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Tuning the structural stability of LiBH₄ through boron-based

compounds towards superior dehydrogenation

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Abstract

The remarkable destabilization effects of H_3BO_3 , HBO_2 , and B_2O_3 on dehydrogenation of $LiBH_4$ are revealed in this work. The effectiveness for destabilizing the structural stability is in the trend of $H_3BO_3 > HBO_2 > B_2O_3$. Besides, through optimizing the molar ratio of LiBH₄ and H_3BO_3 and the milling treatment, the destabilization effect, especially for dehydrogenation kinetics, is further enhanced. In an instance, at temperature as low as 110 °C, 5.8 wt.% hydrogen can be liberated in seconds from 2LiBH₄-H₃BO₃ prepared through pre-milling. The investigation reveals that each LiBH₄-H₃BO₃, LiBH₄-HBO₂ and LiBH₄-B₂O₃ systems undergo multiple dehydrogenation stages corresponding to different destabilization mechanism. The reaction at lower temperature is ascribed to the H⁺…H⁻ coupling mechanism which should be enhanced by the $[OH]^{-}$ interaction mode. Pre-milling treatment of LiBH₄ and H₃BO₃ also promotes the $H^+ \cdots H^-$ interaction which may be originated from the increasing contact area as a result of the fine particle, and therefore probably reduced the reaction activation energy. Consequently, it gives rise to the superior dehydrogenation performance of lower temperature, rapid kinetics, pure hydrogen and high capacity, which are required for the off-board hydrogen energy vehicle application.

Key words: hydrogen storage, destabilization, dehydrogenation, lithium borohydride, borate acid

1. Introduction

Light weight element materials such as Mg-based hydride, alanate, amide and borohydride are regarded as important hydrogen storage materials especially in the hydrogen energy vehicle application [1-4]. Recently, alkali metal borohydrides have received much attention as promising candidates because of their high hydrogen capacity [5, 6]. Among them, LiBH₄ has been studied most comprehensively since 2003 due to the high hydrogen gravimetric density and volumetric density of 18.4 wt.% and 121 kg/m³, respectively [7]. Thermogram shows that pristine LiBH₄ undergoes three endothermic steps at 108-112, 258-286 and 483-600 °C [8]. The first stage corresponds to the reversible polymorphic transformation without any hydrogen emission, and the second stage is attributed to the fusion of LiBH₄ accompanying with a minor dehydrogenation of approximately 2 wt.%. The main dehydrogenation starts at 380 °C liberating 80% hydrogen in LiBH₄. This major dehydrogenation reaction is as following:

$$LiBH_4 \rightarrow LiH + B + 3/2H_2$$
 (1)

However, the extremely high thermodynamic stability and sluggish kinetic barrier originating from the $[BH_4]^-$ structural stability of LiBH₄ hampers its application as hydrogen storage material [9, 10]. Therefore, destabilization of the structural stability through altering the reaction path was proposed to augment the hydrogen storage performance of LiBH₄ by Vajo et al. in 2005 [11]. Since then, extensive efforts have been paid for establishing destabilized LiBH₄ systems with enhanced properties, such as LiBH₄-MgH₂/CaH₂/YH₃/NdH₂, LiBH₄-SiO₂/TiO₂/SnO₂, and so on [11-31]. The destabilization reaction normally is LiBH₄ + MH_x \rightarrow LiH + MB_x + H₂ for the LiBH₄-metal hydride systems, while it is a redox reaction of LiBH₄ + MO_x \rightarrow LiMO_x + B + H₂ for the LiBH₄-metal oxide systems. Besides, the dehydrogenation pathway also can be controlled by confining LiBH₄ in highly ordered nanoporous carbon leading to lower dehydrogenation temperature [32, 33]. Since the thermodynamic stability of metal borohydrides was reported to correlate with Pauling electronegativity of cation [34], new perspective of elemental substitution had been employed to LiBH₄ leading different and sophisticated destabilization reactions [35]. A variety of novel complexes were synthesized with tunable dehydrogenation temperature, such as $Li_{m-4}Zr(BH_4)_m$ (m=4, 5, 6), LiK(BH₄)₂, Li₄Al₃(BH₄)₁₃, etc. [36-42] Besides, anion substitution study of Li₈B₈H_{32-x}F_x from theoretical calculation suggested a lower dehydrogenation temperature of 100 °C for LiBH_{3.75}F_{0.25} [43].

