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The dehydrogenation mechanism and reversibility of LiBH₄ doped by active Al* derived from AlH₃

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Abstract: A detailed analysis of the dehydrogenation mechanism and reversibility of LiBH₄ doped by active Al* derived from AlH₃ was performed by thermogravimetry (TG), differential scanning calorimetry (DSC), mass spectral analysis (MS), powder X-ray diffraction (XRD), scanning electronic microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The results show that the dehydrogenation of LiBH₄/Al* is a five-step reaction: (1) LiBH₄ + Al → LiH + AlB₂ + "Li-Al-B-H" + B₂H₆ + H₂; (2) the decomposition of "Li-Al-B-H" compounds liberating H₂; (3) 2LiBH₄ + Al → 2LiH + AlB₂ + 3H₂; (4) LiBH₄ → LiH + B + 3/2H₂; (5) LiH + Al → LiAl + 1/2H₂. And the reversibility of LiBH₄/Al* composite is based on equation as follows: LiH + LiAl + AlB₂ + 7/2H₂ ↔ 2LiBH₄ + 2Al. The extent of dehydrogenation reaction between LiBH₄ and Al* greatly depends on the precipitation and growth of reaction products (LiH, AlB₂ and LiAl, etc.) on the surface of Al*. A passivation shell of Al* formed by these products is the kinetic barrier to the dehydrogenation of LiBH₄/Al* composite.

Keywords: LiBH₄; Al; dehydrogenation mechanism; kinetic properties; reversibility

1. Introduction

Hydrogen is recognized as an ideal energy vector with the advantages of high combustion value and zero pollution [1-3]. However, the storage of hydrogen is still challenging for its on-board application. Hydrogen energy can be stored in gas, liquid and solid forms, among which solid hydrogen storage is the safest. Currently, complex metal hydrides are considered as the most promising hydrogen storage materials due to their large hydrogen storage capacities [4-6].

Lithium borohydride (LiBH₄) has drawn much attention for on-board hydrogen storage due to its theoretical hydrogen storage capacity as high as 18.5wt.%, which far exceed the requirement of vehicle hydrogen storage material by the US department of energy [7,8]. Unfortunately, LiBH₄ is thermodynamically stable and the dehydrogenation is only initiated when temperature is above 400 °C under 1 bar H₂. The reversibility of LiBH₄ is poor and the rehydrogenation requires a temperature over 600 °C under 155bar H₂ [9,10]. Various methods have been developed to improve the dehydrogenation properties and reversibility of LiBH₄. Some researchers [11-13] found that thermodynamic destabilization of LiBH₄ could be achieved by adding reactive hydride composites (RHC) to change the dehydrogenation steps of it. For instance, Vajo et al [9]. reported that the dehydrogenation reaction enthalpy was much lower than that of the pure LiBH₄ by doping with MgH₂. The formation of MgB₂ during dehydrogenation reaction destabilized LiBH₄ and the reversibility of LiBH₄-MgH₂ composite was also better than pure LiBH₄. After that, many metal hydrides or complex hydrides have been employed to improve the hydrogen storage properties of LiBH₄ [14-22].

The metallic activity of Al and Mg is close. According to the theoretical calculation based on phase diagram, the decomposition temperature of LiBH₄/Al composite was predicted to be
significantly lower than that of pure LiBH₄ [23]. So Al has been popularly employed as another destabilization agent to improve the hydrogen desorption properties of LiBH₄. The Al source can be either a metallic Al or a complex hydrides containing Al [24-26]. However, the metallic Al is usually coated with an oxide layer, which greatly limits the improvement of dehydrogenation and reversibility of LiBH₄. And the utilization of Al-containing hydrides will inevitably introduce the influence of other atoms on the de/rehydrogenation reaction. In order to investigate the mechanism and influence of pure Al on the dehydrogenation and reversibility of LiBH₄, an as-prepared Al (denoted Al*) derived from AlH₃ was employed as destabilization agent. The hydrogen desorption properties and mechanism of LiBH₄/Al* composite were studied systematically, along with kinetic investigations using a Sievert-type apparatus. Kissinger method was used to calculate the activation energy of the main dehydrogenation step of LiBH₄/Al* composite and its reversibility was also discussed.

