Research Article

Effects of Ti-Based Additives on the Hydrogen Storage Properties of a LiBH$_4$/CaH$_2$ Destabilized System

Hongwei Yang, Adeola Ibikunle, and Andrew J. Goudy

Department of Chemistry, Delaware State University, Dover, DE 19901, USA

Correspondence should be addressed to Andrew J. Goudy, agoudy@desu.edu

Received 26 May 2010; Accepted 5 August 2010

1. Introduction

LiBH$_4$ has attracted considerable attention for hydrogen storage in the past few years because it can theoretically release 13.6 wt% hydrogen when it decomposes to LiH and B [1]. However, the enthalpy of this reaction is about 72 kJ/mole H$_2$, and therefore the dehydrogenation of LiBH$_4$ initiates at about 400°C and has its maximum at around 600°C, which is too high to be able to meet DOE’s goals for on-board hydrogen storage systems [2]. By adopting a so-called “destabilization” concept first developed by Reilly and Wiswall [3], Vajo et al. [4, 5] modified the thermodynamics of LiBH$_4$ by coupling LiBH$_4$ and MgH$_2$ together with a small amount of TiCl$_3$ added as catalyst. The addition of MgH$_2$ as a destabilizing reactant changes the reaction pathway and thus reduces the enthalpy of dehydrogenation. Compared with pure LiBH$_4$, the mixture of MgH$_2$/LiBH$_4$ not only had a lower dehydrogenation temperature but more importantly achieved reversibility under moderate conditions. A similar strategy was also applied in mixing LiBH$_4$ with other destabilizing additives, such as LiNH$_2$ [6], metal oxides, and metal chlorides [7, 8].

There are a large number of reaction schemes that could form a destabilized hydrogen storage system. One of reaction schemes that has the potential to meet DOE’s goals for hydrogen storage is the destabilization of LiBH$_4$ using CaH$_2$ as destabilizing reactant, according to the following reaction:

$$6\text{LiBH}_4 + \text{CaH}_2 \rightarrow 6\text{LiH} + \text{CaB}_6 + 10\text{H}_2 \quad (1)$$

This reaction can theoretically release about 11.7 wt% hydrogen. In addition, the enthalpy for this reaction, calculated by Alapati et al. [9, 10], is about 47 kJ/mol H$_2$, which falls within the range of 30–60 kJ/mol estimated for a reversible hydrogen storage system.

Yang et al. [11] reported that samples of 6LiBH$_4$ + CaH$_2$ released about 5.1 wt% of hydrogen at 395°C and that the formation of decomposition product, CaB$_6$, was confirmed by XRD. However, they found that the dehydrogenated sample was not capable of being reversed under 150 bar H$_2$ and 350°C. Barkhordarian et al. [12] had a similar result that a ball milled sample of 6LiH + CaB$_6$ failed to hydrogenate even under a more harsh condition (400°C, 350 bar H$_2$ for 1440 min). In contrast, Pinkerton and Meyer [13] reported that samples of 6LiBH$_4$ + CaH$_2$ + 0.25 TiCl$_3$ prepared by ball milling released about 9.1 wt% of hydrogen during a TGA scan and that the dehydrogenated samples were successfully rehydrogenated under 83 bar H$_2$ and 400°C. In their study, TiCl$_3$ was added as a catalyst in order to increase the kinetics of hydrogen release and
rehydrogenation. However, it is well known that catalyst additives reduce hydrogen storage capacity even though they could lower the dehydrogenation temperature and improve the reversibility. Therefore, it is desirable to know how the amount of a given additive will affect the hydrogen storage properties of the system of interest. In our research, we first examined the effects of three different Ti-based additives on the dehydrogenation temperature of the LiBH₄/CaH₂ system. Much of the work has focused on the effects of additive content on the reversible hydrogen storage properties of the LiBH₄/CaH₂ system, including not only the dehydrogenation temperature, but also the reversibility and the activation energy of dehydrogenation for the system.