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More recently, new complexes and/or systems were synthesized and investigated according to H⁺...H⁻ interaction mechanism which show enhanced dehydrogenation behavior, such as LiBH₄·NH₃, LiBH₄·NH₃BH₃, LiBH₄-LiNH₂ [44-50]. Motivated by this mechanism and to reveal the synergetic effect of coexistence of oxygen and hydrogen atoms on the dehydrogenation of LiBH₄, H₃BO₃ containing [OH]⁻ unit were selected and introduced into LiBH₄, including HBO₂/B₂O₃ for comparison. Besides, the preparation parameters of stoichiometric ratio and pre-milling treatment were also investigated for further strengthening the destabilization effect. Fascinating result was achieved in the case of 2LiBH₄-H₃BO₃ system prepared by pre-milled LiBH₄ and H₃BO₃, in which 5.8 wt.% hydrogen with high purity was liberated at temperature as low as 110 °C in seconds. Table 1 shows the comparison of dehydrogenation performance of typical LiBH₄-additive systems. It clearly declares that high dehydrogenation temperature or hydrogen purity is the main challenge for these investigated systems. Significantly, the 2LiBH₄-H₃BO₃ system may be used as off-board hydrogen storage material requiring the comprehensive performance of lower dehydrogenation temperature, rapid kinetics, high hydrogen

Table 1 Comparison of dehydrogenation performance of typical LiBH₄-additive systems

No.	System	Capacity (wt.%)	Temperature (°C)	Advantages	Disadvantages	Ref.
1	2LiBH ₄ -H ₃ BO ₃	5.8	110	lower dehydrogenation temperature; fast kinetics; high hydrogen purity and capacity	limited reversibility	This work
2	LiBH ₄ -MgH ₂	8	440	fact bination apparian	high dehydrogenation temperature; in some cases, destabilization effect is limited by back pressure and/or nanosized effect	[11]
3	LiBH ₄ -YH ₃	7.2	350	reversibility; high hydrogen purity and		[15]
4	LiBH ₄ -NdH ₂	6.0	370			[16]
5	LiBH ₄ -CaH ₂	7.7	427	capacity		[55]
6	LiBH ₄ -SiO ₂	7	350		high dehydrogenation temperature; irreversibility	[7]
7	LiBH ₄ -TiO ₂	3	250	hydrogen purity: high		[12]
8	LiBH ₄ -SnO ₂	3	400	- capacity in some cases		[17]
9	LiBH ₄ -Fe ₂ O ₃	6	200	capacity in some cases		[12]
10	$Li_4Al_3(BH_4)_{13}$	21.6	40-80	lower dehydrogenation	impure hydrogen involving B ₂ H ₆ ; irreversibility; - thermodynamic unstability of some - compounds at room temperature	[38]
11	LiZn ₂ (BH ₄) ₅	35.0	-35-150	temperature; fast		[37]
12	LiSc(BH ₄) ₄	4.3	177-400			[56]
13	LiBH ₄ ·NH ₃	36	280	relative lower dehydrogenation	impure hydrogen involving NH ₃ /c-(NHBH) ₃ or others; limited reversibility	[44]
14	LiBH ₄ ·NH ₃ BH ₃	34	100-450	temperature in some cases; fast kinetics		[45]

purity and capacity.

