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Improved Dehydrogenation Properties of Ti-Doped LiAlH₄: Role of Ti Precursors

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ABSTRACT: The dehydrogenation properties of LiAlH₄ doped with different Ti precursors (Ti, TiO₂, and TiCl₃) via ball milling are investigated. The results not only show significant decreases in the decomposition temperatures (T_{dec}) and activation energies (E_A) of the first two dehydrogenation reaction steps of LiAlH₄ by doping with TiO₂ or TiCl₃ but also reveal how each Ti precursor affects the dehydrogenation process. Although doping LiAlH₄ with TiCl₃ induced the largest decrease in T_{dec} and E_A, TiO₂-doped LiAlH₄ produced a decrease in T_{dec} and E_A that is quite close to the TiCl₃-doped sample as well as superior short-term stability, suggesting that doping with TiO₂ has certain advantages over doping with TiCl₃. Further, the underlying mechanisms associated with the Ti precursors during the dehydrogenation reaction of LiAlH₄ have been studied using quasi in situ X-ray photoelectron spectroscopy. The results reveal that the Ti⁴⁺ and Ti³⁺ reduction processes and the segregation of Li cations to the surface of LiAlH₄ during ball milling play critical roles in the improved dehydrogenation properties observed.

1. INTRODUCTION

Lithium alanate (LiAlH₄) is a promising candidate for compact and lightweight hydrogen storage and thermal energy storage (TES) systems due to its high hydrogen storage capacity (with 7.9 wt % accessibility below 250 °C), very high equilibrium hydrogen pressure at relatively low temperatures, and moderate reaction enthalpy. In general, unmodified LiAlH₄ decomposes in three reaction steps (reactions R1b–R3) upon heating after an initial melting step, R1a.¹

\[
\text{LiAlH}_4(s) \rightarrow \text{LiAlH}_4(l) \quad (\text{R1a})
\]

\[
3\text{LiAlH}_4(l) \rightarrow 3\text{LiH}_2(s) + 2\text{Al}(s) + 3\text{H}_2(g) \quad (\text{R1b})
\]

\[
\text{Li}_2\text{AlH}_4(s) \rightarrow 3\text{LiH}(s) + \text{Al}(s) + 1.5\text{H}_2(g) \quad (\text{R2})
\]

\[
\text{LiH}(s) \rightarrow \text{Li}(l) + 0.5\text{H}_2(g) \quad (\text{R3})
\]

Upon decomposition, the theoretical \( \text{H}_2 \) release of R1b is 5.3 wt %, while R2 and R3 release 2.6 wt % each. The enthalpies for hydrogen release in R1b and R2 at room temperature are \( \Delta H = -9.1 \) and \( +27.0 \) kJ/mol \( \text{H}_2 \), respectively, while the decomposition temperatures (\( T_{dec} \)) for R1b, R2, and R3 are reported to be between 112–220, 127–260, and 400–450 °C, respectively.¹ Most applied studies focus on R1b and R2 because the \( T_{dec} \) of R3 is too high and not considered important for practical applications. However, the utilization of R1b and R2 is still plagued by a host of shortcomings, notably slow kinetics and desorption temperatures that are higher than what are required in automotive proton exchange membrane (PEM) fuel cell (80 °C) and many TES systems (<100 °C). Other challenges that need to be addressed include the existence of an exothermic reaction step (reaction R1b) that significantly reduces the TES density of LiAlH₄ and the elucidation of the role of additives in the dehydrogenation process.

From the literature, the \( T_{dec} \) and the activation energies (\( E_A \)) of LiAlH₄ are significantly decreased by ball milling with a number of additives such as metal chlorides,²–⁷ metals,⁸–⁹ metal carbide,¹⁰ metal oxides,¹¹,¹² alloys,¹³ and carbon nanotubes/nanofibers.¹⁴ Other methods to improve the dehydrogenation properties of LiAlH₄ include confinement of hydrides in a nanoporous scaffold¹⁵,¹⁶ and the modification through solid-state alloying with elements that destabilize the hydride.¹¹,¹⁷,¹⁸ To determine the most active catalytic additive, a number of experiments have been performed. Balema et al.¹⁹ studied the transformation of LiAlH₄ to Li₄AlH₈ in the presence of Ti- and Fe-based catalysts and established that the Ti-based catalysts have higher activity than Fe-based catalysts. Another study by Kojima et al.²⁰ aimed at determining the catalytic effects of various metal chlorides revealed that the activity, defined in terms of the hydrogen desorption capacity, decreases in the

