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A fleeting glimpse of the dual roles of SiB_4 in promoting the hydrogen storage performance of $LiBH_4$

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In this study, the positive effects and dual roles of SiB_4 on the dehydrogenation and rehydrogenation performance of the $LiBH_4–SiB_4$ system are reported. Characterizations were performed through temperature programmed desorption mass spectrometry (TPD-MS), isothermal kinetics measurements, and XRD and FTIR analyses. For the hydrogen desorption from $LiBH_4$, SiB_4 played the role of a catalyst to kinetically facilitate the structural destabilization of $LiBH_4$ and its intermediate phase $Li_2B_{12}H_{12}$. Accordingly, a dehydrogenation capacity of 2.24 at. H/f.u. $LiBH_4$ (close to 10.3 wt% H) was attained at a relative temperature of 350 °C. For 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 us to take into account the explicit role(s) of the employed components during the dehydrogenation and rehydrogenation reactions when designing a desirable $LiBH_4$-based system.

1. Introduction

Solid-state hydrogen storage technology is particularly promising for on-demand large-scale hydrogen application, such as hydrogen energy vehicles and portable energy-storage equipment.[1] Along these lines, physical methods using MOFs, COFs, carbon, *etc.*, and chemical means employing lightweight materials such as Mg-based alloys, chemical hydrides, complex hydrides, *etc.* have been developed to efficiently store substantial amounts of hydrogen.[2–4] Unfortunately, the performance of these chemicals and their derivatives are still far from the technical requirements for onboard hydrogen storage systems.[5,6] Moreover, a limited understanding of the fundamental principles lying behind the interaction between materials and hydrogen stalls the accessibility of desired hydrogen storage materials (HSMs). Hence, researchers have made great efforts to push forward the scientific knowledge in order to accelerate the practical progress of HSMs, particularly complex hydrides having extremely high capacity of over 10 wt% H.[7]

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

(i) Synthesizing derivatives *via* chemically combining counterparts.

These $LiBH_4$-based derivatives feature high hydrogen capacity and low dehydrogenation temperatures with rapid kinetics. However, the irreversibility resulting from difficulty in reconstructing these compounds needs to be addressed. Enlightened by a theoretical prediction that the higher electronegativities x_p of metal cations (M^{n+}) substituting Li^+ cations could result in lower dehydrogenation temperatures,[8,9] various novel substituted compounds with a general formula of $LiM_x(BH_4)_y$ have been developed and their flexible structural properties and modifiable dehydrogenation performances have been reported.[10–14] For instance, $LiZn_2(BH_4)_5$ and $LiAl(BH_4)_4$ quickly decomposed at 127 °C and 67 °C, respectively.[10,15] Anion substitution of H^- by F^- or of $[BH_4]^-$ by Cl^- was also predicted to have capability towards adjustable thermodynamic performance.[16,17] Stemming from the idea that hydridic H^- interacting with protonic H^+ would advance the hydrogen storage performance, ammoniated $LiBH_4$

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($LiBH_4 \cdot nNH_3$), hydrazine-assisted $LiBH_4$ ($LiBH_4 \cdot nNH_2NH_2$) and ammonia borane-assisted $LiBH_4$ ($LiBH_4 \cdot nNH_3BH_3$) were then experimentally demonstrated to be remarkable HSMs.[18–20] Taking $LiBH_4 \cdot nNH_3$ 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 physical mixing with other components.

These systems have the main virtues of remarkable reversibility and fast dehydrogenation rate. However, a major obstacle for these systems right now is the high dehydrogenation temperature that demands further improvement. Inspired by a strategy involving reactive hydride composites (RHCs) having alternative dehydrogenation pathways,[22] intensive attention was directed to selecting suitable binary or ternary compounds and employing them to form new $LiBH_4$-based destabilization systems. Experimental trials on materials such as metal hydrides (*e.g.*, MgH_2, CaH_2, YH_3, and LaH_2),[23–25] metal halides (*e.g.*, NdF_5, SrF_2, TiF_3, $LaCl_3$, and $CeCl_3$),[26–29] metal chalcogenides (*e.g.*, Fe_3O_4, TiO_2, SiO_2, CoS, and MoS),[30–33] and chemical/complex hydrides (*e.g.*, $LiNH_2$, $Mg(NH_2)_2$, $NaBH_4$, KBH_4, and $Ca(BH_4)_2$)[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 these new systems.[42–47] For instance, for a graphene-wrapped nanostructured $LiBH_4$–MgH_2 system, 8.9 wt% hydrogen was attained in 1 hour at 350 °C without degradation over 25 cycles,[23] which was drastically superior to that of 1.8 wt% hydrogen production in 4 hours at 450 °C over 10 cycles for the bulk $LiBH_4$–MgH_2 system.[48]

Although establishing $LiBH_4$-based HSMs with favorable performance is admittedly important, exposing the mechanism behind the dehydrogenation and rehydrogenation behaviors of these systems is also vital to guide the design of novel HSMs. Recently, intensive attention has paid to the catalytic efficiency of boron-based compounds, such as *h*-BN, NiB, NbB_2, TiB_2, and CoNiB, for tuning the hydrogen storage performance of HSMs.[49–52] In our previous study, an insight into the linear relationship between the catalytic efficiency and the cation electronegativity of MgB_2/TiB_2/FeB/SiB_4 was reported.[53] However, the real role of SiB_4 was still uncertain due to the coexistence of dehydrogenated products of B or intermediate phase $Li_2B_{12}H_{12}$, which can serve as boron sources for the rehydrogenation of the $LiBH_4$–SiB_4 system. Accordingly, the revisited system was investigated in this study, and the dual roles of SiB_4 in the dehydrogenation and rehydrogenation processes of $LiBH_4$ were found. This finding implied that a more preferable hydrogen storage performance could be achieved in $LiBH_4$-based materials, particularly comprising higher stoichiometry of B, such as SiB_6. To be specific, higher the content of B in the component, higher would be the preservation of the catalyst for dehydrogenation, and lower would be the depletion of the reactant for rehydrogenation. Thus, a superior balance can be achieved *via* this boron-designed approach to advance efficient designs of $LiBH_4$-based HSMs.

