Cooperative Catalysis on the Dehydrogenation of NdCl3 Doped LiBH4-MgH2 Composites

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To improve the dehydrogenation properties of LiBH4, the MgH2 and NdCl3 were added with different modes by ball-milling, and their influences on the decomposition of LiBH4 were investigated by performing X-ray diffraction (XRD) analysis and dehydriding kinetic measurements. The results show that adding either NdCl3 or MgH2 alone could not promote the decomposition of LiBH4. But for the NdCl3 doped LiBH4-MgH2 composites, not only the decomposition of MgH2 is accelerated, but also the dehydrogenation rate and capacity of LiBH4 are greatly enhanced. The kinetic improvement is attributed to a cooperative catalytic role arising from dual addition of MgH2 and NdCl3. The NdH2 phase, resulting from reaction between MgH2 and NdCl3, might be responsible for the enhanced dehydrogenation of LiBH4.

Keywords: hydrogen storage materials, LiBH4, MgH2, NdCl3, cooperative catalysis

1. Introduction

Safe and efficient hydrogen storage technology is still a key bottleneck for the development of hydrogen energy, especially as an energy carrier for mobile applications. Despite considerable research over the past decades, access to hydrogen storage materials with high reversible capacity and excellent cyclic performance under moderate conditions remains a significant challenge.

Complex hydrides composed of light elements, such as NaAlH4, LiNH2, LiBH4 and ammonia borane, have been of special interest as solid-state hydrogen storage media because of their high gravimetric and volumetric hydrogen capacities, which probably meet the targets set by US Department of Energy for on-board proton exchange membrane fuel-cell driven vehicles. Among various complex hydrides, LiBH4 was firstly investigated as a hydrogen storage candidate by Züttel et al., which desorbed hydrogen up to 13.5 mass% through the decomposition into LiH. However, the sluggish desorption kinetics and harsh rehydrogenation conditions up to 600°C and 35 MPa hydrogen pressure have to be overcome prior to practical applications. Over the past few years, doping a variety of additives, such as metal oxides, chlorides and hydrides, have been attempted to improve the thermal stability as well as the kinetics and reversibility of LiBH4. The strategy of destabilization is to alter the reaction route of LiBH4 and thereby decrease the reaction enthalpy and energy activation. Yu et al. found that a redox reaction between LiBH4 and oxides greatly lowered the dehydrogenation temperature, and the order of destabilization effect was Fe2O3 > V2O5 > Nb2O5 > TiO2 > SiO2. Zhang et al. destabilized LiBH4 with SiO2/TiF3 and decreased the onset dehydrogenation temperature by about 100°C from that of LiBH4-SiO2, and the addition of TiF3 reduced the energy activation via a preferential reaction with LiBH4 at their interface. Vajo et al. showed that LiBH4 could be rehydrogenated at temperature over 350°C by adding MgH2, the formation of MgB2 accounted for a lowered reaction enthalpy by 25 kJ/(mol H2). In situ X-ray diffraction measurement also revealed the importance of the MgB2 platelets acting as nucleation substrate as well as the limitation to reaction rate. To further improve the dehydrogenation/rehydrogenation kinetics, catalytic transition-metal-based additives were added. In the LiBH4-MgH2-Nb2O5 composite system, Fan et al. demonstrated that the intermediate compound NbH2, which was in situ synthesized in the milling process, enhanced the reversible reaction kinetics through promoting the formation of MgB2. Furthermore, the addition of transition-metal additives might result in spontaneous formation and decomposition of transition-metal borides during dehydrogenation/rehydrogenation cycle, the resultant nanoparticles of transition-metal compounds were highly dispersed in the composite and acted as efficient catalysts. Similar catalytic boride compounds were also found in other systems, such as AlB2 in the LiBH4-Al composite system, and NiB in the LiBH4-Ni composite system.

Nevertheless, to destabilize LiBH4 and enhance its kinetic performances, exploring new methods and mechanisms are still matters of great interest. Hereby, we demonstrates that a novel rare-earth metal chloride NdCl3, which has been proved to be an effective catalyst for the decomposition of NaAlH4, plays catalytic role on the dehydrogenation of LiBH4-MgH2 composites, and a cooperative catalytic mechanism is revealed in the LiBH4-MgH2-NdCl3 system through detailed investigations on the microstructure and dehydrogenation properties.

2. Experimental

Commercial powders of LiBH4 (>90%), MgH2 (>95%) and NdCl3 (>99.9%) were purchased from Alfa Aesar Co. and used without additional purification. LiBH4 and MgH2 were mixed with the molar ratio 2 : 1, 1 : 1 and 1 : 2, with and without addition of 20 mass% NdCl3. Afterward, the powder mixtures were milled in a vibratory mill (QM-1SP, Nanjing, China) at 1200 rpm for 300 min with ball-to-powder...
weight ratio 20 : 1. To avoid temperature over rising, milling time of 5 min was alternated with 5 min of rest.