2. Experimental Section

The starting materials used in this research were all greater than 95 percent pure. They were obtained from Sigma Aldrich and used without further purification. All samples were handled in a Vacuum Atmospheres argon-filled glove box to protect them from exposure to air and moisture. The glove box was capable of achieving less than 1 ppm oxygen and moisture.

Ball milling was used for the preparation of samples. The milling was carried out in a SPEX 8000M Mixer Mill that contained a 25 mL stainless steel milling pot with ball to powder ratio equal to 10:1. Prior to analyses, the LiBH₄/CaH₂ mixtures with various additives were placed in the milling pot with three 11 mm diameter balls under an argon atmosphere. Each reaction mixture was ball milled for up to 10 hours.

Simultaneous thermal analysis, a combination of Thermal Gravimetric and Differential Thermal Analysis (TG/DTA), was conducted to determine the thermal stability and the hydrogen capacity of the mixtures using a Perkin Elmer Diamond TG/DTA. This technique can measure both actual mass and heat flux of the samples at the same time, which leads to a more correct interpretation and correlation between the two types of signals collected. This instrument was placed inside of an argon-filled glove box so that samples could be analyzed with virtually no exposure to air and moisture. Because of the effects of the heating rate with regards to the TGA decomposition onset temperature, the samples were always heated at 4 degrees per minute to study the thermal stability and the hydrogen capacity. The heating rate was set at 1, 4, 10, and 15 degree per minute when the activation energy of the samples was investigated.

Temperature-programmed desorption (TPD) measurements were done by using a Sieverts-type apparatus manufactured by the Advanced Materials Corporation. About 1.0 g of sample was used, and the temperature was ramped from ambient to 500°C at a rate of 5°C/min. The rehydrogenation processes were conducted at 450°C under 100 bar of pressure for 15 hrs in the same Sieverts apparatus.

X-ray powder diffraction analyses were used to determine phase purity and to determine if a reaction had occurred. A Panalytical X’Pert Pro MPD Analytical X-Ray Diffractometer Model PW3040 Pro was used for these analyses. Analyses were done using copper K-alpha radiation. Samples were covered with a Mylar film to protect them from air and moisture. Since the Mylar has three peaks in the 2θ range of 20 to 28 degrees, they were manually excluded from the XRD raw data file.

3. Results and Discussion

3.1. Thermal Decomposition Properties. In this study, LiBH₄/CaH₂ mixtures were ball milled with 4 mol% of three different additives, TiCl₃, TiF₅, and TiO₂, respectively. These additives were chosen because they have been found to have the ability to lower the desorption temperatures in other complex hydrides such as the alanates. One of the goals of this study was to determine how well they would work for the LiBH₄/CaH₂ system. TG/DTA measurements were done on these samples to find the effect of these additives on lowering the hydrogen desorption temperature and affecting the hydrogen capacity of these samples. It was shown from the DTA results in Figure 1(a) that each curve contains three distinct endothermic peaks. The first two peaks, observed around 110°C and 280°C, correspond to the polymorphic phase transformation from an orthorhombic to a hexagonal structure and the melting of LiBH₄, respectively. The third endothermic peak corresponds to the hydrogen release reaction of each mixture. The position of this peak represents the temperature at which the dehydrogenation reaction has the maximum rate. It can be seen from Figure 1(a) that the as-milled mixtures of LiBH₄/CaH₂ with 4 mol% of TiCl₃, TiF₅, and TiO₂ show the maximum dehydrogenation rate at 438, 442, and 454°C, respectively. This indicates that TiCl₃ is relatively more effective in lowering the hydrogen desorption temperature of the LiBH₄/CaH₂ mixtures than the other two additives though the dehydrogenation temperatures of all three mixtures are still high for on-board hydrogen storage purposes. It can also be seen that the third exothermic peak may actually consist of two or more dips. The reason for this is unknown but, since the mechanism for decomposition may consist of more than one step, the extradips could possibly be caused by different steps in the mechanism.

