

CATALYZED LiBH₄ AND MgH₂ FOR HYDROGEN STORAGE

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Introduction

Because of global warming and oil price crisis, alternative energies such as hydrogen have gained much attention for decades. In this case, hydrogen produces energy by reacting with oxygen within a fuel cell. Air is the major source of oxygen while hydrogen sources could be from a hydrogen storage system. High-pressure gas tank, liquidified hydrogen, carbon nanomaterial, and metal hydride are the examples. The metal hydride material shows a number of advantages namely safety, weight, hydrogen capacity, and reversibility.

LiBH₄ is one of the candidates due to its extremely high theoretical hydrogen capacity of 18.4 wt%. Nevertheless, the hydride is rather stable for viable applications since it decomposes to produce hydrogen at temperatures higher than 400°C, and its reversibility is still an issue [1]. Recently, two independent groups, Vajo et. al. [2] and Bösenberg et. al. [3], destabilized LiBH₄ by mixing with MgH₂. The overall reaction is as follows:



The theoretical hydrogen storage capacity is reduced to 11.4 wt%. The decomposition consists of two steps. The first step corresponds with MgH₂ decomposition, while the later step is with the decomposition of both LiBH₄ and LiBH₄/Mg to from MgB₂ and LiH. In addition, hydrogen desorption temperature is reduced to 350°C and reversibility is much improved as compared with pure LiBH₄.

In this work, the hydrogen desorption behaviors of the LiBH₄/MgH₂ mixture were explored by investigating the effects of doping the hydride mixture with different catalysts namely metallic Ti, TiCl₃, VCl₃, HfCl₄, and ZrCl₄. In addition, effect of the milling time for the sample preparation was also studied.

Experimental

To prevent air and moisture, all preparation steps were performed under nitrogen atmosphere. The as-received metal hydrides, a 2:1 molar ratio of LiBH₄ (95%, Acro) and MgH₂ (90%, Acro) were mixed together with a 3 mol% catalyst – metallic Ti (99.99%, mesh 325), TiCl₃ (99.99%), VCl₃ (99.99%), HfCl₄ (99.99%), and ZrCl₄ (99.99%) purchased from Sigma-Aldrich – by using a centrifugal ball mill (Retsch, model S100, ball to powder ratio of 40:1) at a speed 300 rpm for 1 h. For the Ti-LiBH₄/MgH₂ mixture, the milling time was increased to 5 and 10 h.

The hydrogen desorption behaviors of the samples were examined by using the TPDRO 1100 (ThermoFinnigan) directly connected to an MS to measure the released hydrogen and the DSC 822 (METTLER TOLEDO). For both apparatuses, the sample temperature was ramped from 50 to 500°C by using a heating rate of 5°C min⁻¹.

Results and the discussion

Initial hydrogen desorption behavior of each catalyzed LiBH₄/MgH₂ mixture was assessed using TPD-MS. The results, which cover the temperature range of 50-500°C, are shown in Figure 1.

All catalyzed LiBH₄/MgH₂ mixtures release hydrogen more than two steps. In particular, one of these steps, at the temperature range of 250-350°C, is the hydrogen desorption from MgH₂. The small desorption peaks at 100°C found only with the LiBH₄/MgH₂ and TiCl₃-LiBH₄/MgH₂ mixtures are probably resulted from the reaction among the starting materials during the milling process. Moreover, the TiCl₃-LiBH₄/MgH₂ mixture starts to release hydrogen at the lowest temperature of 260°C, which is about 40°C lower than that of the LiBH₄/MgH₂ mixture.

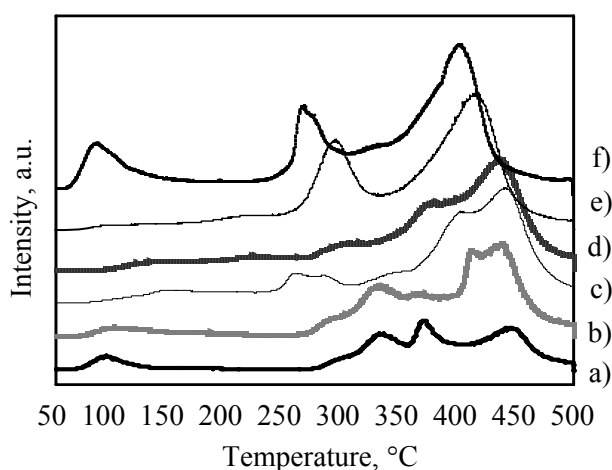


Fig. 1. TPD-MS profiles of a) $\text{LiBH}_4/\text{MgH}_2$, b) $\text{Ti-LiBH}_4/\text{MgH}_2$, c) $\text{HfCl}_4\text{-LiBH}_4/\text{MgH}_2$, d) $\text{VCl}_3\text{-LiBH}_4/\text{MgH}_2$, e) $\text{ZrCl}_4\text{-LiBH}_4/\text{MgH}_2$, and f) $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$.

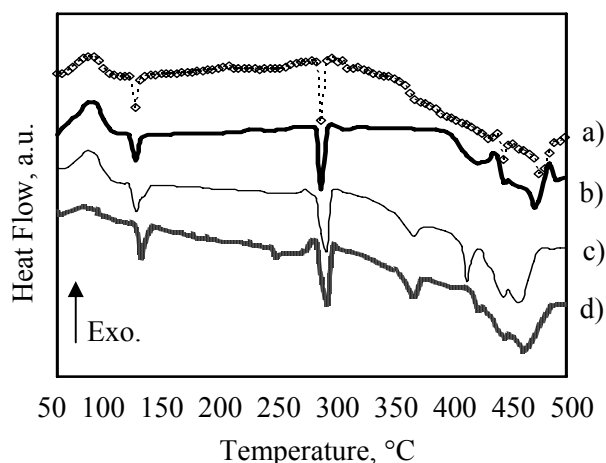


Fig. 2. DSC patterns of the $\text{Ti-LiBH}_4/\text{MgH}_2$ mixture after milling for a) 1 h (pre-milled Ti for 10 h), b) 1 h, c) 5 h, and d) 10 h.

As the milling time was reported to affect the kinetics of hydrogen desorption from MgH_2 containing Ti [4], the milling time was increased from 1 to 5 and 10 h. The DSC patterns of the effect from the milling time are shown in Figure 2. It was found that, after the increase in the milling time, both endothermic peaks at around 115 and 286°C, which represent the phase transition and melting point of LiBH_4 , respectively, are shift to higher temperatures. In addition, the starting hydrogen desorption temperature is reduced from 400°C for the $\text{Ti-LiBH}_4/\text{MgH}_2$ mixture milled 1 h to 350°C for both the $\text{Ti-LiBH}_4/\text{MgH}_2$ mixture

milled for 5 and 10 h. Metallic Ti was also pre-milled for 10 h before mixing with the hydride mixture and milled for 1 h. Interestingly, the mixture also exhibits the same desorption temperature as the $\text{Ti-LiBH}_4/\text{MgH}_2$ mixture milled for 10 h. This implies that the hydrogen desorption temperature may depend on both particle size and surface area of Ti.

Conclusions

The hydrogen desorption temperature of the $\text{LiBH}_4/\text{MgH}_2$ mixture could be reduced by doping a suitable type and size of catalyst. At the same milling time of 1 h, the $\text{TiCl}_3\text{-LiBH}_4/\text{MgH}_2$ mixture gave the lowest hydrogen desorption temperature while the $\text{Ti-LiBH}_4/\text{MgH}_2$ mixture gave the highest hydrogen desorption temperature. However, the hydrogen desorption temperature might be improved by reducing the particle size of the catalyst.

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