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following order: TiCl₃ > ZrCl₄ > VCl₃ > NiCl₂ > ZnCl₂. In general, Ti-based additives appear to provide the best benefit in terms of enhanced dehydrogenation kinetics and reduction in Tₑₙ. The principal Ti additives that have been studied include Ti metal,¹¹ TiO₂,¹¹ TiCl₃,²² TiCl₃·1/3AlCl₃,⁴,⁵ TiCl₄, and TiC.¹⁰

In spite of extensive experimental work on Ti-doped LiAlH₄, no prior systematic study has focused on the effect of various Ti precursors on the dehydrogenation reaction of LiAlH₄ and conflicting views on the role of Ti additives in the dehydrogenation reaction remain. For instance, a number of studies¹,²,⁵,¹⁹ have shown that ball milling LiAlH₄ with TiCl₄, TiCl₃, or TiCl₃·1/3AlCl₃ at room temperature can induce the transformation of LiAlH₄ to Li₃AlH₆. Conversely, Chen et al.⁴ reported no transformation of LiAlH₄ during ball milling with TiCl₃·1/3AlCl₃. As noted, there is little agreement on the role of additives in the dehydrogenation of alanates. Sun et al.²³ attributed the remarkable enhancement of the dehydrogenation reaction of alanates to the destabilization of alanate caused by the substitutution of Ti into the lattice of the alanate. Conversely, more recent studies by Canton et al.²⁴ and Ares Fernandez et al.²⁵ showed no change of structural parameters upon doping with various metal halides. With regard to the exact nature of the active specie, Balema et al.¹⁹ attributed the high catalytic activity of TiCl₃ and TiCl₄ to the microcrystalline intermetallic Al₃Ti that forms during milling, but the subject is far from settled as a variety of other Ti species such as Ti⁰,⁴,²⁶,²⁷ TiH₂,²⁸ TiO₂,¹¹ and Ti cations⁴ have been proposed as the active specie. The lack of understanding of the dehydrogenation mechanism of Ti-doped LiAlH₄ and particularly the role of the different Ti precursors is impeding its development and eventual application and could potentially lead to a reduced interest in LiAlH₄.

Here we provide a systematic study of the dehydrogenation properties and stability of TiCl₃-, TiO₂-, and Ti-doped LiAlH₄. The role of the Ti during the dehydrogenation of LiAlH₄ was investigated using spectroscopic methods. The present results on the chemical evolution of the various elements after ball milling and after dehydrogenation of LiAlH₄ samples enable quantitative and further insights into the roles of the different Ti precursors.
2. EXPERIMENTAL SECTION

The starting materials, LiAlH₄ (98% purity), TiCl₃ (99.995% purity), and TiO₂ (anatase) nanopowder (<100 nm, 99.9% purity), were purchased from Sigma-Aldrich (St. Louis, MO), while Ti metal nanopowder (<100 nm in size and 99.9% purity) was purchased from American Elements. Each material was used as received with no additional purification. Samples were handled in an Ar glovebox with the amount of oxygen and water vapor present being less than 10 and 0.1 ppm, respectively. LiAlH₄ was mixed with 0.5, 5, and 10 mol % of Ti, TiO₂, and TiCl₃ in a 65 cm³ stainless steel vial containing 30 stainless steel grinding balls (0.7 cm in diameter). The ball-to-powder weight ratio was 40:1, which falls within the commonly utilized range of 10:1 to 100:1. Each LiAlH₄-additive mixture was ball milled using a SPEX SamplePrep 8000 M Mixer/Mill (high-energy shaker/vibratory mill). The standard ball milling time was 90 min, and LiAlH₄ samples milled without any additive are designated as “BM90 min”. All samples, except those aged for six months, were characterized within a few hours after milling.