2. Experimental section

Commercial $LiBH_4$ (≥95%, Sigma Aldrich), SiB_4 (Sigma Aldrich) and LiH (Chemical Reagent Co., Tianjin) were used directly as raw materials. Later, SiB_4 was milled to 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 samples were detected *via* temperature programmed desorption mass spectrometry (TPD-MS, Hiden Qic20) with a heating range was from 50 °C to 700 °C at a rate of 4 °C min^{-1} with an argon purge rate of 60 mL min^{-1}. The dehydrogenation kinetics was determined 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 were executed by the same apparatus under the conditions of a hydrogen pressure of 10 MPa and a temperature of 250 °C or 400 °C. The phase analysis was performed by X-ray diffraction measurement (XRD, Philips X'Pert X-ray diffractometer) with Cu Kα radiation and tube parameters of $V = 40$ kV, $I = 40$ mA. The samples were covered with a 3 M 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 $LiBH_4$ in particular.

3. Results and discussion

3.1 Catalytic role of SiB_4 on dehydrogenation of $LiBH_4$

Fig. 1 exhibits the dehydrogenation behavior of the $LiBH_4$–SiB_4 system together with $LiBH_4$ for comparison. As revealed by the TPD-MS results, $LiBH_4$ started to release hydrogen at its melting point of 280 °C and sluggishly reached a dehydrogenation peak at 439 °C, similarly to the reported result.[9] After introducing SiB_4 into $LiBH_4$, dehydrogenation was initiated at 201 °C and a broadened plateau between 307 °C and 437 °C was clearly observed. This result demonstrates that the dehydrogenation of $LiBH_4$ took place at its solid state, which should be ascribed to the enhanced interaction between SiB_4 and $LiBH_4$. It noteworthy that the volcano-like dehydrogena-

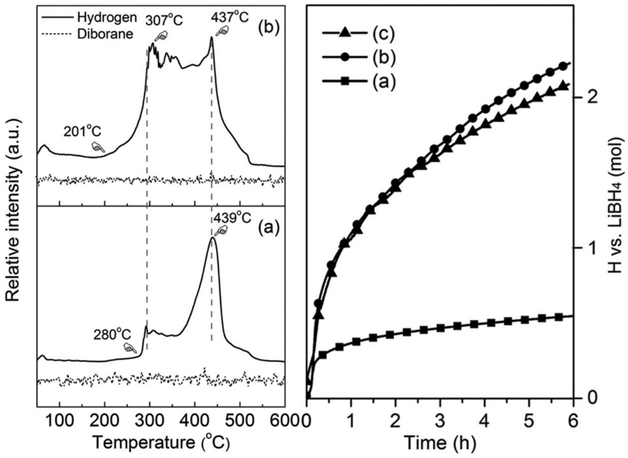

Fig. 1 TPD-MS (left) and isothermal kinetics at 350 °C (right) of $LiBH_4$ (a), $LiBH_4$–SiB_4 system for the 1st dehydrogenation (b) and 2nd dehydrogenation (c). Dehydrogenation of $LiBH_4$ was greatly promoted with the assistance of SiB_4, as indicated by the faster kinetics.

tion behavior shows faster kinetics indicated by a sharper slope of the profile in contrast to that of pure $LiBH_4$. It is also noticeable that these enhanced kinetics happen only at a point near the melting point of $LiBH_4$, therefore demonstrating that the molten state of $LiBH_4$ significantly intensifies the dehydrogenation process with the assistance of SiB_4. Irrespective of whether SiB_4 was used, the dehydrogenation of both the systems ended at around 550 °C and pure hydrogen without the by-product diborane (B_2H_6) was acquired.

As for the isothermal dehydrogenation behavior, $LiBH_4$ displayed a slow dehydrogenation kinetics and released only about 0.50 at. H/f.u. $LiBH_4$ (close to 2.7 wt% H) within 6 hours. In contrast, faster dehydrogenation kinetics and higher capacity of 2.24 at. H/f.u. $LiBH_4$ (close to 10.3 wt% H) with a continuously rising trend were achieved in the $LiBH_4$–SiB_4 system. This result certainly indicates that SiB_4 had a positive influence on promoting the dehydrogenation of $LiBH_4$. Significantly, the $LiBH_4$–SiB_4 system had a superior reversible capacity of 2.16 at. H/f.u. $LiBH_4$ (close to 9.9 wt% H) when it was rehydrogenated at a moderate condition of 10 MPa and 400 °C H_2. This system outperforms the direct rehydrogenation of $LiBH_4$ from its dehydrogenated products of LiH and B (15.5 MPa and 600 °C).[54]

Fig. 2 shows the XRD patterns and FTIR spectra of the investigated samples, and mainly reveals the dehydrogenation mechanism under the $LiBH_4$–SiB_4 system. As revealed by the XRD patterns, only the diffraction peaks from $LiBH_4$ and SiB_4 are clearly observed in the curve (c), thus indicating that the milled $LiBH_4$–SiB_4 system comprises these two crystalline components. The significantly reduced diffraction intensity and broadened peak of milled $LiBH_4$ and SiB_4, in contrast to that of the raw samples in curve (a) and (b) respectively, indicated the reduction of their grain size resulting from the severe milling effect. This concludes that the $LiBH_4$–SiB_4 system was a physical mixture of $LiBH_4$ and SiB_4.

