₂. It outperforms that of 15.5 MPa and 600 °C for the direct rehydrogenation of LiBH₄ from its dehydrogenating product of LiH and B[54].

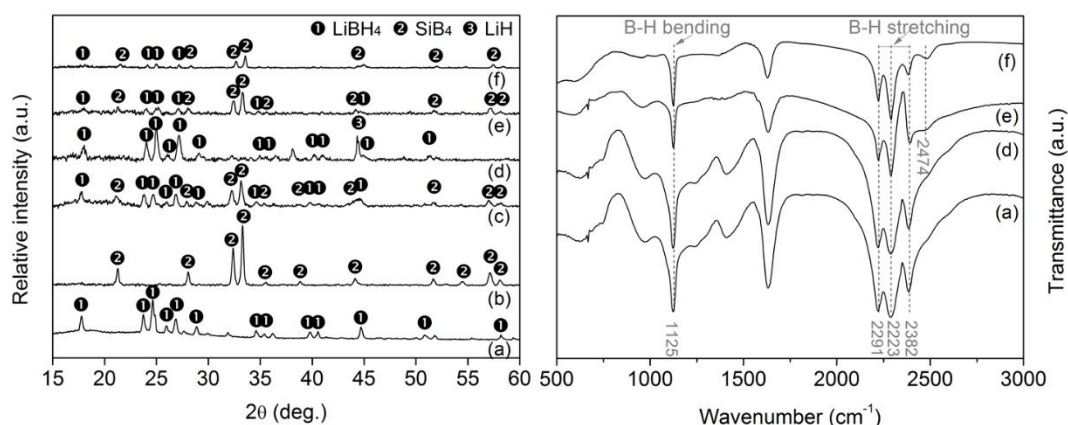
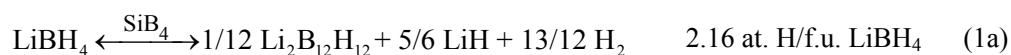


Figure 2 XRD patterns (left) and FTIR spectra (right) of LiBH₄ (a), SiB₄ (b), LiBH₄-SiB₄ system after milling (c), LiBH₄ after dehydrogenation (d), LiBH₄-SiB₄ system after dehydrogenation (e) and rehydrogenation (f). SiB₄ played a role of a catalyst to facilitate the dehydrogenation of LiBH₄.

Figure 2 shows the XRD patterns and FTIR spectra of the investigated samples mainly to reveal the dehydrogenation mechanism under the LiBH₄-SiB₄ system. As revealed by the XRD patterns, only diffraction peaks from LiBH₄ and SiB₄ were clearly observed in curve (c) and it accordingly demonstrated the milled LiBH₄-SiB₄ system was comprised of these two crystalline components. The obviously reduced diffraction intensity and broadened peak of LiBH₄ and SiB₄, in contrast to that of raw ones in curve (a) and (b) respectively, indicated the reduction of their grain size resulting from the fierce milling effect. It concludes that the LiBH₄-SiB₄ system was a physical mixture of

LiBH₄ and SiB₄.

As seen from curve (d), the diffraction peak intensity of dehydrogenated LiBH₄ was almost unchanged compared with the raw LiBH₄, and it accordingly demonstrated that few LiBH₄ came into dehydrogenation. This observation is in line with its dehydrogenation behavior as shown in Figure 1. Besides, LiH phase was observed indicated by its high-intensity diffraction peak, and elemental B derived from LiBH₄ should be in an amorphous state resulting in its absence of diffraction peak. It was in good agreement with other reported works[54, 55]. After the LiBH₄-SiB₄ system was subjected to dehydrogenation treatment, the diffraction peaks of LiBH₄ with extremely lower intensity became almost invisible as shown in curve (e). It also can be seen that the diffraction intensity of SiB₄ was retained and any other diffraction peaks from boron-containing phases were absent. This result indicates that SiB₄ did not react with LiBH₄ to form other crystalline phases. Hereon, one should be aware of that LiH and B phases in the dehydrogenated LiBH₄-SiB₄ system should have an amorphous structure, and it accordingly gave rise to the disappearance of their diffraction peaks in the XRD pattern. Furthermore, the FTIR result of curve (e) revealed that only the characteristic B-H vibrations from the residual LiBH₄ with bending modes at 1125 cm⁻¹ and stretching modes at 2291/2223/2382 cm⁻¹, and a B-H bond vibration from amorphous Li₂B₁₂H₁₂ located at 2474 cm⁻¹ were clearly detected[56]. According to these phase analysis, it was found that SiB₄ played a role of a catalyst to kinetically facilitate the dehydrogenation of LiBH₄. Combining the aforementioned phase analysis with the dehydrogenation behavior of releasing 2.24 at. H/f.u. LiBH₄ at 6 hours and having a growing capacity versus time as shown in Figure 1, the possible catalytic reaction for the dehydrogenation of LiBH₄-SiB₄ system is proposed in reaction (1). On this occasion, it is believed that SiB₄ could catalyze the hydrogen liberation from LiBH₄ and Li₂B₁₂H₁₂ simultaneously.