Differential scanning calorimetry (DSC) analyses were performed using a Simultaneous DSC-TGA instrument (SDT 2960 TA Instruments). All measurements were carried out with 7−15 mg of sample at atmospheric pressure and repeated to ensure reproducibility. The temperature was linearly increased from room temperature (~25 °C) to 500 °C at a rate of 5 °C/min in a stream (75 sccm) of research grade Ar (99.999%) to reduce oxidation. The apparent activation energies, Eₐ, of the dehydrogenation reactions, R1b and R2, were determined using the Kissinger method, and the detailed analysis is presented elsewhere. The TA Instruments Universal Analysis software was used to determine the onset temperature (T_onset) and T_dec after each experiment. T_onset represents the intersection of the tangent line with the maximum slope and the DSC baseline, while T_dec represents the temperature at the maximum heat flow.

FTIR spectroscopy was carried out using a Bruker infrared spectrometer equipped with an attenuated total internal reflection (ATR) module. The spectral resolution was 4 cm⁻¹. Scans were performed between 4000 and 400 cm⁻¹. Morphological characterization of the as-received and milled LiAlH₄ was conducted using a Hitachi S5200 field emission scanning electron microscopy (FESEM).

The dehydrogenation behavior of as-received, milled, and doped LiAlH₄ samples was studied via quasi in situ X-ray photoelectron spectroscopy (XPS) using a Kratos Ultra XPS system with a monochromatic Al Kα source (hν = 1486.6 eV) operated at 12 kV and 10 mA. The sample was loaded on the holder in the glovebox and transported in a sealed bag to reduce contamination from oxygen and water vapor. The Kratos XPS is equipped with a heating stage in the outer sample treatment chamber (STC; vacuum level ~2.0 × 10⁻⁷ Torr during heating). Samples were placed in the STC and heated to 300 °C at a rate of ~50 °C/min and maintained at this temperature, while H₂ desorption was monitored using a residual gas analyzer. After dehydrogenation, the sample was transferred again under vacuum to the analysis chamber for spectral acquisition. All samples were analyzed before and after the dehydrogenation process. The C 1s peak (binding energy = 284.6 eV) was used as charge reference for energy calibration. Spectral analysis was performed using CasaXPS software. Least square fitting of high energy resolution spectra was performed using mixed Gaussian–Lorentzian for curve fitting.

3. RESULTS AND DISCUSSION

Ball Milling and Effects of Ti, TiO₂, and TiCl₃ Additives on T_dec and Eₐ. Mechanical ball milling is one of the preferred processing routes for modifying metal hydrides due to its ability to create metastable phases, high density of grain boundaries that may act as nucleation centers, and new surfaces that can promote hydride–additive interactions.7,31−34 Figure 1a shows the DSC profiles for as-received LiAlH₄ and LiAlH₄ milled for 90 min (BM90 min). The DSC profile of the as-received LiAlH₄ consists of an endothermic peak at 172 °C (R1a, melting phase) and an exothermic peak at 185 °C (R1b), accompanied by two endothermic peaks at 243 (R2) and 430 °C (R3). Also, the DSC profile of the as-received LiAlH₄ is characterized by an exotherm near 149 °C, which the literature attributes to interactions between LiAlH₄ and surface hydroxyl impurities. Conversely, the DSC profiles for the milled samples are characterized by an exothermic peak and two endothermic peaks with the melting transformation R1a clearly suppressed. Langmi et al.22 also observed that melting is suppressed after doping LiAlH₄ with low levels of homogeneously dispersed Ti catalyst; the phenomenon is attributed to the lowering of the T_dec of R1b below the melting point of LiAlH₄ resulting in the disassociation of the melting–decomposition–solidification events. We should note that, in cases where melting of LiAlH₄ is suppressed, the transformation associated with reaction R1b changes from LiAlH₄(l) → Li₃AlH₆(s), whereby solid Li₃AlH₆(s) reacts directly without first forming an intermediate liquid Li₃AlH₆(l).

