Hydrogen Sorption Behavior of the ScH₂–LiBH₄ System: Experimental Assessment of Chemical Destabilization Effects

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The hydrogen storage reaction ScH₂ + 2LiBH₄ → ScB₂ + 2LiH + 4H₂ (8.91 wt %), based on the thermodynamic destabilization of LiBH₄, is predicted to have a reaction enthalpy of ΔH₃₀⁰K = 34.1 kJ/mol H₂. The isothermal kinetic desorption behavior in this system was measured. At temperatures up to 450 °C, less than 5 wt % H₂ is released, which is half of the theoretical capacity. Powder X-ray diffraction data indicate that LiBH₄ has decomposed into LiH in the final desorption product, but the data provide no evidence that ScH₂ has participated in the reaction. Magic angle spinning NMR (MAS NMR) results do not show that the expected ScB₂ equilibrium product phase has formed during desorption. While the addition of 2 mol % TiCl₃ catalyst does improve desorption kinetics at 280 °C, it does not otherwise assist the destabilization reaction. The calculated reaction enthalpies suggest that this system should be of interest at moderate temperatures, but the large heats of formation of the reactant phases in this system appear to play a critical role in determining overall kinetics. Furthermore, the formation of a Li₂B₁₂H₁₂ intermediate phase was determined by MAS NMR, which is an undesirable stable product if reaction reversibility is to be accomplished.

Introduction

Technologically relevant solid-state hydrogen storage materials must have gravimetric storage capacities significantly exceeding 6 wt % to meet the requirements promoted by the U.S. Department of Energy for applications such as fuel-cell powered vehicles.¹ Complex metal hydrides of the light elements have been the subject of intense research as materials meeting these strict gravimetric and volumetric criteria. One promising material is LiBH₄, which can release a maximum of 13.8 wt % hydrogen upon thermal decomposition:

LiBH₄ → LiH + B + 3/2H₂

(1)

However, LiBH₄ is too stable to release and reabsorb hydrogen at ambient temperature and pressure. The standard reaction enthalpy for the decomposition of LiBH₄ in the liquid state is 61.1 kJ/mol H₂, which translates to a 1 bar equilibrium pressure at 400 °C.²,³

Chemical destabilization of LiBH₄ offers a versatile way to lower the desorption enthalpy.³⁻⁸ Recent work has focused on adding an additional metal (M) or metal hydride (MH₂) species which reacts to form a stable metal boride phase, lowering the overall reaction enthalpy.⁷⁻⁸ Vajo et al. demonstrated that adding MgH₂ to LiBH₄ lowered the dehydrogenation enthalpy by 25 kJ/mol and also made the system reversible.³ Motivated by such successes, a comprehensive evaluation of potential chemically destabilized metal hydride systems was initiated, using density functional theory (DFT) to evaluate formation and reaction enthalpies.¹⁰,¹¹ A significant result from this study was the identification of ScH₂ as a destabilizing agent for LiBH₄ with ideal thermodynamics.³ The identified decomposition pathway:

ScH₂ + 2LiBH₄ → ScB₂ + 2LiH + 4H₂

(2)

has a calculated reaction enthalpy at 300 K of ΔH₃₀⁰K = 34.1 kJ/mol after the zero point energy correction.³ This system can release 8.91 wt % H₂ upon completion, and calculations predict the system to have an equilibrium pressure of 1 bar at around 57 °C.