2. Materials and Methods

The LiBH₄ powder (95% purity; Acros Organics) and Al powder (99% purity; Sinopharm Group) were employed as raw materials. AlH₃ was synthesized as follows: LiAlH₄ and AlCl₃ were dissolved in diethyl ether at a molar ratio of 3:1. After a period of reaction based on equation (1), the precipitate LiCl was filtered off and the filtrate containing AlH₃ was separated from mixture. The pure AlH₃ was then obtained from the filtrate by dried and de-ethers in vacuum. Finally, AlH₃ was completely dehydrogenated to obtain active Al* by heating to 200°C and holding for 2.5h. The dehydrogenation curves of AlH₃ and XRD patterns of AlH₃ before and after dehydrogenation are shown in Figure 1(a) and 1(b), respectively.

\[
3\text{LiAlH}_4 + \text{AlCl}_3 \rightarrow 4\text{AlH}_3 + 3\text{LiCl} \downarrow
\]

The commercial Al powder was used for comparison with the as-prepared Al* in this study. The LiBH₄/Al and LiBH₄/Al* composites were synthesized by ball-milling using a QM-3SP4 planetary ball mill (Nanjing Nanda Instrument Plant). The ball to powder ratio was 45:1. The milling process was carried out at 400 rpm for 30 min under a 0.1 MPa argon atmosphere. To prevent the temperature from rising too fast during long-term milling, the milling process was paused every 6 min for cooling. All of the samples were handled in a Mikrouna glove box filled with high purity argon (99.999%) and controlled H₂O (<0.5 ppm) and O₂ (<0.1 ppm) concentrations for preventing contamination.

The morphologies of the as-received Al and as-prepared Al* were observed by a field emission scanning electronic microscopy (SEM, Hitachi S4800). The characterization of hydrogen desorption properties of the LiBH₄/Al and LiBH₄/Al* samples was carried out on a Sieverts-type apparatus [27]. The thermal events during dehydrogenation of the samples were investigated by thermogravimetry.

![Figure 1. The dehydrogenation curves (a) of AlH₃ and XRD patterns (b) of AlH₃ before and after dehydrogenation.](image-url)
/differential scanning calorimeter (TG/DSC, Netzsch STA449F3). For the isothermal hydrogen
desorption measurements, the samples were rapidly heated to a set temperature (i.e., 100°C, 350°C,
500°C and 600°C) and held for 3h under flowing argon of 50 ml/min. For the non-isothermal
dehydrogenation (i.e., the temperature programmed desorption, TPD) measurements, the samples
were heated gradually from room temperature to 600°C with a heating rate of 5°C/min. The
hydrogen desorption spectra were collected synchronously using a mass spectrometer (MS,
Netzsch QMS403C). The phase of the as-prepared samples and the dehydrogenation product of
them at various temperatures were identified by X-ray diffraction technique (XRD, X’Pert Pro,
Cu-Kα) and fourier transform infrared spectroscopy (FTIR, Beuker-Vector22). During XRD
measurements, the samples were sealed with a polypropylene membrane to avoid exposure to any
moisture or oxygen.

3. Results and Discussion

3.1. Dehydrogenation mechanism of the LiBH₄/Al* composite

The SEM images of the as-received Al particles and as-prepared Al* particles are shown in
Figure 2. It can be seen that the particle size of the as-received Al is about 100 μm, while the particle
size of active Al* derived from AlH₃ is only 1% of it. A sharp reduction in the particle size means a
significant increase in the specific surface area.

Figure 2. SEM images of the as-received Al particles (a) and as-prepared Al* particles (b).