2. Experimental

LiBH₄ (95%, Sigma Aldrich) and H₃BO₃ (99.5%, Yongda chemical agent, China) were used as starting materials. By heating H₃BO₃, HBO₂ was obtained at temperature 150 °C for 20 h under air atmosphere, and B₂O₃ was acquired at 250 °C for 6 h under vacuum condition. LiBH₄-48.4 wt.% H₃BO₃/HBO₂/B₂O₃ composites were synthesized by hand milling for 10 minutes using a mortar and pestle, both LiBH₄ and H₃BO₃ were as-received. LiBH₄-H₃BO₃ with molar ratio of 1:2/2:1/3:1 was prepared under the same conditions, in this occasion as-received LiBH₄ and H₃BO₃ and pre-ball milled LiBH₄ and H₃BO₃ were used. The pre-ball milling was performed by a vibratory ball mill (QM-3C, Nanjing Nanda Instrument Plant) at rotation speed of 600 rpm for 1 h. The samples were loaded into a stainless steel vessel together with hardened stainless steel balls and the weight ratio of balls to powders was 120:1.

The gaseous species released from the composites were detected by a mass spectrometer (MS, Hiden-Qic 20) under temperature-programmed desorption mode (TPD). The composites were heated from room temperature to 500 °C with a heating rate of 4 °C min⁻¹ and high purity argon purge of 60 mL/min. Dehydrogenation kinetics measurement was performed on a Sievert-type apparatus (PCT-Pro 2000, Setaram) under static vacuum. Due to the limited volume of the sample container, 0.1 g sample was applied to the apparatus in each measurement. The dehydrogenation content was calculated with respect to the total weight of the composites. Phase analysis was executed on an X-ray diffractometer (XRD, Philips X'Pert, Cu K α radiation). The composites were wrapped with a 3M film to avoid the air and moisture contamination, which caused a scattering peak at 20~18° in XRD pattern. The background induced by this plastic film was removed from the acquired XRD patterns for each sample. Fourier transform infrared spectra (FTIR, Vector 33, Bruker) were recorded from 32 scans at 4000 cm⁻¹-400 cm⁻¹ using 4 cm⁻¹ resolution. The background was subtracted from the spectra. All the samples were handled in a glove box under high purity argon atmosphere. The O₂ and H₂O levels were below 1 ppm.

3. Results and discussions

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LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites

3.1 Microstructure of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites



Figure 1 XRD patterns (1) and FTIR spectra (2) of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites using as-received LiBH₄ and H₃BO₃ (a), pre-milled LiBH₄ and H₃BO₃ (b). LiBH₄-H₃BO₃ composites were mixture of LiBH₄ and H₃BO₃.

In this section, the effect of molar ratio of LiBH₄ : H₃BO₃ (1:2, 2:1, 3:1) and pre-milling treatment of LiBH₄ and H₃BO₃ was systematically investigated to reveal the synergistic effect of oxygen and hydrogen atoms on the destabilization performance. Figure 1 shows the XRD patterns and FTIR spectra of the LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites. The diffraction peaks from LiBH₄ and H₃BO₃ were clearly identified in all composites. With the increasing molar ratio of H₃BO₃, the diffraction intensity of LiBH₄ became weaker while that of H₃BO₃ became stronger. Besides, small diffraction peaks of LiH were detectable in the composites using pre-ball milled LiBH₄ and H₃BO₃. This indicates the occurrence of self-decomposition of LiBH₄ [51] or side reaction between LiBH₄ and H₃BO₃ during the milling process. As revealed by FTIR spectra, the vibrations from H₃BO₃ of O-H bond at 3216 cm⁻¹ and B-O bond at 1354, 1019 and 587 cm⁻¹ were visible. It is interesting that in the LiBH₄-2H₃BO₃ composite new vibrations from B-O bond at

1445, 812, 645 and 548 cm⁻¹ and B-H bond at 1194 cm⁻¹ were detected which were also originated from H₃BO₃ [52]. The vibration shifting indicates that the interaction of $[BH_4]^- \cdots [OH]^-$ distorts the characteristic vibrations of B-H bond and O-H bond in LiBH₄ and H₃BO₃, and it also would be beneficial to the dehydrogenation enhancement as revealed in the following measurements. The characteristic vibrations of B-H bond at 2385, 2291, 2223 and 1125 cm⁻¹ from LiBH₄ gradually became weaker with its decreasing molar ratio. Therefore, the LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites were mainly a mixture of LiBH₄ and H₃BO₃ using either as-received components or pre-milled ones.