Structural characterization for the studied samples was carried out by powder X-ray diffraction (XRD) using Philips X’Pert X-ray diffractometer with Cu Kα radiation. The powders for XRD experiments were filled in a glass holder and sealed with a 3M scotch tape. Dehydrogenation properties were measured by a Sieverts apparatus (Advance Materials Corporation). Samples were heated in a vacuum chamber with a constant volume, and the evolution of hydrogen pressure as function of time was recorded to evaluate the isothermal dehydrogenation kinetics at 330°C.

To prevent LiBH₄ exposed to air, all sample handlings were performed in a glove box under high pure argon atmosphere with water and oxygen concentration less than 3 ppm.

3. Results and Discussions

Figure 1 shows the dehydrogenation properties of as-milled LiBH₄-MgH₂ composites with different molar ratios of LiBH₄ to MgH₂ (2 : 1, 1 : 1, 1 : 2) at 330°C, the dehydridding properties of both pure LiBH₄ and pure MgH₂ milled under same milling conditions were also compared. As seen from Fig. 1, pure LiBH₄ hardly decomposed and pure MgH₂ desorbed hydrogen very slowly at this temperature, while the milled LiBH₄-MgH₂ composites show enhanced dehydridding kinetics, especially for the second step of hydrogen release. Furthermore, the two-step hydrogen release characteristic implied that the decomposition reactions of LiBH₄ and MgH₂ proceeded respectively. From the XRD patterns (Fig. 2) for the dehydrogenated LiBH₄-MgH₂ composites, the presence of Mg peaks and the absence of MgH₂ peaks indicated that MgH₂ decomposed completely. By comparing the diffraction intensity of LiBH₄ peaks for the LiBH₄-MgH₂-MgB₂ composite after milling (Fig. 6(a)) and after dehydrogenation (Fig. 2(c)), it can be concluded that LiBH₄ partially decomposed at this temperature. Thereby, LiBH₄ should contribute to the first step dehydrogenation with lower desorption capacity although the incubation of MgH₂ may be included in this phase, while the second step dehydrogenation can be assigned to the decomposition of MgH₂. In addition, no diffraction peaks of reaction products such as MgB₂ were detected, which means that no reaction occurred in the LiBH₄-MgH₂ composites, which is not like previous reports on the LiBH₄-MgH₂ system. It should be due to relative low dehydrogenation temperature in our experiment. The present MgO indicates that small amount of oxidation is unavoidable in our experiments. In summary, the dehydrogenation properties of LiBH₄ could not be greatly improved by adding MgH₂.

When adding 20 mass% NdCl₃ into the LiBH₄-MgH₂ composites, the dehydrogenation characteristic was remarkably changed. Figure 3 displays the dehydridding kinetic curves of the NdCl₃ doped LiBH₄-MgH₂ composites with different molar ratios at 330°C, the LiBH₄-MgH₂-NdCl₃ composites showed faster dehydrogenation rate as well as larger desorption capacity despite fewer practical mass of hydrides in comparison with undoped LiBH₄-MgH₂ composites. Unlike the two-step hydrogen release process of LiBH₄-MgH₂ composites, the NdCl₃ doped LiBH₄-MgH₂ desorbed hydrogen rapidly and reached equilibrium state in 30 min. As seen from the XRD patterns (Fig. 4) for the dehydrogenated LiBH₄-MgH₂-NdCl₃ composites, the ab-

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Fig. 1 Dehydriding curves at 330°C of pure LiBH₄ and the LiBH₄-MgH₂ composites with different molar ratios.

Fig. 2 XRD patterns of LiBH₄-MgH₂ composites after dehydrogenation.

Fig. 3 Dehydriding curves at 330°C of NdCl₃ doped LiBH₄-MgH₂ composites.
sence of MgH$_2$ peaks and the presence of weak LiBH$_4$ peaks indicated that all of MgH$_2$ and most of LiBH$_4$ decomposed completely. The results indicate that the NdCl$_3$ plays catalytic role on the dehydrogenation of LiBH$_4$-MgH$_2$ composites, especially on the dehydrogenation of the LiBH$_4$ constituent. The existence of LiCl (Fig. 4) suggested that NdCl$_3$ reacted with LiBH$_4$ and facilitated its dehydrogenation. It is worth noting that diffraction of LiCl becomes stronger with smaller ratio of LiBH$_4$ to MgH$_2$, it appeared that NdCl$_3$ could not directly react with LiBH$_4$. In addition, trace NdH$_2$ phase is identified by a fairly weak diffraction peak at 28.2° in Fig. 4(c), which reveals the chemical state of Nd.