It is important to note, however, that first principles DFT calculations provide no information about either the reaction mechanism or the activation barriers. It is likely that the rate limiting steps would involve the breakdown of ScH₂ (ΔH = 200 kJ/mol) and the formation of ScB₂ (ΔH = 248 kJ/mol), both of which are very stable compounds. While DFT has proved accurate in reproducing experimental H₂ equilibrium pressures for the destabilized MgH₂–LiBH₄ system,¹⁰ it is uncertain whether it will work as well for a reaction system containing reactant and product phases that are considerably more stable. High energy ball-milling can improve reaction kinetics to some degree by reducing diffusion distances and increasing the concentration of reaction interfaces, but it does not necessarily mitigate the large activation barriers to ScH₂ and ScB₂ decomposition. The aim of the present work is to experimentally investigate the destabilized LiBH₄–ScH₂ system and evaluate the importance of kinetic barriers in determining hydrogen absorption and desorption behavior. Hydrogen sorption properties are studied with isothermal kinetics measurements, while reaction products are characterized by powder
X-ray diffraction (XRD), magic angle spinning nuclear magnetic resonance (MAS NMR), and Raman spectroscopy.

Experimental Details

ScH₂ was synthesized by heating small scandium ingots (99.9%, Stanford Materials Corporation) in ultrahigh purity (UHP) grade H₂ at 350 °C. The resulting formation of scandium hydride was rapid and highly exothermic. Hydrogenation was allowed to proceed for 3 h to ensure equilibration. Volumetric analysis and X-ray diffraction both indicate that the reaction product is ScH₂. Roughly 10 g of a 2:1 molar mixture of LiBH₄ (95% purity, Sigma Aldrich) and ScH₂ was loaded under argon atmosphere into a sealed 80 mL stainless steel vessel containing five 0.5 in. diameter stainless steel balls. The vessel was sealed with a rubber gasket in a high purity argon glovebox. The argon-filled vessel was then loaded into a Fritsch-pulverizette 6 planetary mill. Different mixtures were milled at 400 rpm for either 1 or 10 h. For possible catalytic enhancement of the reaction rates, 2 mol % of TiCl₃ (Sigma Aldrich) was added to one sample prior to milling. All samples were handled in argon atmosphere gloveboxes (Vacuum Atmospheres Corporation) to prevent air and moisture contamination.

Isothermal kinetic desorption measurements were conducted on a custom built stainless steel Sieverts apparatus equipped with a 3000 psi MKS pressure gauge. In a typical experiment, a 1 g sample was loaded under argon atmosphere into a 14 mL stainless steel reactor assembly sealed with a 0.5 in. Swagelok VCR filter gasket connection. The reactor was then mounted on the Sieverts system and enclosed in a thick, tight-fitting aluminum collar, and an Omega temperature controller. The furnace setup included a Watlow band heater fastened around the aluminum collar, two thermocouples inserted into holes in the aluminum collar, and an Omega temperature controller. The quantity of desorbed hydrogen was determined by volumetric measurements. Weight percents are reported with respect to the fully hydrogenated samples, excluding the weight of the catalyst. Reabsorption was not attempted due to difficulties in extracting the desorption products.

Powder X-ray diffraction (XRD) patterns were acquired on a PANalytical X’pert PRO X’celerator diffractometer using Cu Kα radiation (λ = 1.5418 Å). All samples were sealed in 1.0 mm glass capillary tubes in an argon glovebox. Raman spectroscopy measurements were performed on a Renishaw M1000 Micro-Raman spectrometer, operating at 1 cm⁻¹ spectral resolution with a 514.5 nm argon laser, 1800 mm grating, and 20× LWD objective.

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed using a Bruker Avance 500 MHz spectrometer equipped with a Bruker 4 mm boron-free cross-polarization (CP) MAS probe. The spectral frequencies were 500.23, 160.5, 121.6, and 73.6 MHz for the ¹H, ¹¹B, ⁴⁵Sc, and ⁶Li nuclei, respectively. Samples were loaded into 4 mm ZrO₂ rotors, and each was sealed with a tight fitting kfel-F cap in an argon glovebox and spun at 13 kHz. The one-dimensional (1D) ¹¹B, ⁴⁵Sc, and ⁶Li MAS NMR spectra were acquired after a short (~0.5 µs) single pulse (i.e., <π/12 for ¹¹B) with application of a strong ¹H decoupling pulse of the two-pulse phase modulation (TPPM) scheme.¹² The NMR shifts were reported in parts per million (ppm) with respect to “zeroes” set to standard external references: tetramethylsilane (TMS) for ¹H, BF₃-ethylamine for ¹¹B, 1.0 M LiCl aqueous solution for ⁶Li, and 1.0 M Sc(NO₃)₃·HNO₃ aqueous solution for ⁴⁵Sc nuclei.