3.2 Dehydrogenation of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites

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Figure 2 TPD-MS of H₂ evolution of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites using as-received LiBH₄ and H₃BO₃ (a), pre-milled LiBH₄ and H₃BO₃ (b), pristine LiBH₄ and H₃BO₃ (c). The composites exhibited similar dehydrogenation behavior with three stages.

Figure 2 shows the TPD-MS results of H₂ evolution for LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites using as-received LiBH₄ and H₃BO₃, pre-milled LiBH₄ and H₃BO₃, without any poisonous B₂H₆ emission (data not shown here). These composites exhibited similar dehydrogenation behavior which can be divided into three dehydrogenation stages of <150 °C (first stage), 270-325 °C (second stage) and >325 °C (third stage). This behavior is different from that of pristine LiBH₄ and H₃BO₃ that implies the interaction between these two compounds. Pristine LiBH₄ starts to liberate hydrogen at about 280 °C and reach its peak point at 440 °C, and

pristine H₃BO₃ liberates hydrogen from 120 °C reaching the peak temperature at 198 °C. When using as-received LiBH₄ and H₃BO₃, the dehydrogenation peak temperatures were 108 °C/300 °C/351 °C for LiBH₄-3H₃BO₃, 51-96 °C/298 °C/383 °C for LiBH₄-2H₃BO₃, and 83 °C/301 °C/405 °C for LiBH₄-H₃BO₃. By changing into pre-milled LiBH₄ and H₃BO₃, the peak temperatures were relatively reduced to 85 °C/290 °C/340 °C for LiBH₄-3H₃BO₃, 94 °C/296 °C/379 °C for LiBH₄-2H₃BO₃, and 92 °C/285 °C/394 °C for LiBH₄-H₃BO₃. Significantly, it is necessary to emphasize that the dehydrogenation peak temperatures are significantly lower (<110 °C) for those composites at first stage. Therefore, we focus on the improvement effectiveness at this stage for further kinetics measurement, and to reveal the hydrogen emission whether comes from the H⁺...H⁻ interaction mechanism or not.



Figure 3 Isothermal dehydrogenation at 110 °C of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites using as-received LiBH₄ and H₃BO₃ (a), pre-milled LiBH₄ and H₃BO₃ (b). The composites prepared from pre-milled LiBH₄ and H₃BO₃ exhibited better dehydrogenation kinetics.

Figure 3 shows the isothermal dehydrogenation kinetics at 110 °C for LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites using as-received LiBH₄ and H₃BO₃, and pre-milled LiBH₄ and H₃BO₃. Pristine LiBH₄ liberates none of any hydrogen at this extremely lower temperature as revealed in Figure 2c. The extremely sharp dehydrogenation curves clearly indicate that hydrogen was rapidly released within seconds from the composites. 3.2 wt.%, 4.8 wt.% and 3.9 wt.% hydrogen was liberated

and H₃BO₃. 3.3 wt.%, 5.8 wt.% and 5.2 wt.% hydrogen was acquired from LiBH₄-3H₃BO₃, LiBH₄-2H₃BO₃ and LiBH₄-H₃BO₃ respectively by using pre-milled LiBH₄ and H₃BO₃. These results declare that the dehydrogenation effectiveness is in the order of 2LiBH₄-H₃BO₃>LiBH₄-2H₃BO₃>3LiBH₄-H₃BO₃, and the pre-milled ones show much better performance. This should be attributed to the reduced reaction activation energy originating from the increasing contact area between refining particles of LiBH₄ and H_3BO_3 (see ESI). Table 2 shows the theoretical dehydrogenation capacity and observed value from LiBH₄-H₃BO₃ composite under different molar ratio. It is clear that the observed capacity is very closed to the theoretical value of $H^+ \cdots H^-$ interaction mechanism, which indicates the liberated hydrogen is produced from hydrogen atoms combined from LiBH₄ and H₃BO₃.