Our high-energy milling process suppresses melting of LiAlH₄ and decreases T_dec of R1b and R2 by 39 and 27 °C, respectively. Also, as summarized in Table 1, milling decreases Eₐ of R1b and R2 from 89.2 and 99.9 kJ/mol to 82.3 and 72.3 kJ/mol, respectively. The slight decreases in T_dec and Eₐ

<table>
<thead>
<tr>
<th>samples</th>
<th>T_dec of R1b (°C)</th>
<th>T_dec of R2 (°C)</th>
<th>Eₐ of R1b (kJ/mol)</th>
<th>Eₐ of R2 (kJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>LiAlH₄</td>
<td>185</td>
<td>243</td>
<td>89.2</td>
<td>99.9</td>
</tr>
<tr>
<td>LiAlH₄ − BM90 min</td>
<td>146</td>
<td>216</td>
<td>82.3</td>
<td>72.3</td>
</tr>
<tr>
<td>LiAlH₄ + 0.5 mol % Ti</td>
<td>142</td>
<td>204</td>
<td>76.3</td>
<td>65.4</td>
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<tr>
<td>LiAlH₄ + 0.5 mol % TiO₂</td>
<td>126</td>
<td>201</td>
<td>38.5</td>
<td>39.3</td>
</tr>
<tr>
<td>LiAlH₄ + 0.5 mol % TiCl₃</td>
<td>108</td>
<td>187</td>
<td>26.3</td>
<td>38.4</td>
</tr>
<tr>
<td>LiAlH₄ + 5 mol % Ti</td>
<td>117</td>
<td>205</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlH₄ + 5 mol % TiO₂</td>
<td>116</td>
<td>203</td>
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<tr>
<td>LiAlH₄ + 5 mol % TiCl₃</td>
<td>117</td>
<td>198</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlH₄ + 10 mol % Ti</td>
<td>117</td>
<td>198</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlH₄ + 10 mol % TiO₂</td>
<td>117</td>
<td>182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiAlH₄ + 10 mol % TiCl₃</td>
<td>117</td>
<td>161</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 1. Summary of T_dec and Eₐ Values of As-Received LiAlH₄, Milled LiAlH₄, and LiAlH₄ Milled with Different Amounts of Ti-Based Additive for 90 min*
observed after milling in the absence of an additive indicates that the defects created during milling and/or decrease in grain size are playing active roles in the dehydrogenation process. The DSC profiles and FESEM images of samples milled for different durations are presented in the Supporting Information (Figure S1).

The DSC scans of as-received LiAlH4 milled with 0.5, 5, and 10 mol % of Ti, TiO2, and TiCl3 for 90 min are shown in Figure 1b, c, and d, respectively. In general, the melting phase is suppressed in all cases, which can be attributed to high-energy ball milling, as observed in Figure 1a. Also, there is a reduction in $T_{\text{dec}}$ of R1b and R2 with increasing amounts of additive, although, as shown in Table 1, the additives have higher effects on the downshift of R1b than R2. The DSC profiles of LiAlH4 milled with 0.5, 5, and 10 mol % Ti in Figure 1b show thermal peaks associated with R1b, R2, and R3. Milling LiAlH4 with the lowest amount of Ti (0.5 mol %) reduces $T_{\text{dec}}$ of R1b and R2 by 43 and 39 °C, while milling with the highest amount of Ti (10 mol %) reduces $T_{\text{dec}}$ of R1b and R2 by 68 and 45 °C, respectively. For LiAlH4 milled with various amounts of TiO2 (Figure 1c), thermal peaks associated with R1b, R2, and R3 are also observed, except for samples milled with 10 mol % TiO2 that lacks a well-defined peak for R1b. Milling LiAlH4 with 0.5 mol % TiO2 decreases the $T_{\text{dec}}$ of R1b and R2 by 59 and 42 °C, while the $T_{\text{dec}}$ of R2 for samples milled with 10 mol % TiO2 decreases by 61 °C. In the case of LiAlH4 milled with various amounts of TiCl3 (Figure 1d), the DSC profiles reveal two striking differences: (1) Thermal peaks associated with R1b are absent for samples with high TiCl3 amount (5 and 10 mol %), suggesting that the high reactivity of the TiCl3-doped LiAlH4 may have led to R1b occurring during ball milling. (2) There is a significant reduction in $T_{\text{dec}}$ of R1b and R2 for LiAlH4 doped with the lowest amount of TiCl3 (0.5 mol %); this sample produced the largest reduction in $T_{\text{dec}}$ from 185 to 108 °C for R1b and from 243 to 187 °C for R2. In terms of lowering $T_{\text{dec}}$, the activity of the additives decreases in the following order: TiCl3 > TiO2 > Ti. From the DSC profiles, the $T_{\text{onset}}$ for both 5 mol % TiO2- and 0.5 mol % TiCl3-doped LiAlH4 samples, while difficult to precisely quantify, are well under 100 °C.