Figure 1(b) contains TGA results for the as-milled LiBH₄/CaH₂ mixtures with 4 mol% of additives as mentioned above. It can be seen that dehydrogenation of the LiBH₄/CaH₂ mixtures starts from around 250°C, which is much lower than that of pure LiBH₄. All mixtures continue slowly releasing about 1 wt% of hydrogen until the temperature increases up to 400°C, after which dehydrogenation of these mixtures proceeds at a much faster rate. It is shown that the mixtures with three different additives all release about 11-12 wt% hydrogen. This amount is close to the theoretical value of 11.7 wt%. It is known that the presence of additives may reduce the amount of released hydrogen. However, 4 mol% is a relatively small amount of additive, which reduces the theoretical hydrogen capacity of LiBH₄/CaH₂ mixtures by 0.4 wt% if the mass of additives is the only factor to be taken into account. Such a small change may not be detected in TGA measurements. When the amount of additives is increased, however, their effects on hydrogen capacity will become more obvious and thus measurable.
In a further attempt to determine how the amount of Ti-based additives affects the hydrogen desorption process of LiBH₄/CaH₂ mixtures, a study was done by ball milling LiBH₄/CaH₂ mixtures with 4, 10, and 25 mol% of TiCl₃, respectively. The DTA results in Figure 2(a) show that for the samples with 4, 10, and 25 mol% of TiCl₃, the endothermic peak corresponding to the maximum dehydrogenation rate occurs at 438, 428 and 411 °C, respectively. Attempts to explain this result will be made later in this paper.

TGA curves in Figure 2(b) show the change in hydrogen capacity of the mixtures with different amount of additives. It can be seen that the samples with 4, 10, and 25 mol% of TiCl₃ release about 11.2, 9.7, and 8.1 wt% of hydrogen, respectively. As expected, all of the numbers are lower than the theoretical value of 11.7 wt%. It is clearly seen from Figure 2(b) that the samples with larger amounts of additives will release less hydrogen than the ones with smaller amounts of additives even though the former ones release hydrogen at a lower temperature than the later ones. Two types of reasons are generally taken into account for the reduced hydrogen capacity of the samples. Firstly, the physical presence of TiCl₃ additives lowers the hydrogen capacity of the samples. Secondly, chemical reaction of TiCl₃ with LiBH₄/CaH₂ mixtures during the ball milling could further decrease the hydrogen capacity. This is supported by a calculation based on HSC chemistry [14], which shows that TiCl₃ reacts with LiBH₄/CaH₂ to form LiCl, TiB₂, and CaCl₂, releasing hydrogen at the same time. The reduction in hydrogen capacity as a function of TiCl₃ additives is illustrated in Figure 3. The total loss of hydrogen capacity is obtained by comparing the TGA data with the theoretical value of 11.7 wt% for LiBH₄/CaH₂ mixtures. The reduction in capacity due to the physical presence of TiCl₃ additives, which is represented by the grey bars in Figure 3, is calculated based on the amount of TiCl₃ added to each mixture. The reduction caused by the chemical reaction of TiCl₃ with LiBH₄/CaH₂ mixtures, which is represented by the dark bars, is estimated by taking the difference between the total loss of capacity and that contributed from the physical presence of the additives. It can be seen from Figure 3 that at a lower level of TiCl₃ additives, there is a very small contribution to the total hydrogen capacity reduction as
4

Figure 3: Hydrogen capacity reduction of the LiBH₄/CaH₂ mixture with 4, 10, and 25 mol% of TiCl₃ additive.