Table 2 Dehydrogenation capacity of LiBH ₄ -H ₃ BO ₃ composites at 110 °C. (unit: wt.%)								
Molar ratio of LiBH ₄ :H ₃ BO ₃	3:1	2:1	1:2					
Theoretical capacity of composite	11.8	10.4	6.9					
Theoretical capacity of H ⁺ -H ⁻	4.7(3H ⁺ -3H ⁻)	5.7 (3H ⁺ -3H ⁻)	5.5 (4H ⁺ -4H ⁻)					
Observed capacity	3.3	5.8	5.2					

3.3 Microstructure of dehydrogenated LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites



Figure 4 XRD patterns (1) and FTIR spectra (2) of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites after dehydrogenation at 110 °C, using as-received LiBH₄ and H₃BO₃ (a), pre-milled LiBH₄ and H₃BO₃ (b). Destabilization reaction between LiBH₄ and H₃BO₃ occurred during dehydrogenation.

Figure 4 shows the XRD patterns and FTIR spectra of LiBH₄-H₃BO₃ (1:2, 2:1, 3:1) composites after dehydrogenation at 110 °C using as-received LiBH₄ and H₃BO₃, and pre-milled LiBH₄ and H₃BO₃. In the XRD patterns, only diffraction peaks from LiBH₄ and HBO₂ were clearly identified. By increasing the molar ratio of H₃BO₃, the intensity of LiBH₄ decreased whereas that of HBO₂ increased, especially for LiBH₄-2H₃BO₃ composite using pre-milled components. These results suggest that more LiBH₄ had been consumed under higher molar ratio of H₃BO₃ leading to increasing dehydrogenation capacity (see Figure 3). FTIR spectra reveal the characteristic B-H vibrations at 2385, 2291, 2223 and 1125 cm⁻¹ indicating partial LiBH₄ retained in the dehydrogenated composites. Besides, the B-O vibration peaks appeared at range of 1500-1200 cm⁻¹, 1100-900 cm⁻¹, 760-500 cm⁻¹ should be originating from the reaction product HBO₂. Herein, it is worthwhile to note that the reaction products of Li-B-O-H and/or Li-B-O

should exist in this lower-temperature dehydrogenated products, although their B-O and B-H bond vibrations was hard to be distinguished from that of HBO₂ and LiBH₄ due to the overlapping profiles. Therefore, the destabilization reaction between LiBH₄ and H₃BO₃ with molar ratio of 1:2, 2:1, 3:1 at 110 °C was proposed as following:

$$LiBH_4 + H_3BO_3 \rightarrow (1-x)LiBH_4 + HBO_2 + Li-B-O-H/Li-B-O + H_2$$
(2)

In our work, pristine H_3BO_3 was found to self-decompose into HBO_2 and B_2O_3 when heating up. In particularly, HBO_2 emerged in the dehydrogenated products (equation 2). Therefore, it is of interest to further reveal the promotion effect of HBO_2 and B_2O_3 on the dehydrogenation behavior of LiBH₄. And then HBO_2 and B_2O_3 was prepared and introduced into LiBH₄ and the results were shown in the following section.

LiBH₄-H₃BO₃/HBO₂/B₂O₃ composites

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3.4 Microstructures of LiBH₄-H₃BO₃/HBO₂/B₂O₃ composites

Figure 5 XRD patterns (a) and FTIR spectra (b) of pristine LiBH₄, LiBH₄-H₃BO₃, LiBH₄-HBO₂ and LiBH₄-B₂O₃ composites. The composites were mixtures of LiBH₄ and H₃BO₃/HBO₂/B₂O₃.