As seen from curve (d), the diffraction peak intensity of dehydrogenated $LiBH_4$ was almost unchanged compared with that of raw $LiBH_4$, accordingly demonstrating that few $LiBH_4$ molecules underwent dehydrogenation. This observation is in line with its dehydrogenation behavior, as shown in Fig. 1. Moreover, the LiH phase was observed, as indicated by its high-intensity diffraction peak, and elemental B derived from $LiBH_4$ should be in the amorphous state, resulting in the absence of its diffraction peak. This finding is in good agreement with other reported studies.[54,55] After the $LiBH_4$–SiB_4 system was subjected to dehydrogenation, the diffraction peaks of $LiBH_4$ with significantly lower intensity became almost invisible, as shown in curve (e). It also can be seen that the diffraction intensity of SiB_4 was retained and any other diffraction peaks from boron-containing phases were absent. This result indicates that SiB_4 did not react with $LiBH_4$ to form other crystalline phases. Hereafter, it should be noted that the LiH and B phases in the dehydrogenated $LiBH_4$–SiB_4 system should have an amorphous structure, and accordingly gives rise to the disappearance of their diffraction peaks in the XRD pattern. Furthermore, the FTIR spectrum of the $LiBH_4$–SiB_4 system (curve (e)) revealed that only the characteristic B–H

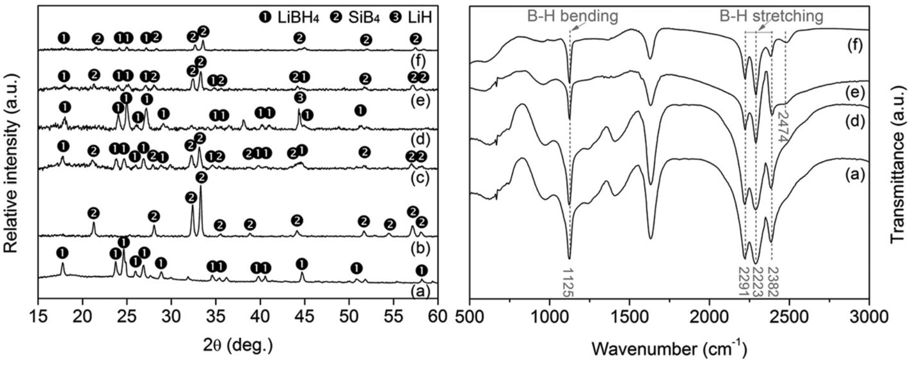

Fig. 2 XRD patterns (left) and FTIR spectra (right) of $LiBH_4$ (a), SiB_4 (b), $LiBH_4$–SiB_4 system after milling (c), $LiBH_4$ after dehydrogenation (d), $LiBH_4$–SiB_4 system after dehydrogenation (e) and $LiBH_4$–SiB_4 system after rehydrogenation (f). SiB_4 played the role of a catalyst to facilitate the dehydrogenation of $LiBH_4$.

vibrations from the residual $LiBH_4$ with bending modes at 1125 cm^{-1} and stretching modes at 2291/2223/2382 cm^{-1} and a B–H bond vibration from amorphous $Li_2B_{12}H_{12}$ located at 2474 cm^{-1} are clearly detected.[56] According to the phase analysis, it was found that SiB_4 played the role of a catalyst to kinetically facilitate the dehydrogenation of $LiBH_4$. Combining the aforementioned phase analysis with the dehydrogenation behavior for the release of 2.24 at. H/f.u. $LiBH_4$ at 6 hours and having an increasing trend of capacity *versus* time as shown in Fig. 1, the possible catalytic reaction for the dehydrogenation of the $LiBH_4$–SiB_4 system is proposed in reaction (1a) and (1b). It is believed that SiB_4 could catalyze the hydrogen liberation from $LiBH_4$ and $Li_2B_{12}H_{12}$ simultaneously.

$$\begin{aligned} &LiBH_4 \xleftrightarrow{SiB_4} 1/12\,Li_2B_{12}H_{12} + 5/6\,LiH + 13/12\,H_2 \\ &\qquad 2.16\,\text{at. H/f.u. } LiBH_4 \end{aligned} \tag{1a}$$

$$\begin{aligned} &Li_2B_{12}H_{12} \xleftrightarrow{SiB_4} 2LiH + 12B + 5H_2 \\ &\qquad 3.00\,\text{at. H/f.u. } LiBH_4 \end{aligned} \tag{1b}$$

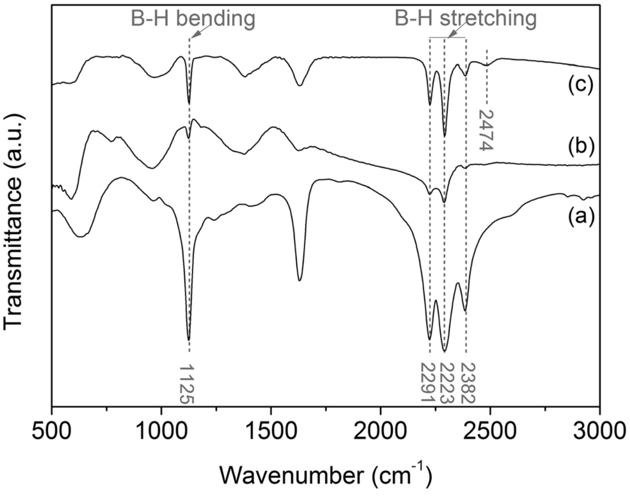

Fig. 3 FTIR spectra of $LiBH_4$ (a), LiH–SiB_4 systems hydrogenated at 250 °C (b) and 400 °C (c). $LiBH_4$ was unexpectedly found in the LiH–SiB_4 system hydrogenated at moderate conditions.