Results

The hydrogen desorption capacity and desorption rate for each ScH₂ + 2LiBH₄ mixture were studied with kinetic desorption measurements using a set of isothermal temperature steps (Figure 1). Samples were heated inside an initially evacuated 72 mL volume to temperatures ranging from 280 to 450 °C. For samples maintained at 450 °C, the release of 4.5 wt % hydrogen over 20 h was recorded. This is roughly half of the 8.91 wt % desorption capacity predicted for the reaction listed in eq 2. Longer milling times resulted in a small enhancement of the desorption capacity (an increase of less than 0.5 wt %) with no observable change in desorption kinetics. The composition of the desorbed gas was sampled using a residual gas analyzer (Stanford Research Systems, model RGA200) and found to contain over 99% hydrogen. Dehydrogenation occurred between 350 and 450 °C, roughly the same temperature range as the decomposition of lithium borohydride.²,¹¹ The 4.5 wt % H₂ release at 450 °C is consistent with decomposition due solely
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(a) Bloch decay $^{11}$B MAS NMR spectra with neat LiBH$_4$ (from Sigma Aldrich, as received) added as a reference. Note that a $^{11}$B MAS NMR spectrum of the ScB$_2$ + 2LiH system after absorption treatment at high H$_2$ pressure (896 bar; see text) is also included, where the broader spinning sidebands in this spectrum are due to unreacted ScB$_2$. (b) $^{11}$B MAS and CPMAS NMR spectra (contact time = 0.1 ms) of desorbed sample. (c) $^{45}$Sc MAS NMR spectra with pure ScB$_2$. (d) $^6$Li MAS NMR spectra.

Figure 3. NMR spectra of milled and dehydrogenated ScH$_2$ + 2LiBH$_4$. (a) Bloch decay $^{11}$B MAS NMR spectra with neat LiBH$_4$ (from Sigma Aldrich, as received) added as a reference. Note that a $^{11}$B MAS NMR spectrum of the ScB$_2$ + 2LiH system after absorption treatment at high H$_2$ pressure (896 bar; see text) is also included, where the broader spinning sidebands in this spectrum are due to unreacted ScB$_2$. (b) $^{11}$B MAS and CPMAS NMR spectra (contact time = 0.1 ms) of desorbed sample. (c) $^{45}$Sc MAS NMR spectra with pure ScB$_2$. (d) $^6$Li MAS NMR spectra.

to LiBH$_4$. (Excluding the mass of the unreacted ScH$_2$, this would give 9 wt %, which is consistent with desorption measurements taken on catalyzed LiBH$_4$.13) Desorption measurements were also performed with an initial hydrogen backpressure of 7 bar, which was not found to enhance reaction kinetics or increase the hydrogen gas yield. Desorption of a ScH$_2$ + 2LiBH$_4$ + 0.02TiCl$_3$ sample was measured to assess the effect of metal catalyst on desorption capacity and kinetics. At 280 °C, the desorption capacity was increased 5-fold in the Ti-containing sample (overall desorption capacity was still low, at 0.5 wt %). However, at 350 and 450 °C, the presence of TiCl$_3$ did not appear to enhance the desorption rate or desorption capacity.