Figure 5 shows the XRD patterns (a) and FTIR spectra (b) of pristine LiBH₄, LiBH₄-H₃BO₃,

LiBH₄-HBO₂, and LiBH₄-B₂O₃ composites. As shown in Figure 5a, diffraction peaks from H_3BO_3 were identified, whereas that of HBO₂ and B_2O_3 were invisible possibly due to their amorphous structures. The diffraction peaks of LiBH₄ in the composites were also detectable. Some unknown

peaks in the diffraction patterns were originated from the impurities in LiBH₄. FTIR spectra in Figure 5b shows the characteristic vibrations of B-H bond from LiBH₄ at 2385, 2291, 2223 and 1125 cm⁻¹. However, the B-H, O-H, B-O bond vibrations from H₃BO₃, HBO₂, B₂O₃ were hard to distinguish due to the overlapping peak. Only broad peaks of B-O bond at 1354, 1019 and 587 cm⁻¹ were identified in LiBH₄-H₃BO₃ composite. These results indicate that those composites were mixtures of LiBH₄ and H₃BO₃, HBO₂, or B₂O₃ without any newly formed compounds.

3.5 Dehydrogenation of LiBH₄-H₃BO₃/HBO₂/B₂O₃ composites



Figure 6 TPD-MS of H₂ (a) and B₂H₆ (b) evolution of pristine LiBH₄, LiBH₄-H₃BO₃, LiBH₄-HBO₂ and LiBH₄-B₂O₃ composites. Dehydrogenation temperatures of LiBH₄ were dramatically reduced in the presence of H₃BO₃/HBO₂/B₂O₃.

Figure 6 shows the H₂ and B₂H₆ evolution from LiBH₄-H₃BO₃, LiBH₄-HBO₂, LiBH₄-B₂O₃ composites, together with pristine LiBH₄ for comparison. It is obvious that pure hydrogen was released from those composites without any poisonous B₂H₆ emission. When introducing H₃BO₃, HBO₂, or B₂O₃ into LiBH₄, the dehydrogenation behaviors were significantly enhanced. For LiBH₄-H₃BO₃, the peak temperature was greatly lower to 108 °C followed with two small peaks at 300 °C and 351 °C. For LiBH₄-HBO₂, the composite exhibits multiple dehydrogenations around 74 °C and the temperature between 300 °C and 350 °C. Hydrogen releasing from LiBH₄-B₂O₃

takes place at the temperatures between 300 °C and 400 °C with a predominant peak at 307 °C. It is obvious that these composites show similar dehydrogenation behavior at lower temperature (< 150 °C) for LiBH₄-H₃BO₃ and LiBH₄-HBO₂ composites and at higher temperature (300-400 °C) for three composites which implies the similar destabilization reaction.



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Figure 7 Isothermal dehydrogenation of LiBH₄-H₃BO₃ (a), LiBH₄-HBO₂ (b), LiBH₄-B₂O₃ (c), together with pristine LiBH₄ for comparison. Dehydrogenation kinetics of LiBH₄ was significantly enhanced by doping with H₃BO₃/HBO₃/HBO₂/B₂O₃.

Figure 7 shows the isothermal dehydrogenation kinetics of pristine LiBH₄ at 350 °C, LiBH₄-H₃BO₃ at 110 °C and 350 °C, LiBH₄-HBO₂ at 75 °C and 340 °C, LiBH₄-B₂O₃ at 300 °C and 360 °C. These dehydrogenation temperatures were reasonably selected according to the TPD-MS results. As shown in Figure 7, pristine LiBH₄ exhibited sluggish dehydrogenation kinetics resulting in a lower dehydrogenation capacity of 2.0 wt.% at 350 °C. Fortunately, the situation was greatly changed by introducing boron-based compound such as H₃BO₃, HBO₂, and B₂O₃. LiBH₄-H₃BO₃ composite released 3.2 wt.% and 8.6 wt.% hydrogen at 110 °C and 350 °C

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TPD-MS result (see Figure 6a). LiBH₄-HBO₂ composite released only 0.5 wt.% hydrogen at 75 °C and 6.6 wt.% hydrogen at 340 °C. 5.2 wt.% and 5.8 wt.% hydrogen was released from the LiBH₄-B₂O₃ composite at 300 °C and 360 °C respectively. Combined with TPD-MS results in Figure 6, the results indicate that the effectiveness of boron-based compounds on improving the dehydrogenation of LiBH₄ is in the order of H₃BO₃>HBO₂>B₂O₃. It undoubtedly declares that the higher $[OH]^-$ content is, the stronger destabilization effect will been obtained. Table 3 shows the dehydrogenation capacity comparison between theoretical and observed values, and it implies that some of the hydrogen-containing compounds exist in the dehydrogenated product which was revealed in the following.