3.2 Reactant role of SiB_4 on rehydrogenation of $LiBH_4$

As shown in Fig. 1, the superior reversibility of the $LiBH_4$–SiB_4 system leads us to investigate the rehydrogenation of $LiBH_4$. With the coexistence of B, $Li_2B_{12}H_{12}$, and SiB_4 serving as boron sources, three types of rehydrogenation reactions possibly took place during the rehydrogenation process of the $LiBH_4$–SiB_4 system. B reacted with LiH and H_2 to generate $LiBH_4$, $Li_2B_{12}H_{12}$ reacted with LiH and H_2 to produce $LiBH_4$, and SiB_4 probably reacted with LiH and H_2 to form $LiBH_4$. As reported in previous studies, elemental B necessitates extremely harsh conditions of 15.5 MPa and 600 °C to combine with LiH and consequently form $LiBH_4$ due to the chemical inertness of B.[55,57] Moreover, the intermediate phase $Li_2B_{12}H_{12}$ necessitated the conditions of 100 MPa and 500 °C to be rehydrogenated into $LiBH_4$ because of its high thermal stability and low chemical reactivity, thus causing a high reaction kinetic barrier.[58] Therefore, it seems that these two reactions did not occur in our study, where the applied rehydrogenation parameters were 10 MPa and 400 °C. Thus, the superior reversible performance of the $LiBH_4$–SiB_4 system should not be attributed to the direct rehydrogenation of B and/or $Li_2B_{12}H_{12}$ 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 us to determine its explicit effect. Subsequently, controlled experiments were performed *via* hydrogenating the LiH–SiB_4 system.

The LiH–SiB_4 system was subjected to a hydrogenation condition of 10 MPa and 250 °C or 400 °C. The corresponding results *via* FTIR spectroscopy are shown in Fig. 3. It is surprising that the B–H bending mode at 1125 cm^{-1} and stretching modes at 2291/2223/2382 cm^{-1}, which are in good agreement with that of $LiBH_4$, were clearly detected, and their vibration peak intensity increased along with the increase in hydrogenation temperature. This demonstrates that the B state in the SiB_4 was easily changed by chemically reacting with H atoms under moderate conditions, and the higher temperature could further enhance the formation of the $[BH_4]^-$ unit of $LiBH_4$. Moreover, the weak vibration peak located at 2474 cm^{-1} disclosed the formation of the intermediate phase $Li_2B_{12}H_{12}$ in small quantities only when the hydrogenation treatment was executed at 400 °C. This result proves that the formation of $LiBH_4$ was prior to that of $Li_2B_{12}H_{12}$ in the hydrogenating LiH–SiB_4 system. $Li_2B_{12}H_{12}$ was suspected to be produced from the reaction between $LiBH_4$ and B_2H_6 where B_2H_6 possibly originated from the combination of H atoms from H_2 and B atoms from SiB_4.[59,60] Accordingly, the above experimental results certainly indicate that SiB_4 played the role of a reactant in this hydrogenating LiH–SiB_4 system, and it is plausible to conclude that the superior reversibility of the $LiBH_4$–SiB_4 system originated from the contribution of the above-mentioned reaction.

$$SiB_4 + 4LiH + 6H_2 \rightarrow 4LiBH_4 + Si \tag{2}$$

To further figure out the possibility of this declaration, the quantity calculation in the hydrogenation reactions was performed. It was assumed that 1 mol $LiBH_4$ 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. This result indicated that 0.19 mol SiB_4 is required to generate $LiBH_4$ according to reaction (2). In fact, in the experimental design of the $LiBH_4$–SiB_4 system, the component molar ratio was $LiBH_4 : SiB_4 = 1 : 0.3$. Due to 0.19 mol being less than 0.3 mol, it was reasonable to conclude that the quantity of SiB_4 was sufficient for the occurrence of reaction (2) in the rehydrogenation process of the $LiBH_4$–SiB_4 system, and the consumption of SiB_4 was calculated to be 63%. In addition, as shown in Fig. 2, the diffraction peak intensity of SiB_4 was reduced after the system's rehydrogenation (curve f) in contrast to that for

Table 1 The quantity calculations for the hydrogenation reactions

Hydrogenation reactions		$LiBH_4 \xleftrightarrow{SiB_4} LiH + B + 3/2\,H_2$ [a]	$SiB_4 + 4LiH + 6H_2 \rightarrow 4LiBH_4 + Si$
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 ratio of SiB_4	According to reaction	—	**63%**
	According to XRD	—	**58%**

[a] It was assumed that 1 mol $LiBH_4$ completely dehydrogenated into LiH and B, which is a combination of reactions (1a) and (1b).