To reveal the catalytic role of NdCl$_3$ on the dehydrogenation of LiBH$_4$-MgH$_2$ composites, the LiBH$_4$ and the MgH$_2$ was respectively milled with 20 mass% NdCl$_3$ under same milling conditions, and their dehydrogenation properties at 330°C were compared with those of LiBH$_4$-MgH$_2$ composite (molar ratio 1:1) with and without addition of NdCl$_3$. The result, shown in Fig. 5, demonstrates different catalytic effect of NdCl$_3$ on the decomposition of MgH$_2$ and LiBH$_4$. The NdCl$_3$ doped LiBH$_4$ showed negligible catalytic hydrogen kinetics improvement, while for the NdCl$_3$ doped MgH$_2$, the incubation period almost disappears and the desorption process speeds up greatly comparing with those of pure MgH$_2$ and the MgH$_2$ constituent of LiBH$_4$-MgH$_2$ (Fig. 1). In summary, since the individual addition of NdCl$_3$ or MgH$_2$ could not catalyze the dehydrogenation of LiBH$_4$, it is reasonable to propose that there exists a cooperative catalytic effect in the LiBH$_4$-MgH$_2$-NdCl$_3$ composites owing to joint addition of NdCl$_3$ and MgH$_2$.

To quantitatively reveal this so-called cooperative catalytic effect, the dehydrogenation capacities of LiBH$_4$-MgH$_2$-NdCl$_3$ composites were compared and shown in Table 1. When considering the theoretical hydrogen release capacities of LiBH$_4$ and MgH$_2$ (13.9 and 7.7 mass%, respectively) and their purities, the total theoretical capacities of LiBH$_4$-MgH$_2$ composites having molar ratio 2:1, 1:1, 1:2 are 10.6, 9.8, 9.1 mass% respectively, which are far greater than the measured values (2.8, 3.9, 5.3 mass% respectively). We also notice that the practical desorption capacities of LiBH$_4$-MgH$_2$ composites are close to theoretical values (2.7, 4.0, 5.3 mass%, respectively) of the MgH$_2$ constituent in the LiBH$_4$-MgH$_2$ composites, and it should be related with partial decomposition of MgH$_2$ during milling, which was confirmed by the XRD pattern for as-milled LiBH$_4$-2MgH$_2$ composite (Fig. 6(a)). When adding NdCl$_3$ to the LiBH$_4$-MgH$_2$ composites with molar ratio 2:1, 1:1, 1:2, the total dehydrogenation capacities increases up to 3.3, 4.5, 5.8 mass% respectively. By subtracting the fraction of NdCl$_3$, the re-calculated dehydrogenation contents are 4.1, 5.6, 7.2 mass% respectively, which are greater than theoretical capacity of the MgH$_2$ constituent in the LiBH$_4$-MgH$_2$ composites. Obviously, the dehydrogenation of the LiBH$_4$ constituent in the LiBH$_4$-MgH$_2$-NdCl$_3$ composites was catalyzed. With increasing amount of MgH$_2$, the LiBH$_4$...
undertook more decomposition and contributed more to the total dehydrogenation capacity. Therefore, it is further proved that this cooperative catalytic role should arise from dual addition of MgH$_2$ and NdCl$_3$.

Combining with XRD analysis above mentioned, we infer that the catalytic role of NdCl$_3$ is realized through reacting with MgH$_2$, which results in the formation of NdH$_2$ phase. The existence of NdH$_2$ is further confirmed by the XRD pattern (Fig. 6(b)) of dehydrogenated MgH$_2$-50 mass% NdCl$_3$. It is believed that the in situ formed NdH$_2$ phase might catalyze the dehydrogenation of LiBH$_4$. The more doping content of MgH$_2$, the more fraction of NdH$_2$, and thus better catalytic effect on the decomposition of LiBH$_4$ was obtained.

4. Conclusions

The dehydrogenation properties of LiBH$_4$-MgH$_2$ composites with and without addition of NdCl$_3$ were investigated. Individually adding NdCl$_3$ or MgH$_2$ could not promote the decomposition of LiBH$_4$, only the NdCl$_3$ doped LiBH$_4$-MgH$_2$ composites showed enhanced dehydrogenation kinetics and high desorption capacity, which was attributed to a cooperative catalytic effect originating from reaction between MgH$_2$ and NdCl$_3$, the resultant NdH$_2$ phase might act as real catalysts on the dehydrogenation of LiBH$_4$. Further work to reveal the detailed catalytic mechanism of NdH$_2$ and to improve the hydrogen storage properties of LiBH$_4$ is under way.

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