To investigate the effect of doping LiAlH4 with 0.5 mol % additive (Ti, TiO2, or TiCl3) on the kinetics of reactions R1b and R2, the nonisothermal Kissinger method was used;30 the respective $E_A$ values are summarized in Table 1. The comparison of their respective $E_A$ values is limited to samples with 0.5 mol % Ti additive because, as discussed earlier, R1b occurs either partially or completely during milling for samples milled with higher amounts of TiO2 or TiCl3. The $E_A$ values for R1b increase in the following order: LiAlH4/TiCl3 < LiAlH4/TiO2 < LiAlH4/Ti < as-received LiAlH4; a similar trend was observed for the $E_A$ of R2. We should note that the $E_A$ values of R1b and R2 for as-received LiAlH4 observed in our study compare favorably with previously reported values reported by Andreassen et al. (80 and 100 kJ/mol for R1b and R2, respectively)31 and Rafi-ud-din et al. (86 and 101 kJ/mol for R1b and R2, respectively).32 Interestingly, Table 1 reveals that the trends in $E_A$ for R1b and R2 correlate well with their respective downshifts in $T_{\text{dec}}$. This observation supports the hypothesis that reactions R1b and R2 are kinetically limited. Also, the $E_A$ values obtained in our work for TiO2-doped LiAlH4 and TiCl3-doped LiAlH4 using the Kissinger method are among the lowest in the literature. The positive effect of TiO2 and TiCl3 additives on the dehydrogenation properties of LiAlH4 is consistent with previous studies.14,11 We should note that the comparison between the dopants has revealed that TiO2 can provide a reasonable downshift in $T_{\text{dec}}$ and kinetic enhancement of reactions R1b and R2 that is quite close to TiCl3. The high activity of TiO2 is particularly important given the shortcomings of Ti halides as catalysts or additives. As observed in Figure 1d and by Resan et al.,35 doping LiAlH4 with TiCl3 or TiCl4 results in a significant decrease in the amount of desorbed H2 due to the elimination of R1b. The high activity shown by TiO2, especially in decreasing $T_{\text{dec}}$ of R1b and $E_A$ of R1b and R2, suggests that it could become a better alternative to TiCl3, if the doping procedure is further improved.

**Stability and Dehydrogenation Behavior.** The successful application of LiAlH4 will require a good understanding of the transformation of LiAlH4 or lack thereof during processing and storage. From the literature, it is clear that the stability of as-received LiAlH4 and modified LiAlH4 is an intensely debated subject. For instance, Balem et al.36 reported that as-received LiAlH4 does not undergo decomposition during high-energy ball milling at ambient temperatures, whereas Ares et al.37 showed that, during milling, the increase in the local temperature and pressure induced by shocks led to the decomposition of LiAlH4. Also, LiAlH4 doped with some catalytic additives has been shown to undergo decomposition during milling.1,4,7,19 XPS and IR spectroscopy in ATR mode were used to investigate the stability of as-received LiAlH4, milled LiAlH4, and LiAlH4 doped with 0.5 and 10 mol % Ti, TiO2, or TiCl3. Both XPS and IR spectroscopy have been used in this study because they provide complementary results, allowing us to have a good understanding of the stability and the dehydrogenation process. Figure 2a shows high resolution XPS spectra of Al 2p and Li 1s regions for LiAlH4 before and after heating, while Figure 2b shows a similar spectrum of LiAlH4 after milling for 90 min. The binding energy (BE) for
Al$^{3+}$ is 74 eV, while that of metallic Al is 72 eV.$^{38}$ As expected, the Al 2p peak of as-received LiAlH$_4$ is centered at 74 eV, indicating the sample is composed mainly of LiAlH$_4$ (Figure 2a). After heating, there is the appearance of a metallic peak at 72 eV, suggesting the occurrence of reaction R1b; this observation is further confirmed by the presence of a plasmon loss feature of metallic Al at 88 eV. As Figure 2b shows, the shape and the BEs of the Al 2p and Li 1s spectra for milled LiAlH$_4$ and as-received LiAlH$_4$ are identical, and the spectral features associated with metallic Al are absent, suggesting that reaction R1b did not take place.