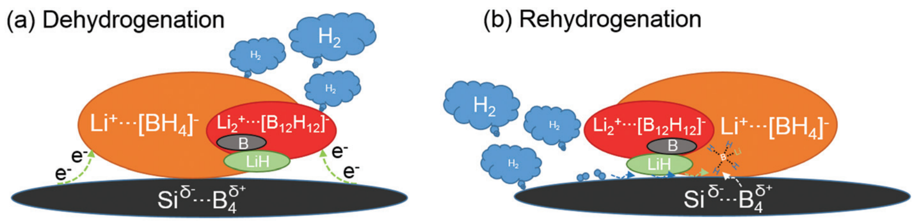

Fig. 4 Sketch of the hypothetical dehydrogenation (a) and rehydrogenation (b) mechanisms of the $LiBH_4$–SiB_4 system.

the dehydrogenated SiB_4 (curve e). According to these XRD patterns, 58% SiB_4 was estimated to be spent in the rehydrogenated sample. Table 1 summarized the calculation analysis in those two hydrogenation reactions. The fact that the calculated value of 63% was quite close to the actual value of 58% assures us that SiB_4 did react with LiH to form $LiBH_4$ under the applied rehydrogenation conditions and accordingly, a superior reversibility of $LiBH_4$–SiB_4 was achieved with only a slight capacity reduction.

Combining the aforementioned analysis, we attempted to elucidate the catalysis mechanism of SiB_4 for the dehydrogenation and rehydrogenation processes of $LiBH_4$–SiB_4, as sketched in Fig. 4. For the dehydrogenation catalyzed by SiB_4, the catalysis mechanism is explained by the non-compensated electronic structure of SiB_4 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 $LiBH_4$ and the intermediate phase $Li_2B_{12}H_{12}$ to release substantial amounts of hydrogen *via* providing sufficient electrons to $[BH_4]^-$ and $[B_{12}H_{12}]^-$ anions, and then produce the dehydrogenated products LiH and B.[8] With regard to the rehydrogenation, SiB_4 was a reactant and cooperated with LiH and hydrogen to generate $LiBH_4$ with a calculated reaction enthalpy change of -65 kJ mol^{-1} H_2. It is well known that the enthalpy change of rehydrogenating B and LiH into $LiBH_4$ was reported to be -67 kJ mol^{-1} H_2, which was quite close to our value.[61] Therefore, the experimental result indicates that SiB_4 was more reactive than elemental B to react with LiH and form $LiBH_4$. This should result from a different boron state with a high chemical activity for SiB_4 compared with that of 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 B and LiH under moderate rehydrogenation conditions of this study.

4. Conclusion

In this study, the effect of SiB_4 on the dehydrogenation and rehydrogenation performance of $LiBH_4$ was investigated and the corresponding mechanism was proposed. With the assistance of SiB_4, hydrogen emission from $LiBH_4$ was drastically promoted. 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 rehydrogenation treatment under moderate conditions of 10 MPa H_2 and 400 °C, superior reversibility of 2.16 at. H/f.u. $LiBH_4$ was attained. During these two processes, SiB_4 was found to act differently. It played the 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 the $[BH_4]^-$ and $[B_{12}H_{12}]^-$ units and led to destabilization of the structure. As for the rehydrogenation, SiB_4 acted as a reactant to generate $LiBH_4$ by reacting with LiH and hydrogen owing to the higher reactive nature of SiB_4 than that of elemental B. These experimental results assert that during the dehydrogenation and rehydrogenation reaction processes, the roles of the components adopted in the design of new $LiBH_4$-based hydrogen storage materials could change, which would certainly influence the hydrogen storage behavior of $LiBH_4$.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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References

1 T. He, P. Pachfule, H. Wu, Q. Xu and P. Chen, Hydrogen carriers, *Nat. Rev. Mater.*, 2016, **1**(12), 16059.

2 X. B. Yu, Z. W. Tang, D. L. Sun, L. Z. Ouyang and M. Zhu, Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications, *Prog. Mater. Sci.*, 2017, **88**, 1–48.

3 Z. H. Lu, J. P. Li, A. L. Zhu, Q. L. Yao, W. Huang, R. Y. Zhou, R. F. Zhou and X. S. Chen, Catalytic hydrolysis of ammonia borane via magnetically recyclable copper iron nanoparticles for chemical hydrogen storage, *Int. J. Hydrogen Energy*, 2013, **38**(13), 5330–5337.

4 Q. L. Yao, Z. H. Lu, W. Huang, X. S. Chen and J. Zhu, High Pt-like activity of the Ni-Mo/graphene catalyst for hydrogen evolution from hydrolysis of ammonia borane, *J. Mater. Chem. A*, 2016, **4**(22), 8579–8583.

5 https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles.

6 H. L. Chu, S. J. Qiu, Y. J. Zou, C. L. Xiang, H. Z. Zhang, F. Xu, L. X. Sun and H. Y. Zhou, Improvement on hydrogen desorption performance of calcium borohydride diammoniate doped with transition metal chlorides, *J. Phys. Chem. C*, 2015, **119**(2), 913–918.

7 Z. H. Lu and Q. Xu, Recent progress in boron and nitrogen based chemical hydrogen storage, *Funct. Mateir. Lett.*, 2012, **5**(1), 1230001.

8 K. Miwa, N. Ohba, S.-I. Towata, Y. Nakamori and S.-I. Orimo, First-principles study on lithium borohydride $LiBH_4$, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **69**(24), 245120.