Figure 3 presents different simultaneous signals for the dehydrogenation of LiBH₄/Al and
LiBH₄/Al* samples: the thermogravimetry (TG) signal, DSC signal and hydrogen signal plotted over
the temperature. It can be seen from Figure 3a that the dehydrogenation curves of LiBH₄/Al and
LiBH₄/Al* composites are almost the same before 350°C, and they both liberate about 0.1 wt.% of H₂.
After being heated to 350°C, the dehydrogenation rate of LiBH₄/Al* is obviously faster than that of
LiBH₄/Al. Finally, the total dehydrogenation amount of LiBH₄/Al and LiBH₄/Al* samples at 600°C
reached 5.5 wt.% and 6.2 wt.%, respectively. It can be ascribed to the Al* derived from AlH₃ has
larger specific surface area, and the oxide-free surface of Al* possess higher chemical reactivity. So
that the dehydrogenation reaction of LiBH₄/Al* is more sufficient than LiBH₄/Al.

The DSC/MS curves of LiBH₄, LiBH₄/Al and LiBH₄/Al* were displayed in Figure 3b, 3c and 3d,
respectively. The endothermic peak in the DSC curve of pure LiBH₄ (Figure 3b) at 112°C
corresponds to the crystal transformation from orthorhombic phase (o-LiBH₄) to hexagonal phase
(h-LiBH₄), while the endothermic peak at 288°C corresponds to the melting of h-LiBH₄ [28]. LiBH₄ is
dehydrogenated in the temperature range of 400°C to 550°C, in which the dehydrogenation rate
reached the maximum around 481°C. So the endothermic peak at this temperature is ascribed to the
decomposition of LiBH₄ based on equation (2).

$$\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + 3/2\text{H}_2 \uparrow$$  \hspace{1cm} (2)
There are three endothermic peaks at 465°C, 482°C and 530°C in the DSC curve of LiBH₄/Al sample (Figure 3c). Each endothermic peak corresponds to a hydrogen evolution peak in the MS curve. The endothermic peak at 482°C is in good agreement with that of the decomposition of LiBH₄ mentioned above. Compared with figure 3b, the new endothermic peaks at 465°C and 530°C should be related to the reaction of LiBH₄ and the added Al. According to the work of other researchers [29-31], the endothermic peak at 465°C is ascribed to LiBH₄ reacts with Al forming LiH, AlB₂ and liberating H₂ (equation (3)), and the endothermic peak at 530°C is attributed to the reaction of LiH with Al to form LiAl alloy and H₂ (equation (4)).

$$2\text{LiBH}_4 + \text{Al} \rightarrow 2\text{LiH} + \text{AlB}_2 + 3\text{H}_2 \uparrow$$ \hspace{1cm} (3)

$$\text{LiH} + \text{Al} \rightarrow \text{LiAl} + \frac{1}{2}\text{H}_2 \uparrow$$ \hspace{1cm} (4)

It can be seen from Figure 3d that the dehydrogenation behavior of LiBH₄/Al* is more sophisticated than that of LiBH₄/Al. There is a tiny endothermic peak appeared at 376°C in the DSC curve of LiBH₄/Al* composite, accompanied by a small amount of H₂ and B₂H₆ desorption reflected in the MS curve. What’s more, there are four endothermic peaks of dehydrogenation locate at 434°C, 450°C, 472°C and 560°C. In order to investigate the mechanism of these thermal events, XRD and FTIR analyses were conducted on the solid products of LiBH₄/Al* sample at different dehydrogenation temperatures (e.g. 100°C, 350°C, 500°C and 600°C). The results are shown in Figure 4 and Figure 5, respectively. It can be seen from Figure 4(a) that no new phase was detected when the sample was heated to 100°C. The shrinkage of the diffraction peaks of LiBH₄ is related to its crystal transformation. When the sample was heated to 350°C, some tiny diffraction peaks of AlB₂ and an unknown phase appeared. The unknown phase, marked “?” was also reported by
Finally, the product LiH reacted with Al* to form LiAl alloy and H₂ based on equation (4) when the excess molten LiBH₄ underwent self-decomposition to form LiH, B and H₂ (equation (2)) around reaction stopped when the surface of Al* was completely wrapped by LiH and AlB₂. Therefore, the encapsulated Al* occurred around 450°C and Al* rose to 434°C completely wrapped by these reaction products to form a passivation shell. When the temperature of AlB₂ and "Li-Al-B-H" compounds on the surface of Al*, the reaction stopped when Al* was releasing B₂H₆ and H₂ based on equation (6) around 376°C. Then the molten LiBH₄ reacted with Al* to form LiH, AlB₂ and "Li-Al-B-H" compounds while from orthorhombic phase (o-LiBH₄) to hexagonal phase (h-LiBH₄) at 112°C dehydrogenation reaction based on equation (5). In addition, AlB₂ is generally considered to be a product which makes the dehydrogenation system reversible, while B₂H₆ is a toxic gas which may be an problem for the future application of LiBH₄/Al* system.