Absorption of H$_2$ by a milled ScB$_2$ + 2LiH + 0.02TiCl$_3$ mixture was also investigated. Starting with a 135 bar back-pressure of H$_2$, a 0.8 g sample was heated to 300 °C for 48 h. No statistically significant hydrogen uptake was determined from a volumetric analysis. Powder XRD and MAS NMR analysis also failed to detect the formation of either H$_2$ absorption product LiBH$_4$ or ScH$_2$. A subsequent absorption was performed with a 896 bar H$_2$ pressure, with the sample kept at 460 °C for 48 h. A $^{11}$B MAS NMR spectrum (see Figure 3a) of this sample revealed the presence of a small peak at –41 ppm, indicating very limited LiBH$_4$ formation (~3 mol %) in the reaction product. We note, however, that this pressure falls well out of the range of interest for technologically relevant metal hydride storage systems.

Figure 2 shows the powder XRD measurement results of the ScH$_2$ + 2LiBH$_4$ mixture (a) before milling, (b) after milling for 10 h, and (c) after desorption at 450 °C for 20 h. The XRD pattern of the 450 °C desorption product reveals the presence of LiH and unreacted ScH$_2$. LiH is an expected decomposition product of LiBH$_4$, and there is no evidence that ScH$_2$ has reacted. A large X-ray background was also present due to the melting and resolidification of LiBH$_4$ in the amorphous phase, as well as the formation of amorphous intermediate phases.14 No peaks from the theoretically expected9–11 reaction product ScB$_2$ could be detected in the desorbed material.

Because a large fraction of the desorption product is amorphous, MAS NMR was utilized to complement to the powder XRD results. Figure 3 shows the $^{11}$B, $^{45}$Sc, and $^6$Li MAS NMR data for the ScH$_2$ + 2LiBH$_4$ mixture after milling and after dehydrogenation (450 °C for 20 h). From the $^{11}$B NMR spectra, no noticeable change of the LiBH$_4$ peak was observed after ball-milling. $^{11}$B MAS and CPMAS spectra (Figure 3a and b) show the formation of elemental boron in the amorphous phase (broad shoulder at ~5 ppm) and the formation of an intermediate phase (with a peak at ~12 ppm) that was recently identified as [B$_3$H$_8$]$_2^-$ species. We note also that some
unreacted LiBH₄ is still present (seen from the peak at around -40 ppm) in the dehydrogenated product. Unreacted ScH₂ is still present in the desorption product, ScB₂ or other Sc compounds are not detectable in the ⁴⁵Sc MAS NMR spectra presented in Figure 3c. Note that the ⁴⁵Sc MAS NMR signal was significantly reduced after the desorption reaction, which we tentatively attribute to inhomogeneous separation of ScH₂ and LiBH₄ phases during the desorption reaction and correspondingly nonuniform distribution of ScH₂ particles in the resulting NMR sample. ⁶Li MAS NMR spectra (shown in Figure 3d) also provide a distinctive signature of phase changes from LiBH₄ (~0.1 ppm) to Li₂B₂H₁₂ (~0.5 ppm). The presence of LiH was confirmed by independent ⁶Li CPMAS NMR measurements (not shown) because extremely long spin–lattice relaxation behavior inhibited its observation during recording of the MAS spectra in Figure 3d. As in the XRD data, the NMR results identify the decomposition products of LiBH₄ but provide no evidence that ScH₂ has reacted to form the ScB₂ product destabilization phase.

Raman spectroscopy was used to probe the chemical composition of a ScH₂ + 2LiBH₄ mixture desorbed at 400 °C for 20 h (Figure 4). It was found that the desorption product segregated into two phases that could be distinguished by their white and dark colors. The dark phase and the as-milled mixture were not Raman active. However, the Raman spectrum from the white phase bore striking similarities to the spectrum of dehydrogenated LiBH₄. The B–H bending and stretching modes of LiBH₄ around 1300 and 2300 cm⁻¹ are present in both samples and, as observed previously, are not affected by decomposition at temperatures below 400 °C.¹⁴ The broad peak at 1100 cm⁻¹ corresponds to Raman modes from B–B bonding in amorphous boron. The additional B–H bending and stretching modes around 500–1000 and 2500 cm⁻¹ are consistent with the calculated and measured B–H vibrational modes in Li₂B₂H₁₂.¹⁶ These results lead us to believe that the ball-milled ScH₂ + 2LiBH₄ mixture segregates back into its initial components upon the melting and solidifying of LiBH₄. The dark phase consists of ScH₂, while the white phase contains LiBH₄ and its thermal decomposition products.