9 Y. Nakamori, K. Miwa, A. Ninomiya, H. W. Li, N. Ohba, S.-I. Towata, A. Züttel and S.-I. Orimo, Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativites: First-principles calculations and experiments, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**(4), 045126.

10 D. B. Ravnsbæk, Y. Filinchuk, Y. Cerenius, H. J. Jakobsen, F. Besenbacher, J. Skibsted and T. R. Jensen, A Series of Mixed-Metal Borohydrides, *Angew. Chem., Int. Ed.*, 2009, **48**(36), 6659–6663.

11 D. B. Ravnsbaek, C. Frommen, D. Reed, Y. Filinchuk, M. Sorby, B. C. Hauback, H. J. Jakobsen, D. Book, F. Besenbacher, J. Skibsted and T. R. Jensen, Structural studies of lithium zinc borohydride by neutron powder diffraction, Raman and NMR spectroscopy, *J. Alloys Compd.*, 2011, **509**, S698–S704.

12 X. B. Xiao, W. Y. Yu and B. Y. Tang, First-principles study of a double-cation alkali metal borohydride LiK(BH4)2, *J. Phys.: Condens. Matter*, 2008, **20**(44), 445210.

13 M. Paskevicius, L. H. Jepsen, P. Schouwink, R. Cerny, D. B. Ravnsbaek, Y. Filinchuk, M. Dornheim, F. Besenbacherf and T. R. Jensen, Metal borohydrides and derivatives - synthesis, structure and properties, *Chem. Soc. Rev.*, 2017, **46**(5), 1565–1634.

14 J. S. Hummelshoj, D. D. Landis, J. Voss, T. Jiang, A. Tekin, N. Bork, M. Dulak, J. J. Mortensen, L. Adamska, J. Andersin, *et al.*, Density functional theory based screening of ternary alkali-transition metal borohydrides: A computational material design project, *J. Chem. Phys.*, 2009, **131**(1), 014101–014109.

15 H. W. Li, S.-I. Orimo, Y. Nakamori, K. Miwa, N. Ohba, S.-I. Towata and A. Züttel, Materials designing of metal borohydrides: Viewpoints from thermodynamical stabilities, *J. Alloys Compd.*, 2007, **446–447**, 315–318.

16 L. C. Yin, P. Wang, Z. Z. Fang and H. M. Cheng, Thermodynamically tuning $LiBH_4$ by fluorine anion doping for hydrogen storage: A density functional study, *Chem. Phys. Lett.*, 2008, **450**(4–6), 318–321.

17 O. Zavorotynska, M. Corno, E. Pinatel, L. H. Rude, P. Ugliengo, T. R. Jensen and M. Baricco, Theoretical and Experimental Study of $LiBH_4$-LiCl Solid Solution, *Crystals*, 2012, **2**(1), 144–158.

18 T. He, H. Wu, G. T. Wu, J. H. Wang, W. Zhou, Z. T. Xiong, J. E. Chen, T. Zhang and P. Chen, Borohydride hydrazinates: high hydrogen content materials for hydrogen storage, *Energy Environ. Sci.*, 2012, **5**(2), 5686–5689.

19 J. H. Luo, H. Wu, W. Zhou, X. D. Kang, Z. Z. Fang and P. Wang, $LiBH_4{\cdot}NH_3BH_3$: A new lithium borohydride ammonia borane compound with a novel structure and favorable hydrogen storage properties, *Int. J. Hydrogen Energy*, 2012, **37**(14), 10750–10757.

20 Y. H. Guo, G. L. Xia, Y. Zhu, L. Gao and X. B. Yu, Hydrogen release from amminelithium borohydride, $LiBH_4{\cdot}NH_3$, *Chem. Commun.*, 2010, **46**(15), 2599–2601.

21 X. L. Zheng, Y. S. Chua, Z. T. Xiong, W. D. Chen, Z. J. Jiang, G. T. Wu and P. Chen, The effect of NH_3 content on hydrogen release from $LiBH_4$-NH_3 system, *Int. J. Hydrogen Energy*, 2015, **40**(13), 4573–4578.

22 J. J. Vajo, S. L. Skeith and F. Mertens, Reversible storage of hydrogen in destabilized $LiBH_4$, *J. Phys. Chem. B*, 2005, **109**(9), 3719–3722.

23 G. L. Xia, Y. B. Tan, F. L. Wu, F. Fang, D. L. Sun, Z. P. Guo, Z. G. Huang and X. B. Yu, Graphene-wrapped reversible reaction for advanced hydrogen storage, *Nano Energy*, 2016, **26**, 488–495.

24 H. Wang, H. J. Lin, W. T. Cai, L. Z. Ouyang and M. Zhu, Tuning kinetics and thermodynamics of hydrogen storage

in light metal element based systems – A review of recent progress, *J. Alloys Compd.*, 2016, **658**, 280–300.

25 Y. Li, P. Li and X. H. Qu, Investigation on $LiBH_4$-CaH_2 composite and its potential for thermal energy storage, *Sci. Rep.*, 2017, **7**, 41754.

26 H. Q. Kou, G. Sang, Y. L. Zhou, X. Y. Wang, Z. Y. Huang, W. H. Luo, L. M. Chen, X. Z. Xiao, G. Y. Yang and C. W. Hu, Enhanced hydrogen storage properties of $LiBH_4$ modified by NbF_5, *Int. J. Hydrogen Energy*, 2014, **39**(22), 11675–11682.