Table 3 Dehydrogenation capacity of LiBH ₄ -H ₃ BO ₃ /HBO ₂ /B ₂ O ₃ composites. (unit: wt.%)								
Composite	Theoretical capacity	Observed capacity						
LiBH ₄ -H ₃ BO ₃	11.8	3.2 (110 °C)	8.6 (350 °C)					
LiBH ₄ -HBO ₂	10.6	0.5 (75 °C)	6.6 (340 °C)					
LiBH ₄ -B ₂ O ₃	9.5	/	5.2 (300 °C)/ 5.8 (360 °C)					

3.6 Microstructure of dehydrogenated LiBH₄-H₃BO₃/HBO₂/B₂O₃ composites



Figure 8 XRD patterns (a) and FTIR spectra (b) of pristine LiBH₄, LiBH₄-H₃BO₃, LiBH₄-HBO₂, and LiBH₄-B₂O₃ composites after dehydrogenation. Destabilization effect between LiBH₄ and H₃BO₃/HBO₂/B₂O₃ occurred during dehydrogenation.

Figure 8 shows the XRD patterns and FTIR spectra of pristine LiBH₄, LiBH₄-H₃BO₃, LiBH₄-HBO₂, and LiBH₄-B₂O₃ composites after dehydrogenation. As revealed in Figure 8a, diffraction peaks of Li₄B₂O₅, LiB₃O₁₀H₁₃ and Li₃BO₃ were clearly identified in the dehydrogenated composites of LiBH₄-H₃BO₃ at 350 °C, LiBH₄-HBO₂ at 340 °C, LiBH₄-B₂O₃ at 300 °C and 360 °C. Whereas, a possible diffraction peak of HBO₂ together with peaks of LiBH₄ were detected in the LiBH₄-H₃BO₃ composite dehydrogenated at 110 °C. And only the diffraction peaks of LiBH₄ were detected in the LiBH₄-HBO₂ dehydrogenated at 75 °C. Furthermore, as revealed by FTIR spectra in Figure 8b, the characteristic vibrations of B-H bond at 2385, 2291, 2223 and 1125 cm⁻¹ indicated that partial LiBH₄ was remained in all the dehydrogenated composites. For dehydrogenation of LiBH₄-H₃BO₃ at 350 °C, LiBH₄-HBO₂ at 340 °C and LiBH₄-B₂O₃ at 300 °C/360 °C, the B-H bond vibration at 2474 cm⁻¹ was visible declaring the

formation of $Li_2B_{12}H_{12}[53]$. Besides, bond vibrations from B-O, possibly even the overlapping B-H-O vibration, at range of 1500-1200 cm⁻¹, 1100-900 cm⁻¹, 760-500 cm⁻¹ should be from $Li_4B_2O_5$, Li_3BO_3 and $LiB_5O_{10}H_{13}$ which were revealed in XRD patterns shown in Figure 8a. Unlike these FTIR spectra at high temperatures, not any new vibrations were detected in the spectra of LiBH₄-HBO₂ dehydrogenated at 75 °C.

According to the results above, remarkable dehydrogenation performance of those composites is originated from the destabilization effect between LiBH₄ and H₃BO₃/HBO₂/B₂O₃. Due to the same reaction products from LiBH₄-H₃BO₃, LiBH₄-HBO₂, and LiBH₄-B₂O₃ composites at higher temperatures (>300 °C), the destabilization reaction equation is proposed as following:

$$LiBH_4 + H_3BO_3/HBO_2/B_2O_3 \rightarrow Li_4B_2O_5 + LiB_5O_{10}H_{13} + Li_3BO_3 + Li_2B_{12}H_{12} + H_2$$
(3)