\[
\text{LiBH}_4 + \text{Al} \rightarrow \text{LiH} + \text{AlB}_2 + "\text{Li-Al-B-H}" + \text{B}_2\text{H}_6 \uparrow + \text{H}_2 \uparrow \tag{5}
\]

When the sample was heated to 500°C, the LiBH₄ cannot be detected by the XRD analysis (Figure 4(a)) and the vibrational peaks of B-H stretching (2382 cm⁻¹, 2292 cm⁻¹ and 2224 cm⁻¹) and bending (1125 cm⁻¹) disappeared (Figure 5(a)), indicating that LiBH₄ had been completely consumed in dehydrogenation reaction around 376°C, 434°C, 450°C and 472°C (Figure 3(d)). What’s more, the diffraction peaks of LiAl appeared and the diffraction intensity of LiH and AlB₂ slightly increased, while the peaks of Al weakened and the peaks of unknown components disappeared. Combined with the analyses of LiBH₄ and LiBH₄/Al samples, it can be reasonably assumed that the main dehydrogenation peak of LiBH₄/Al* around 450°C (Figure 3(d)) is attributed to the reaction of LiBH₄ and Al to form LiH, AlB₂ and H₂ based on equation (3). The reaction temperature is lower than that of LiBH₄/Al sample probably because the higher chemical reactivity of Al* reduced the activation energy of the reaction. The dehydrogenation peak around 472°C is ascribed to the self-decomposition of LiBH₄ forming LiH, B and H₂ based on equation (2). However, the diffraction peaks of B are not found in the XRD examination due to that B is in an amorphous state. Then the dehydrogenation peak around 434°C is probably related to the decomposition of the unknown phase, which is deduced to be an complex hydride containing Li-Al-B. Therefore, the equation (5) can be modified to equation (6), where the unknown phase was denoted as “Li-Al-B-H". Finally, the appearance of LiAl indicates that LiH had begun to react with Al* to form LiAl and liberate H₂ (equation (4)) before 500°C.

\[
\text{LiBH}_4 + \text{Al} \rightarrow \text{LiH} + \text{AlB}_2 + "\text{Li-Al-B-H}" + \text{B}_2\text{H}_6 \uparrow + \text{H}_2 \uparrow \tag{6}
\]

Compared with the XRD patterns at 500°C, no new phase was detected when the LiBH₄/Al* sample was heated to 600°C. The increase of the relative diffraction intensity of LiAl implies that the reaction of LiH with Al* continued from 500°C to 600°C. The dehydrogenation rate of this reaction reached a peak at 560°C according to Figure 5(d). The existence of LiH and Al suggests that the LiBH₄/Al* system still dehydrogenated incompletely even at 600°C. In fact, the actual dehydrogenation amount of LiBH₄/Al* sample is only 86.11% of the theoretical value (7.2 wt.%) according to Figure 3(a), indicating that there exists some kinetic barriers in the dehydrogenation reaction of LiBH₄/Al* composite.