27 Y. H. Guo, X. B. Yu, L. Gao, G. L. Xia, Z. P. Guo and H. K. Liu, Significantly improved dehydrogenation of $LiBH_4$ destabilized by TiF_3, *Energy Environ. Sci.*, 2010, **3**(4), 465–470.

28 B. J. Zhang, B. H. Liu and Z. P. Li, Destabilization of $LiBH_4$ by (Ce, La)(Cl, F)(3) for hydrogen storage, *J. Alloys Compd.*, 2011, **509**(3), 751–757.

29 S. X. Zhao, C. Y. Wang, D. M. Liu, Q. J. Tan, Y. T. Li and T. Z. Si, Destabilization of $LiBH_4$ by SrF_2 for reversible hydrogen storage, *Int. J. Hydrogen Energy*, 2018, **43**(10), 5098–5103.

30 X. B. Yu, D. M. Grant and G. S. Walker, Dehydrogenation of $LiBH_4$ destabilized with various oxides, *J. Phys. Chem. C*, 2009, **113**(41), 17945–17949.

31 W. T. Cai, H. Wang, L. F. Jiao, Y. J. Wang and M. Zhu, Remarkable irreversible and reversible dehydrogenation of $LiBH_4$ by doping with nanosized cobalt metalloid compounds, *Int. J. Hydrogen Energy*, 2013, **38**(8), 3304–3312.

32 J. S. Wang, Z. B. Wang, Y. Li, D. D. Ke, X. Z. Lin, S. M. Han and M. Z. Ma, Effect of nano-sized Ce_2S_3 on reversible hydrogen storage properties of $LiBH_4$, *Int. J. Hydrogen Energy*, 2016, **41**(30), 13156–13162.

33 Y. Zhao, Y. C. Liu, H. Q. Liu, H. Y. Kang, K. Z. Cao, Q. H. Wang, C. L. Zhang, Y. J. Wang, H. T. Yuan and L. F. Jiao, Improved dehydrogenation performance of $LiBH_4$ by 3D hierarchical flower-like MoS_2 spheres additives, *J. Power Sources*, 2015, **300**, 358–364.

34 Y. Bai, Z. W. Pei, F. Wu and C. Wu, Role of metal electronegativity in the dehydrogenation thermodynamics and kinetics of composite metal borohydride-$LiNH_2$ hydrogen storage materials, *ACS Appl. Mater. Interfaces*, 2018, **10**(11), 9514–9521.

35 H. Wang, H. J. Cao, C. Pistidda, S. Garroni, G. T. Wu, T. Klassen, M. Dorheim and P. Chen, Effects of Stoichiometry on the H-2-Storage Properties of $Mg(NH_2)_2$-LiH-$LiBH_4$ Tri-Component Systems, *Chem. – Asian J.*, 2017, **12**(14), 1758–1764.

36 Y. Z. Liu, D. Reed, C. Paterakis, L. C. Vasquez, M. Baricco and D. Book, Study of the decomposition of a $0.62LiBH_4$-$0.38NaBH_4$ mixture, *Int. J. Hydrogen Energy*, 2017, **42**(35), 22480–22488.

37 E. Roedern, B. R. S. Hansen, M. B. Ley and T. R. Jensen, Effect of eutectic melting, reactive hydride composites, and nanoconfinement on decomposition and reversibility of $LiBH_4$-KBH_4, *J. Phys. Chem. C*, 2015, **119**(46), 25818–25825.

38 H. Y. Leng, X. L. Zhou, Y. Shi, J. Wei, Q. Li and K. C. Chou, Improved hydrogen desorption properties of Li-N-H system by the combination of the catalytic effect of $LiBH_4$ and microwave irradiation, *Catal. Today*, 2018, **318**, 91–96.

39 P. Javadian, S. P. GharibDoust, H. W. Li, D. A. Sheppard, C. E. Buckley and T. R. Jensen, Reversibility of $LiBH_4$ facilitated by the $LiBH_4$-$Ca(BH_4)_2$ Eutectic, *J. Phys. Chem. C*, 2017, **121**(34), 18439–18449.

40 Y. W. Zhang, X. Z. Xiao, B. S. Luo, X. Huang, M. J. Liu and L. X. Chen, Synergistic effect of $LiBH_4$ and $LiAlH_4$ dddditives on improved hydrogen storage properties of unexpected high capacity magnesium hydride, *J. Phys. Chem. C*, 2018, **122**(5), 2528–2538.

41 S. J. Qiu, H. L. Chu, Y. J. Zou, C. L. Xiang, F. Xu and L. X. Sun, Light metal borohydrides/amides combined hydrogen storage systems: composition, structure and properties, *J. Mater. Chem. A*, 2017, **5**(48), 25112–25130.

42 Y. Zhang, Z. Y. Lan, N. Jian, Z. H. Ren, J. J. Hu, M. X. Gao, H. G. Pan, Y. H. Lu and Y. F. Liu, Mechanistic insights into the remarkable catalytic activity of nanosized Co@ C composites for hydrogen desorption from the $LiBH_4$-$2LiNH_2$ system, *Catal. Sci. Technol.*, 2017, **7**(9), 1838–1847.

43 P. Plerdsranoy, P. Javadian, N. D. Jensen, U. G. Nielsen, T. R. Jensen and R. Utke, Compaction of $LiBH_4$-$LiAlH_4$ nanoconfined in activated carbon nanofibers: Dehydrogenation kinetics, reversibility, and mechanical stability during cycling, *Int. J. Hydrogen Energy*, 2017, **42**(2), 1036–1047.