3.7 Discussion

As revealed in this work, the coexistence of oxygen and hydrogen atoms in the form of $[OH]^-$ show better destabilization effect on reducing the dehydrogenation temperature than that of the LiBH₄-oxide and LiBH₄-metal hydride systems [11-24]. The effect of $[OH]^-$ is implemented through the $[BH_4]^-\cdots[OH]^-$ interaction emerging after milling of LiBH₄ and H₃BO₃ as revealed in Figure 1. Subsequently, we found that the observed capacity of LiBH₄-H₃BO₃ composite is much lower than that of the composite's theoretical value respectively, but very closed to the theoretical capacity calculated from the H⁺-H⁻ coupling mechanism as shown in Table 2 [54]. These indicate that the $[BH_4]^-\cdots[OH]^-$ interaction contributes to the enhancement of H⁺-H⁻ coupling leading to the significant dehydrogenation improvement with respect to lower temperature and fast kinetics as shown in Figure 2 and 3. Herein, it is also worthwhile to point out the tuning method to achieve

superior dehydrogenation performance. Altering the molar ratio of LiBH₄:H₃BO₃ is one of the effective way to control the theoretical molar ratio of H^+/H^- . When three H^+ in H₃BO₃ combines with three H^- in LiBH₄, the 3LiBH₄-H₃BO₃ has a observed capacity of 3.3 wt.%; and 2LiBH₄-H₃BO₃ exhibits the best performance of 5.8 wt.% observed capacity. When four H^+ from H₃BO₃ combines with four H^- from LiBH₄, the observed values is reduced to 5.2 wt.% for LiBH₄-2H₃BO₃. Besides, it also reveals that HBO₂ with less H^- or B₂O₃ without H^- leads to limiting effect on reducing the dehydrogenation temperature and/or kinetics. Another way is to increase the surface energy of the particle of LiBH₄ and H₃BO₃ which will reduce the reaction activation energy. Therefore, the composite from pre-milling treatment of LiBH₄ and H₃BO₃. At the higher dehydrogenation temperature over 300 °C, hydrogen was released from the hydrogen-containing compound Li-B-O-H or probably the reaction between residual LiBH₄ and HBO₂ showing a similar behavior like LiBH₄-B₂O₃ composite.

We also found that the LiBH₄-H₃BO₃ composite showed partial reversibility under appropriate rehydrogenation conditions (see ESI). This arises from the stable chemical stability of the reaction products, and the reversibility improvement was still under way.

4. Conclusion

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Focusing on the comprehensive target of lower dehydrogenation temperature, rapid kinetics, pure hydrogen and high capacity, $H_3BO_3/HBO_2/B_2O_3$ were found to display fascinating improvement effect on the dehydrogenation of LiBH₄ according to destabilization reaction. The destabilization effectiveness is in the trend of $H_3BO_3>HBO_2>B_2O_3$ which indicates the higher [OH]⁻ content benefit for enhancing the destabilization effect. Further investigation on

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LiBH₄-H₃BO₃ was carried out by altering the molar ratio of LiBH₄ : H₃BO₃ and pre-milling treatment of LiBH₄ and H₃BO₃. The destabilization effectiveness is in the trend of $2LiBH_4$ -H₃BO₃>LiBH₄-2H₃BO₃>3LiBH₄-H₃BO₃ and the pre-milled composites exhibit better performance. 5.8 wt.% hydrogen is liberated in seconds at temperature as low as 110 °C from $2LiBH_4$ -H₃BO₃ prepared by pre-milling treatment of LiBH₄ and H₃BO₃. The remarkable destabilization improvement of H₃BO₃ on LiBH₄ is attributed to the H⁺-H⁻ coupling mechanism, and the appropriate molar ratio of [OH]⁻ : [BH₄]⁻ and composite preparation treatment is found to enhance the interaction between H⁺ and H⁻.

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Table of contents

 $LiBH_4$ - H_3BO_3 destabilization system shows significantly lower temperature, rapid kinetics, pure hydrogen and high capacity through $[BH_4]^-\cdots[OH]^-$ interaction.