3.2 Reactant role of SiB₄ on rehydrogenation of LiBH₄

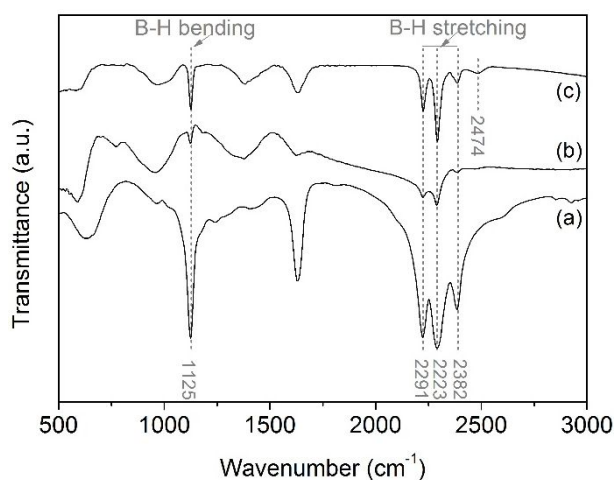
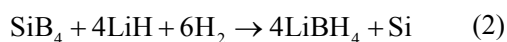


Figure 3 FTIR spectra of LiBH_4 (a), LiH-SiB_4 system hydrogenated at 250 °C (b) and 400 °C (c). LiBH_4 was unexpectedly found in the LiH-SiB_4 system hydrogenated at moderate conditions.

As shown in Figure 1, the superior reversibility of $\text{LiBH}_4\text{-SiB}_4$ system leads us to question the achievement of the rehydrogenation of LiBH_4 . With the coexistence of B, $\text{Li}_2\text{B}_{12}\text{H}_{12}$, and SiB_4 serving as boron sources, three kinds of rehydrogenation reactions possibly took place during the rehydrogenation process of $\text{LiBH}_4\text{-SiB}_4$ system. B reacted with LiH and H_2 to generate LiBH_4 , $\text{Li}_2\text{B}_{12}\text{H}_{12}$ reacted with LiH and H_2 to produce LiBH_4 , and a possible reaction of SiB_4 reacting with LiH and H_2 to form LiBH_4 . As reported by previous works, the elemental B necessitated an extremely harsh condition of 15.5 MPa and 600 °C to combine with LiH and consequently form LiBH_4 , for which it was thought to be inhibited by the chemical inertness of B[55, 57]. Whereas, the intermediate phase $\text{Li}_2\text{B}_{12}\text{H}_{12}$ necessitated conditions of 100 MPa and 500 °C to be rehydrogenated into LiBH_4 , because of its nature of high thermal stability and low chemical reactivity causing high reaction kinetic barrier[58]. It, therefore, seems that these two reactions did not occur in our study in which the applied rehydrogenation parameters were 10 MPa and 400 °C. Thus, the superior reversible performance of $\text{LiBH}_4\text{-SiB}_4$ system should not be attributed to the direct rehydrogenation of B and/or $\text{Li}_2\text{B}_{12}\text{H}_{12}$ by reacting with LiH. In this case, SiB_4 is speculated to play an important role to facilitate the rehydrogenation of LiBH_4 , and it consequently stimulates folks to figure out its explicit effect. Subsequently, controlled experiments were carried out via a hydrogenating LiH-SiB_4 system.