44 P. Javadian, D. A. Sheppard, C. E. Buckley and T. R. Jensen, Hydrogen desorption properties of bulk and nanoconfined $LiBH_4$-$NaAlH_4$, *Crystals*, 2016, **6**(6), 70.

45 W. Zhao, L. J. Jiang, Y. F. Wu, J. H. Ye, B. L. Yuan, Z. N. Li, X. P. Liu and S. M. Wang, Improved dehydrogenation cycle performance of the $1.1MgH_2$-$2LiNH_2$-$0.1LiBH_4$ system by addition of $LaNi_{4.5}Mn_{0.5}$ alloy, *J. Rare Earths*, 2015, **33**(7), 783–790.

46 Y. Zhang, Y. F. Liu, T. Liu, M. X. Gao and H. G. Pan, Remarkable decrease in dehydrogenation temperature of Li-B-N-H hydrogen storage system with CoO additive, *Int. J. Hydrogen Energy*, 2013, **38**(30), 13318–13327.

47 H. L. Chu, S. J. Qiu, L. X. Sun and G. T. Wu, Improved hydrogen desorption properties of Li-Ca-B-N-H system catalyzed by cobalt containing species, *J. Renewable Sustainable Energy*, 2014, **6**(1), 013105.

48 P. Sridechprasat, Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan and S. Kulprathipanja, Catalyzed $LiBH_4$ and MgH_2 mixture for hydrogen storage, *Int. J. Hydrogen Energy*, 2011, **36**(1), 1200–1205.

49 J. Y. Zhu, H. Wang, W. T. Cai, J. W. Liu, L. Z. Ouyang and M. Zhu, The milled $LiBH_4$/h-BN composites exhibiting unexpected hydrogen storage kinetics and reversibility, *Int. J. Hydrogen Energy*, 2017, **42**(24), 15790–15798.

50 J. Shao, X. Z. Xiao, L. X. Chen, X. L. Fan, L. Y. Han, S. Q. Li, H. W. Ge and Q. D. Wang, Enhanced hydriding-dehydriding performance of a $2LiH$-MgB_2 composite by the catalytic effects of Ni-B nanoparticles, *J. Mater. Chem. A*, 2013, **1**(35), 10184–10192.

51 X. L. Fan, X. Z. Xiao, L. X. Chen, X. H. Wang, S. Q. Li, H. W. Ge and Q. D. Wang, High catalytic efficiency of amorphous TiB_2 and NbB_2 nanoparticles for hydrogen storage using the $2LiBH_4$-MgH_2 system, *J. Mater. Chem. A*, 2013, **1**(37), 11368–11375.

52 Y. P. Zhao, L. Z. Ding, T. S. Zhong, H. T. Yuan and L. F. Jiao, Hydrogen storage behavior of $2LiBH_4/MgH_2$ composites improved by the catalysis of CoNiB nanoparticles, *Int. J. Hydrogen Energy*, 2014, **39**(21), 11055–11060.

53 W. T. Cai, Y. Z. Yang, P. J. Tao, L. Z. Ouyang and H. Wang, Correlation between structural stability of $LiBH_4$ and cation electronegativity in metal borides: an experimental insight for catalyst design, *Dalton Trans.*, 2018, **47**(14), 4987–4993.

54 P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Bielmann, C. N. Zwicky and A. Züttel, Stability and reversibility of $LiBH_4$, *J. Phys. Chem. B*, 2008, **112**(3), 906–910.

55 S.-I. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S.-I. Towata and A. Züttel, Dehydriding and rehydriding reactions of $LiBH_4$, *J. Alloys Compd.*, 2005, **404**, 427–430.

56 S. R. H. Jensen, M. Paskevicius, B. R. S. Hansen, A. S. Jakobsen, K. T. Moller, J. L. White, M. D. Allendorf, V. Stavila, J. Skibsted and T. R. Jensen, Hydrogenation properties of lithium and sodium hydride-closo-borate, $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$, composites, *Phys. Chem. Chem. Phys.*, 2018, **20**(23), 16266–16275.

57 O. Friedrichs, F. Buchter, A. Borgschulte, A. Remhof, C. N. Zwicky, P. Mauron, M. Bielmann and A. Züttel, Direct synthesis of $LiBH_4$ and $LiBD_4$ from the elements, *Acta Mater.*, 2008, **56**(5), 949–954.

58 J. L. White, R. J. Newhouse, J. Z. Zhang, T. J. Udovic and V. Stavila, Understanding and mitigating the effects of stable dodecahydro-closo-dodecaborate intermediates on hydrogen-storage reactions, *J. Phys. Chem. C*, 2016, **120**(45), 25725–25731.

59 O. Friedrichs, A. Remhof, S.-J. Hwang and A. Züttel, Role of $Li_2B_{12}H_{12}$ for the formation and decomposition of $LiBH_4$, *Chem. Mater.*, 2010, **22**(10), 3265–3268.

60 A. Remhof, O. Friedrichs, F. Buchter, P. Mauron, A. Züttel and D. Wallacher, Solid-state synthesis of $LiBD_4$ observed by in situ neutron diffraction, *Phys. Chem. Chem. Phys.*, 2008, **10**(38), 5859–5862.

61 R. G. Chen, X. H. Wang, L. Xu, H. Li, C. P. Chen, L. X. Chen and H. G. Pan, Direct preparation of $LiBH_4$ from pretreated LiH+B mixture at high pressure, *J. Alloys Compd.*, 2011, **509**(8), 3481–3485.