3.2. Reversibility. Temperature-programmed desorption (TPD) measurements were used to study the reversibility of LiBH₄/CaH₂ mixtures with TiCl₃ additives. Figure 4(a) shows the results for samples with 4 mol% TiCl₃ after the 1st desorption (as-milled sample) and after the 2nd desorption (rehydrogenated sample). Figure 4(b) contains the results for the samples with 25 mol% TiCl₃ done under the same conditions. It is shown that the two as-milled samples release about 10.9 and 9.2 wt% of hydrogen, respectively, which are close to the data obtained from TGA measurement. The rehydrogenation process was done at 450°C under 100 bar for 15 hrs. It can be seen from Figures 4(a) and 4(b) that both of the rehydrogenated samples with 4 and 25 mol% TiCl₃ preserve most of their hydrogen capacity after the 1st dehydriding-rehydriding cycle. The sample with 4 mol% TiCl₃ releases 9.9 wt% of hydrogen during the second desorption, which is similar to the result from the pressure-composition isotherm (PCI) measurements in our previous report [15]. The sample with 25 mol% TiCl₃ desorbs 8.9 wt% of hydrogen, and a slightly higher number was reported [13] for an identical sample after similar rehydrogenation process. On the other hand, Yang et al. [11] were not able to rehydrogenate the LiBH₄/CaH₂ mixtures without any additives under 150 bar H₂ and 350°C after the sample was successfully dehydrogenated. It is illustrated in Figure 4 that even with a lower amount of TiCl₃ (compared to 20 or 25 mol% in the similar studies [13, 14]), the dehydrogenated LiBH₄/CaH₂ sample is able to be rehydrogenated, which indicates that the presence of additives plays a critical role in overcoming the energy barrier of the rehydrogenation process for LiBH₄/CaH₂ mixtures.

There is also a noteworthy difference in TPD curves between the as-milled and rehydrogenated samples. TPD curves for the as-milled samples show an early stage dehydrogenation process, starting from about 250°C and 200°C for the samples with 4 and 25 mol% TiCl₃, in which about 1-2 wt% hydrogen is released before the dehydrogenation becomes much faster. However, this preliminary dehydrogenation process does not appear in the TPD curves for the rehydrogenated samples, which is more obvious for the sample with 25 mol% TiCl₃. One possible reason is that at the beginning of the TPD, TiCl₃ additives in the as-milled samples may continue to react with LiBH₄/CaH₂ mixtures as happened during the ball milling, resulting in early hydrogen release and some by-products.

XRD measurements were also done on the rehydrogenated LiBH₄ + CaH₂ mixtures. Figure 5 contains spectra for the samples with 0, 4, and 25 mol% TiCl₃ additives, respectively. The XRD patterns show that CaH₂ and LiBH₄ exist in the rehydrogenated sample with no TiCl₃. However, it is obvious that there is also a significant amount of CaB₆ and LiH remaining in this sample after the re-hydrogenation process. On the other hand, the XRD patterns clearly show that the samples with either 4 mol% or 25 mol% of TiCl₃ are able to be rehydrogenated back to LiBH₄ + CaH₂ and that there are no visible peaks from either CaB₆ or LiH. This result indicates that the presence of additives plays a critical role in enhancing the re-hydrogenation process. Unlike the study made by Pinkerton and Meyer [13], however, the LiCl peaks resulting from the reaction between LiBH₄ and TiCl₃ remain in the rehydrogenated sample with TiCl₃. As is shown in Figure 5, the sample with 25 mol% TiCl₃ has stronger LiCl peaks than the one with 4 mol% TiCl₃. This indicates that more LiBH₄ is consumed for the sample with 25 mol% TiCl₃, which causes more H₂ capacity loss for this sample than the one with 4 mol% TiCl₃. It is also found that the peaks identified as CaCl₂ appear in the XRD patterns for both 4 and 25 mol% TiCl₃-containing samples after re-hydrogenation. This is possibly due to the reaction between CaH₂ and TiCl₃ during dehydrogenation/re-hydrogenation.