The LiH-SiB_4 system was subjected to a hydrogenation condition of 10 MPa and 250°C or 400 °C and the results measured by FTIR were shown in Figure 3. It is surprising that the B-H bending

mode at 1125 cm⁻¹ and stretching modes at 2291/2223/2382 cm⁻¹, in good agreement with that of LiBH₄, were clearly detected, and their vibration peak intensity increased along with the increasing hydrogenation temperature. It demonstrates that the B state in the SiB₄ was easily changed by chemically reacting with H atoms at moderate conditions, and the higher temperature could further enhance the formation of [BH₄]⁻ unit of LiBH₄. Besides, weak vibration peak locating at 2474 cm⁻¹ disclosed the formation of intermediate phase Li₂B₁₂H₁₂ in a small quantity only when the hydrogenation treatment was executed at 400 °C. This result proves that the formation of LiBH₄ was prior to Li₂B₁₂H₁₂ in the hydrogenating LiH-SiB₄ system. The Li₂B₁₂H₁₂ was suspected to be produced from the reaction between LiBH₄ and B₂H₆ in which B₂H₆ was possibly originated from the combination of H atoms from H₂ and B atoms from SiB₄[59, 60]. Accordingly, the above experimental results certainly indicate that SiB₄ played a role of a reactant in this hydrogenating LiH-SiB₄ system, and it is plausible to declare that the superior reversibility of LiBH₄-SiB₄ system was originated from a contribution of the abovementioned reaction.



To further figure out the possibility of this declaration, the quantity calculation in the hydrogenation reactions was carried out. It was assumed that 1mol LiBH₄ was completely heated into LiH and B, which was a combination of reactions (1a) and (1b). In this occasion, the available capacity of 10.3 wt.% H resulted in a yield of 0.75 mol LiH, and therefore this result meant that it would spend 0.19 mol SiB₄ to generate LiBH₄ according to reaction (2). Actually, in the experimental design of LiBH₄-SiB₄ system, the component molar ratio was LiBH₄:SiB₄=1:0.3. Due to 0.19 mol less than 0.3 mol, it was reasonable to conclude that the quantity of SiB₄ was sufficient for the occurrence of reaction (2) in the rehydrogenation process of LiBH₄-SiB₄ system, and the consumption of SiB₄ was calculated to be a value of 63%. In addition, as shown in Figure 2, the diffraction peak intensity of SiB₄ was reduced after the system's rehydrogenation (curve f) in contrast to that in the dehydrogenated one (curve e). With a calculation according to these XRD patterns, 58% SiB₄ was estimated to be spent in the rehydrogenated sample. Table 1 summarized the calculation analysis in those two hydrogenation reactions. Owing to that the calculated value of 63% was quite close to the actual one of 58%, it assures us that SiB₄ did react with LiH to form LiBH₄ at the applied rehydrogenation conditions, and accordingly a superior reversibility of LiBH₄-

SiB₄ was achieved with only a little of capacity reduction.

Table 1. The quantity calculation analysis in the hydrogenation reactions

| Hydrogenation reactions | $\text{LiBH}_4 \xleftarrow{\text{SiB}_4} \text{LiH} + \text{B} + 3/2\text{H}_2^*$ | $\text{SiB}_4 + 4\text{LiH} + 6\text{H}_2 \rightarrow 4\text{LiBH}_4 + \text{Si}$ |
|--|---|---|
| available capacity of H ₂ | 10.3 wt. % | / |
| resultant quantity of LiH | 0.75 mol | 0.75 mol |
| reactant quantity of SiB ₄ | / | 0.19 mol |
| theoretical value of SiB ₄ | 0.3 mol | / |
| consumption according to reaction | / | 63% |
| ratio of SiB ₄ according to XRD | / | 58% |

*: It was assumed that 1mol LiBH₄ completely dehydrogenated into LiH and B, which was a combination of reactions (1a) and (1b).