The whole hydrogen desorption process of the LiBH₄/Al* sample, which is schematically shown in Figure 6, can be concluded as follows: As heating in the crucible, LiBH₄ first transformed from orthorhombic phase (o-LiBH₄) to hexagonal phase (h-LiBH₄) at 112°C and melted at 288°C. Then the molten LiBH₄ reacted with Al* to form LiH, AlB₂ and "Li-Al-B-H" compounds while releasing B₂H₆ and H₂ based on equation (6) around 376°C. With the nucleation and growth of LiH, AlB₂ and "Li-Al-B-H" compounds on the surface of Al*, the reaction stopped when Al* was completely wrapped by these reaction products to form a passivation shell. When the temperature rose to 434°C, the decomposition of "Li-Al-B-H" compounds liberated a certain amount of H₂ and the encapsulated Al* exposed some new surfaces. So the main dehydrogenation reaction of LiBH₄ and Al* occurred around 450°C to form LiH, AlB₂ and H₂ based on equation (3). Similarly, the reaction stopped when the surface of Al* was completely wrapped by LiH and AlB₂. Therefore, the excess molten LiBH₄ underwent self-decomposition to form LiH, B and H₂ (equation (2)) around 472°C. Boron (B) are not detected in the XRD examination because it is in an amorphous state. Finally, the product LiH reacted with Al* to form LiAl alloy and H₂ based on equation (4) when the
sample was heated to 560℃. The actual dehydrogenation amount of LiBH₄/Al* sample did not reach the theoretical value since there were still non-contact and unreacted LiH and Al* at 600℃.

Figure 4. XRD patterns (a) of the LiBH₄/Al* sample obtained at different temperatures (room temperature, 100, 350, 500 and 600℃) and expanded XRD pattern of LiBH₄/Al* sample of 600℃ at 2θ range of 36-48º.

Figure 5. FTIR patterns of the LiBH₄/Al* sample (a) obtained at different temperatures (room temperature, 100, 350, 500 and 600℃) and reference substances (b) include KBr, LiH, amorphous B, and LiBH₄.

Figure 6. Schematic diagram of the dehydrogenation process of the LiBH₄/Al* sample.

3.2. Kinetic properties of the dehydrogenation of LiBH₄/Al* composite
The kinetic properties of the dehydrogenation of LiBH₄/Al* composite was studied using the Kissinger method, which assuming that the apparent activation energy (Eₐ) of dehydrogenation reaction is determined by equation (7).

\[
\ln\left(\frac{\beta}{T_m^2}\right) = -\frac{E_a}{RT_m} + C \quad (7)
\]

In this equation, \(\beta\) is the heating rate in thermal analysis and \(T_m\) represents the absolute temperature at the maximum reaction rate. Besides, \(R\) is the universal gas constant and \(C\) also represents a constant. Therefore, the \(E_a\) of the dehydrogenation reaction of LiBH₄/Al* composite can be obtained from the slope of a linearly fitted line in the \(\ln\left(\frac{\beta}{T_m^2}\right)-T_m^{-1}\) spectrum.

During the kinetic investigations, the LiBH₄/Al and LiBH₄/Al* samples were heated to 600°C at the rates of 5°C/min, 10°C/min and 20°C/min, respectively. The MS curves at various heating rates and the Kissinger spectra reflecting the \(E_a\) of the main dehydrogenation reaction are shown in Figure 7. It can be seen that the temperatures for the maximum dehydrogenation rate of LiBH₄/Al* at the heating rates of 5°C/min, 10°C/min and 20°C/min are 449.9°C, 471.1°C and 485.2°C, respectively. All lower than that of LiBH₄/Al at the same heating rates. The \(E_a\) of the main dehydrogenation reaction of LiBH₄/Al* is calculated to be 163.8 kJ/mol, while that of LiBH₄/Al is 243.5 kJ/mol. This is in good agreement with the previous analysis that the larger specific surface area and higher chemical reactivity of Al* can reduce the activation energy and improve the kinetic properties of the dehydrogenation reaction.