The distinct active infrared vibration of LiAlH$_4$ and LiAlH$_4$ makes IR spectroscopy particularly suitable for investigating the occurrence of reaction R1b. [AlH$_4$]$^{-}$ has a tetrahedral structure with active infrared vibrations of the Al–H bond in two regions: Al–H stretching modes occur at 1760 and 1610 cm$^{-1}$ and Li–Al–H bending modes occur at 900 and 830 cm$^{-1}$; on the other hand, the octahedral structure of [AlH$_6$]$^{3-}$ also shows an active infrared vibration in two regions: Al–H stretching modes occur at 1386 and 1276 cm$^{-1}$ and Li–Al–H bending modes at 1000, 950, and 850 cm$^{-1}$. For both as-received and milled LiAlH$_4$ (Figure 2c), the distinct Al–H stretching modes of [AlH$_4$]$^{-}$ observed at 1759 and 1615 cm$^{-1}$ confirm that the sample is LiAlH$_4$ and that reaction R1b did not occur during ball milling. It is clear from the results in Figure 2 that undoped LiAlH$_4$ is stable under our high-energy milling conditions.

The stability of LiAlH$_4$ samples milled with 0.5 and 10 mol % Ti, TiO$_2$, or TiCl$_3$ can be easily discerned from their IR spectra presented in Figure 3. The spectra reveal that some amount of LiAlH$_4$ decomposed to Li$_3$AlH$_6$ during milling. Unlike samples milled with 10 mol % TiO$_2$ or Ti, for samples milled with 10 mol % TiCl$_3$, the stretching and bending modes of [AlH$_4$]$^{-}$ are nonexistent, while the modes associated with [AlH$_6$]$^{3-}$ are weak, indicating the absence of LiAlH$_4$ and the presence of a low amount of Li$_3$AlH$_6$. We attribute this difference in the dehydrogenation behavior to the relatively higher stability of TiO$_2$- and Ti-doped samples. We conclude that LiAlH$_4$ samples milled with TiCl$_3$ are highly reactive, and for the 10 mol % TiCl$_3$-doped samples, reactions R1b and R2 may have occurred completely and partially during ball milling, respectively.

The long-term stability of the modified LiAlH$_4$ samples at room temperature was studied by analyzing the aging behavior of the modified LiAlH$_4$ samples in a glovebox after six months. The respective IR spectra of milled and doped LiAlH$_4$ samples are presented in Figure 4. Complete decomposition of LiAlH$_4$ to Li$_3$AlH$_6$ is apparent for all the doped samples after aging. However, the sample milled without any additive showed higher stability, evidenced by the distinct stretching modes of [AlH$_4$]$^{-}$, indicating the presence of unde decomposed LiAlH$_4$. These results confirm the poor long-term stability of the doped LiAlH$_4$ samples, and therefore, success with Ti-doped LiAlH$_4$ in TES and on-board hydrogen storage systems will require the use of regenerated samples.

The evolution of the XPS spectra of Al 2p and Li 1s regions for LiAlH$_4$ samples doped with Ti, TiO$_2$, or TiCl$_3$ before heating (i.e., after ball milling) and after heating further revealed the effect of the precursors on the dehydrogenation behavior. As shown in Figure 5a, a small peak centered near 72 eV appears after milling LiAlH$_4$ with 0.5 mol % Ti, TiO$_2$, or TiCl$_3$ additive, indicating the formation of a small amount of metallic Al. After heating, as shown in Figure 5b, the intensity of the metallic peak at 72 eV increases, suggesting the occurrence of reaction R1b. On the other hand, as Figure 5c,d shows, milling LiAlH$_4$ with 10 mol % additive results in

![Figure 3](image1.png)

**Figure 3.** FTIR spectra of LiAlH$_4$ milled with (a) 0.5 mol % Ti, TiO$_2$, and TiCl$_3$ and (b) 10 mol % Ti, TiO$_2$, and TiCl$_3$.