Discussion

While the rate limiting steps of the absorption and desorption reactions of simple metal hydrides such as MgH₂ have been identified,¹⁷ the reaction pathways of most destabilization reactions are still not well understood. Based on calorimetric and in situ XRD measurements, desorption in the MgH₂ + 2LiBH₄ system has been found to proceed in two distinct steps:¹⁸

\[
\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2 \quad (3)
\]

\[
\text{Mg} + 2 \text{LiBH}_4 \rightarrow \text{MgB}_2 + 2 \text{LiH} + 3 \text{H}_2 \quad (4)
\]

An equivalent reaction pathway for the ScH₂ + 2LiBH₄ system would not work for the temperature range investigated in this paper. Decomposition of ScH₂ does not occur until 900 °C¹⁹,²⁰ (compared to 275 °C for MgH₂), when thermal decomposition of LiBH₄ should have already occurred independently. In principle, using nanostructured ScH₂ can reduce the decomposition temperature by creating excess surface energies and excess grain boundary enthalpies in the hydride phase. Reductions in the heat of formation of MgH₂ of up to 30% have been estimated for crystallites smaller than 5 nm.²¹ In practice, however, crystal grains with a minimum size of 10–15 nm are typically obtained with high energy ball-milling.²² Our own measurements of XRD peak broadening after ball-milling indicated an average ScH₂ crystallite size larger than 20 nm in the experiments. Moreover, the effect of nanocrystalline ScH₂ is complicated by the low melting point of LiBH₄ (Tₘ = 280 °C). Our results indicate that, above the melting temperature, the milled ScH₂ + 2LiBH₄ mixture segregates back into distinct phases. Another important insight is obtained by studying the desorption of a Sc + LiBH₄ mixture, which avoids the dehydrating of ScH₂. Significantly, it has been found that this reaction results in the formation of ScH₂ rather than ScB₂.⁸ From these results, it could be summarized that ScH₂ is not effective in destabilizing LiBH₄, and until the reaction mechanism is better understood, there is no simple way to surmount the significant thermodynamic and kinetic barriers present in this system.

Conclusions

Hydrogen sorption studies were performed on the ScH₂ + 2LiBH₄ system, which was identified by DFT calculations⁹ as having particularly favorable thermodynamic reaction properties. Our experimental results demonstrate that desorption of H₂ is
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consistent with only thermal decomposition of LiBH₄ and not the reaction ScH₂ + 2LiBH₄ → ScB₂ + 2LiH + 4H₂. The decomposition temperatures range between 350 and 450 °C, which are the same as those for pristine LiBH₄, and neither XRD, MAS NMR, or Raman spectroscopy provide evidence for the reaction of ScH₂ or for the formation of ScB₂. Due to the stability of both ScH₂ and ScB₂, activation barriers in both directions appear to inhibit the predicted reaction at temperatures below 450 °C. Application of a H₂ pressure of ~900 bar to a heated ScB₂ + 2LiH mixture was found to yield a minimal amount (i.e., ~3 mol %) of the desired LiBH₄ phase. Furthermore, our findings suggest that the ball-milled LiBH₄–ScH₂ mixture segregates back into LiBH₄-rich and ScH₂-rich phases after the melting and solidifying of LiBH₄. There was no indication that TiCl₃ assisted the destabilization reaction, although the desorption kinetics were improved as noted previously in the LiBH₄–MgH₂ system.³⁵⁻⁷

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References and Notes