![MS curves and Kissinger spectra](Figure 7.png)

**Figure 7.** MS curves (a), (c) of LiBH₄/Al* and LiBH₄/Al samples at different heating rates (5°C/min, 10°C/min and 20°C/min) and Kissinger spectra (b), (d) that \(\ln\left(\frac{\beta}{T_m^2}\right)\) as a function of \(T_m^{-1}\) for the main dehydrogenation reaction of LiBH₄/Al* and LiBH₄/Al samples.

### 3.3. Reversibility of the LiBH₄/Al* composite
In order to investigate the reversibility of LiBH₄/Al* composite, rehydrogenation test was carried out under 8 MPa H₂ at 400°C. The rehydrogenation curve of the sample is shown in Figure 8. It can be seen that the dehydrogenated LiBH₄/Al* sample quickly absorbed 0.8 wt.% of hydrogen within 2 min at the beginning of test. And then it absorbed 2.6 wt.% of hydrogen in 60 min. After that, it entered the stable hydrogen absorption stage and reached saturation after 480 min. The total rehydrogenation capacity was 5.5 wt.%. Compared with the harsh rehydrogenation conditions reported by other researchers [10], the doping of active Al* derived from AlH₃ effectively improved the reversible hydrogen storage properties of LiBH₄.

![Rehydrogenation Curve](image)

**Figure 8.** The rehydrogenation curve of dehydrogenated LiBH₄/Al* sample under 8 MPa H₂ at 400°C.

The rehydrogenation mechanism exploration was conducted using XRD and FTIR analysis on the rehydrogenated products of LiBH₄/Al* sample, and the results are shown in Fig. 9a and 9b, respectively. It can be seen from the XRD patterns that the diffraction peaks of LiAl, LiH and AlB₂ disappeared, while the diffraction peaks of LiBH₄ reappeared and the diffraction intensity of Al increased after rehydrogenation. Not to mention that the vibrational peaks of B-H stretching (2382 cm⁻¹, 2292 cm⁻¹ and 2224 cm⁻¹) and bending (1125 cm⁻¹) were also detected in the FTIR spectra. Therefore, the reformation of LiBH₄ can be confirmed during the rehydrogenation process. Based on the above analysis, it can be safely concluded that the rehydrogenation process of LiBH₄/Al* is based on equation (8).

\[
\text{LiH} + \text{LiAl} + \text{AlB}_2 + 7/2\text{H}_2 \leftrightarrow 2\text{LiBH}_4 + 2\text{Al} \quad (8)
\]

![XRD and FTIR spectra](image)

**Figure 9.** XRD patterns (a) and FTIR spectra (b) of LiBH₄/Al* sample before and after rehydrogenation.

4. Conclusions
The dehydrogenation of LiBH₄ doped by active Al⁺ derived from AlH₃ has a five-step character:

(1) LiBH₄ + Al → LiH + AlB₂ + "Li-Al-B-H" + B₂H₆ + H₂;
(2) the decomposition of "Li-Al-B-H" compounds liberating H₂;
(3) 2LiBH₄ + Al → 2LiH + AlB₂ + 3H₂;
(4) LiBH₄ → LiH + B + 3/2H₂;
(5) LiH + Al → LiAl + 1/2H₂. And the reversibility of LiBH₄/Al⁺ composite is based on equation as follows: LiH + LiAl + AlB₂ + 7/2H₂ ↔ 2LiBH₄ + 2Al.

The hydrogen desorption kinetics of LiBH₄ were effectively improved by doping with active Al⁺ derived from AlH₃. Higher dehydrogenation capacity, lower activation energy and better reversibility of LiBH₄/Al⁺ can be achieved due to the larger specific surface area and higher chemical reactivity of Al⁺. The extent of dehydrogenation reaction between LiBH₄ and Al⁺ greatly depended on the precipitation and growth of reaction products (LiH, AlB₂ and LiAl, etc.) on the surface of Al⁺. A passivation shell of Al⁺ formed by these products is the kinetic barrier to the dehydrogenation of LiBH₄/Al⁺ composite. Therefore, next work should be focused on cracking the barrier to further improve the hydrogen storage properties of LiBH₄/Al⁺ composite.

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