3.3. Activation Energy of Dehydrogenation. To further understand the effects of TiCl₃ additives on dehydrogenation of LiBH₄/CaH₂ mixtures, the activation energies of dehydrogenation for the samples with different amounts of TiCl₃ additives were investigated using an isothermal method based on the Kissinger equation [16, 17]:

$$\ln \left( \frac{\beta}{T_{\text{max}}} \right) = - \frac{E_a}{R} \left( \frac{1}{T_{\text{max}}} \right) + f_{\text{KAS}}(\alpha),$$  \hspace{1cm} (2)$$

where $T_{\text{max}}$ is the temperature at the maximum reaction rate, $\beta$ the heating rate, $E_a$ the activation energy, $\alpha$ the fraction of transformation, $f_{\text{KAS}}(\alpha)$ a function of the fraction of transformation, and $R$ is the gas constant.
Figure 4: TPD of the as-milled and rehydrogenated LiBH$_4$/CaH$_2$ mixture with (a) 4 mol% and (b) 25 mol% of TiCl$_3$ additive.

Figure 5: XRD patterns of the rehydrogenated LiBH$_4$/CaH$_2$ mixture with a different amount of TiCl$_3$ additive: (a) none, (b) 4 mol%, and (c) 25 mol%.

Figure 6 shows the DTA curves for the as-milled LiBH$_4$/CaH$_2$ mixtures with 25 mol% TiCl$_3$ as a function of constant heating rate. As expected, the endothermic peak corresponding to the maximum rate of dehydrogenation shifts to higher temperatures with increasing heating rate.

Figure 7: Activation plots using Kissinger equation for the LiBH$_4$/CaH$_2$ mixture with 4, 10, and 25 mol% of TiCl$_3$ additive.
temperatures when the heating rate is increased. The same trend is also observed for the samples with lower amount of TiCl3 additives. The plots based on the Kissinger equation are shown in Figure 7. It can be seen that good linear relationships between ln(β/Tmax) and 1/Tmax are present for all three samples with 4, 10, and 25 mol% of TiCl3 and that the activation energy of dehydrogenation can be calculated from the slope of the straight lines in Figure 7. Note that the activation energy for the sample with 4 mol% TiCl3 additives is 141 kJ/mol. As the amount of TiCl3 increases, the activation energy decreases. For the sample with 10 mol% TiCl3, the activation energy is reduced to 126 kJ/mol, while for the sample with 25 mol% TiCl3, the activation energy is further reduced to 110 kJ/mol. This may also explain the fact that higher levels of Ti-based additives lead to lower dehydriding temperatures for the LiBH4/CaH2 mixtures as was shown in TG/DTA measurements.

The reduction in the activation energy observed in this study is believed to be the result of a change in the energy state of the reactants due to addition of TiCl3. However, there has been no clear mechanism to explain the effects of Ti-based catalysts on enhancing the dehydrogenation/rehydrogenation properties of certain complex hydride materials. Some studies on NaAlH4 with Ti precursors show that the transition metal Ti could enter the entire Na+ sublattice as a variable valence species to produce vacancies of de- and rehydrogenation. Further studies are needed to determine the role of TiCl3 additives in the LiBH4/CaH2 system.

4. Conclusions

The hydrogen storage properties of LiBH4/CaH2 mixtures with Ti-based additives have been investigated. TG/DTA results show that TiCl3 is more effective in lowering the hydrogen desorption temperature than TiF3 and TiO2. The results also show that higher amounts of TiCl3 additives lead to lower dehydrogenation temperature but this is offset by a larger reduction in the hydrogen capacity of the mixture. TPD and XRD measurements indicate that a catalytic effect may play a role in the reversibility of this system. It was also found that the activation energy of this system is reduced as the amount of TiCl3 additives increases. This is consistent with the fact that a lower dehydrogenation temperature is observed for mixtures with a higher amount of TiCl3 additives. Further study on the mechanism of this phenomenon is needed.

Acknowledgments

This paper was financially supported by grants from the BP Foundation, the US Department of Energy, and the US Department of Transportation.

References