![Figure 4](image2.png)

**Figure 4.** FTIR spectra of LiAlH$_4$ milled with (a) 0.5 mol % Ti, TiO$_2$, and TiCl$_3$ and (b) 10 mol % Ti, TiO$_2$, and TiCl$_3$. All samples were analyzed after aging for six months.
striking differences in the XPS spectra: (1) There is the presence of a distinct peak at 74 eV and a shoulder at 72 eV for LiAlH₄ milled with 10 mol % TiCl₃ and 10 mol % TiO₂ before heating (Figure 5c); this indicates that a significant reaction resulting in the formation of metallic Al may have occurred during ball milling. Note that, for LiAlH₄ samples doped with a high amount of Ti (10 mol %), the XPS spectrum remains unchanged, with a narrow Al 2p peak centered at 74 eV and a small metallic peak at 72 eV, indicating that Ti metal does not induce the transformation of LiAlH₄ during milling. (2) After heating, the metallic peak becomes more visible for LiAlH₄ milled with 10 mol % Ti, while samples milled with 10 mol % TiO₂ or TiCl₃ showed only small changes in the spectra (Figure 5d). (3) The Al/Li ratio (Table 2) decreases from 6.6 in the as-received state to 6.0 after ball milling and appears to decrease further with an increasing amount of Ti precursor. What is most striking about the LiAlH₄ samples doped with 0.5 and 10 mol % additive is the significant decrease in the Al/Li ratio that is observed for samples doped with either 10 mol % TiO₂ or TiCl₃ compared to samples doped with 10 mol % Ti.

**Role of Ti Precursors.** Even though various Ti compounds have been used to improve the dehydrogenation properties of LiAlH₄, the question of the actual role played by the Ti additives is still unresolved. The development of a more rational approach for modifying Ti-doped LiAlH₄ will require a good understanding of the role of Ti. To advance our understanding of the subject, we have used quasi in situ XPS to study the evolution of the chemical state of Ti before heating (after ball milling) and after heating in the respective LiAlH₄ samples doped with 10 mol % Ti additives (Figure 6). Samples with the highest amount of Ti additive have been used in this study because we were unable to detect Ti in samples with low Ti concentrations. Ismail et al. showed that ion etching of TiO₂-doped LiAlH₄ resulted in better signal-to-noise; this approach was not explored in our work due to the possibility of contaminating or altering the chemistry of the surface.

The Al/Li ratio for the milled LiAlH₄ sample (BM90 min) is 5.9.

### Table 2. Summary of Al 2p and Li 1s Peak Area Ratios (Al/Li) Before and After Heating at 300 °C for As-Received LiAlH₄ (0 mol %) and LiAlH₄ Milled with 0.5 and 10 mol % Ti, TiO₂, and TiCl₃

<table>
<thead>
<tr>
<th>additive</th>
<th>Al/Li ratio (before heating)</th>
<th>Al/Li ratio (after heating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>amount of Ti precursor (mol %)</td>
<td>Ti-doped LiAlH₄</td>
<td>TiO₂-doped LiAlH₄</td>
</tr>
<tr>
<td>0</td>
<td>6.6</td>
<td>6.6</td>
</tr>
<tr>
<td>0.5</td>
<td>5.1</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>4.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The Al/Li ratio for the milled LiAlH₄ sample (BM90 min) is 5.9.
there are shifts toward lower BEs after milling indicating that significant reduction of Ti occurs during ball milling. The broadening of the XPS spectra observed after milling is indicative of the presence of multiple oxidation states. Curve fitting of the Ti 2p spectra using a mixture of Gaussian (70%) and Lorentzian (30%) line shapes to achieve the best fit allowed for the resolution of the various oxidation states of Ti that were formed. It is apparent from the reduction of TiO2 and TiCl3 that the active specie is a reduced form of Ti in agreement with previous studies. In particular, our results reveal that the reduction process that Ti4+ and Ti3+ undergo plays a critical role in improving the dehydrogenation properties because Ti metal, the least effective of the three additives evaluated, does not show the same effect. Due to the high reactivity of Ti and the fact that XPS is a surface analysis technique, the Ti metal (reference material) shows an intense metallic peak component at 454 eV increases, confirming that the bulk is composed mainly of metallic Ti.