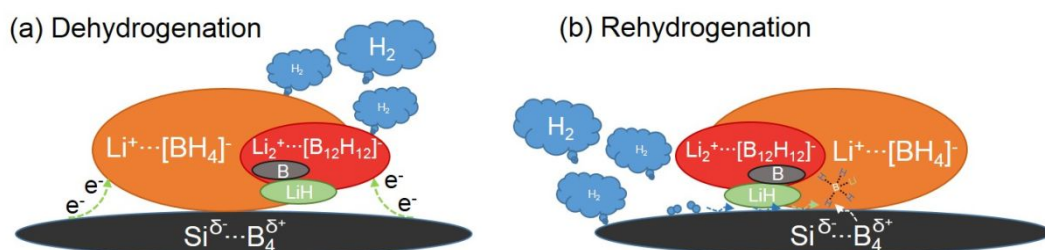


Figure 4 Sketch of the hypothetical dehydrogenation (a) and rehydrogenation (b) mechanisms of LiBH₄-SiB₄ system.

Combining with the aforementioned analysis, the mechanism of SiB₄ on the dehydrogenation and rehydrogenation processes of LiBH₄-SiB₄ is tried to sketch in Figure 4. For the dehydrogenation catalyzed by SiB₄, the catalysis mechanism is explained by a non-compensated electronic structure of SiB₄ in which the electron was transferred from B to Si making B electron-deficient and Si electron-enriched. Thus, the electron-enriched Si sites structurally destabilized the LiBH₄ and intermediate phase Li₂B₁₂H₁₂ to release massive hydrogen via giving sufficient electrons to [BH₄]⁻ and [B₁₂H₁₂]⁻ anions, and then to produce dehydrogenated products of LiH and B[8]. With regard to the rehydrogenation, SiB₄ was a reactant and cooperated with LiH and hydrogen to generate LiBH₄ with a calculated reaction enthalpy change of -65 kJ/mol H₂. As we all know, the enthalpy change of rehydrogenating B and LiH into LiBH₄ was reported to be -67 kJ/mol H₂ which was quite close to the former one[61]. Therefore, the experimental result indicates that SiB₄ was more reactive than elemental B to react with LiH to form LiBH₄. It should be resulted from a different boron state with a high chemical activeness for SiB₄ compared to B leading to a reduced reaction activation

energy. In other words, the formation of LiBH_4 from SiB_4 and LiH was prior to that from its dehydrogenated products of B and LiH under the moderate rehydrogenation conditions of this study.

4. Conclusion

In this study, an interest was attracted by the effect of SiB_4 on the dehydrogenation and rehydrogenation performance of LiBH_4 , and then corresponding mechanism was also proposed. With the assistance of SiB_4 , the hydrogen emission from LiBH_4 was dramatically promoted, and therefore a capacity of 2.24 at. H/f.u. LiBH_4 (close to 10.3 wt.% H) was achieved which was better than that of 0.50 at. H/f.u. LiBH_4 (close to 2.7 wt.% H) for pristine LiBH_4 . After a rehydrogenation treatment under moderate conditions of 10 MPa H_2 and 400 °C, a superior reversibility of 2.16 at. H/f.u. LiBH_4 was acquired. During these two processes, SiB_4 was found to act in different roles. It played a role of a catalyst to facilitate the dehydrogenation of LiBH_4 possibly originating from its non-compensated structure effect. The electron-enriched Si active sites transferred electrons to $[\text{BH}_4]^-$ and $[\text{B}_{12}\text{H}_{12}]^-$ units and led to a destabilizing structural stability. As for rehydrogenation, SiB_4 acted as a reactant to generate LiBH_4 by reacting with LiH and hydrogen, and it was owing to the higher reactive nature of SiB_4 than that of elemental B. These experimental results declare that, during the dehydrogenation and rehydrogenation reaction processes, the roles of a component adopted to design new LiBH_4 -based hydrogen storage materials would be changed, which certainly influence the hydrogen storage behavior of LiBH_4 .

Acknowledgements

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