There is a significant decrease in the surface Al/Li ratio for LiAlH4 samples doped with 10 mol % TiO2 or 10 mol % TiCl3 (Table 2). We attribute the observed increase in the relative intensity of the Li 1s peak to the segregation of Li cations to the surface. The migration of Li to the surface during milling may result in the formation of vacancies that can provide pathways for hydrogen or active site diffusion. We hypothesize that the formation of vacancies destabilizes LiAlH4 by suppressing the highly ionic bond interaction between Li cations and alanate anions. This hypothesis is supported by other studies performed on NaAlH4 an alanate described by Varin et al. as having the same thermal behavior as LiAlH4. It has been shown via ab initio spin-polarized density functional theory calculations on NaAlH4 that the presence of a cationic vacancy elongates and eventually weakens the Al–H bond, thereby enhancing the dehydrogenation process. The efficiency of TiCl3 in improving the dehydrogenation properties of NaAlH4 has been attributed to the formation of vacancies during milling via reduction and the formation of the metal halide.

Figure 7. Schematic of transformation of LiAlH4 during doping with different Ti precursors via ball milling. Milling LiAlH4 with any of the Ti precursors induces reaction R1b, as shown by the formation of Li3AlH6. The underlying mechanisms for the enhanced dehydrogenation properties in TiCl3- and TiO2-doped LiAlH4 involve significant reduction of Ti3+ and Ti4+ and the segregation of Li to the surface during milling (a). The inferior dehydrogenation properties observed in LiAlH4 samples doped with Ti metal is attributed to the absence of both phenomena, that is, reduction of Ti and surface segregation of Li (b).

The active specie could be one or a combination of the following reduced species: a metal, an intermetallic compound (TixAly), and/or mixed Ti states (Ti1+/Ti2+). In addition to the reduction that occurs in the TiO2- and TiCl3-doped samples, we hypothesize that Li cations segregate to the surface of LiAlH4 where they react with the oxide or chloride anions forming Li2O and LiCl, as shown in reactions R4 and R5. As observed in NaAlH4, it is also possible that the formed LiCl may also be acting as an antisinger agent by inhibiting particle growth and maintaining short diffusion distance in the LiAlH4 matrix.

The transformations that LiAlH4 undergoes during ball milling with the respective Ti precursors are illustrated in the schematic in Figure 7. As shown by the XPS and FTIR data, R1b reaction is induced during milling of LiAlH4 with any of the Ti additive. Significant reduction of Ti3+ or Ti4+ and the segregation of Li to the surface occurs during ball milling of LiAlH4 with TiCl3 or TiO2. Conversely, milling LiAlH4 with Ti metal does not result in reduction of Ti and surface segregation.
of Li. The process in achieving these reduced states in samples doped with TiCl₃ and TiO₂ during ball milling is critically important, as it helps to create Li vacancies. We therefore hypothesize that both phenomena, reduction of Ti and surface segregation of Li, work in concert during ball milling to destabilize the alanate and are largely responsible for the observed improvement in the dehydrogenation properties of TiO₂-doped and TiCl₃-doped LiAlH₄.

**CONCLUSIONS**

The results herein elucidate the influence of the different Ti dopants (Ti, TiO₂, and TiCl₃) on stability and the dehydrogenation properties (\(T_{\text{dec}}\) and \(E_\lambda\)). A distinguishing feature of our work is that, unlike previous studies whereby the influence of Ti-based additives on the dehydrogenation properties of LiAlH₄ were studied individually or with other transition metal additives, here we have focused on the effects of various types and amounts of Ti precursors (Ti, TiO₂, and TiCl₃) under identical conditions to allow for meaningful comparison. The efficiency of the Ti precursors in improving the dehydrogenation properties decreases in the order: TiCl₃ > TiO₂ > Ti. Interestingly, the AI/Li ratio of samples doped with LiAlH₄. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**