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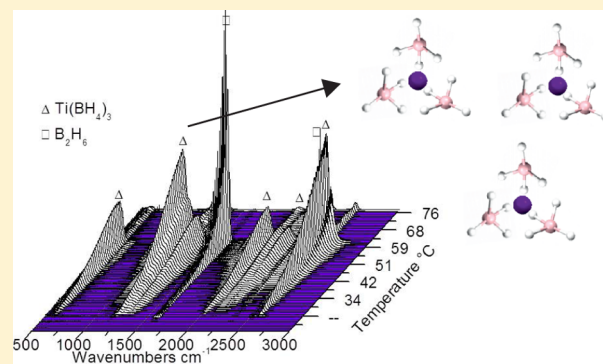
The Role of Ti in Alanates and Borohydrides: Catalysis and Metathesis

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ABSTRACT: Ti catalyzes the hydrogen sorption reaction in alanates and allows the measurement of pressure composition isotherms, that is, the reaction equilibrates at each point of the isotherm. Although some effects of Ti compounds addition to borohydrides have been shown, our measurements show that the hydrogen desorption reaction from borohydrides is not catalyzed by Ti, when the system is exposed to a gas flow. The reabsorption of hydrogen by the products of the desorption reaction requires high temperatures and high pressures. Furthermore, the reaction pathway for the hydrogen desorption is different from the absorption one and as a consequence the borohydrides do not equilibrate with the gas phase during the hydrogen sorption reactions. Ti in borohydrides leads to the formation of stable and volatile Ti-containing species, for example, $(\text{Ti}(\text{BH}_4)_3)$. This is a metathesis reaction, that is, a bimolecular process involving the exchange of bonds between the two reacting chemical species. In this paper, we have investigated via spectroscopy measurements the hydrogen sorption reactions of NaAlH_4 and LiBH_4 with Ti catalyst in view of the changes in the solid phase as well as in the gas phase.



■ INTRODUCTION

The reversibility of complex hydrides has been intensively investigated, since Bogdanovic and co-worker in 1997 discovered the catalytic effect of a few mol % of TiCl_3 in NaAlH_4 . The addition of TiCl_3 accelerates the decomposition of NaAlH_4 and the dopant is not consumed by the hydrogen sorption reaction. The presence of Ti among the decomposition products allows their rehydrogenation, achieving equilibrium of the alanates with the gas phase.¹ TiCl_3 addition was investigated in both alanates and borohydrides,^{2–6} but while the hydrogen sorption reaction of the former becomes totally reversible, the addition of TiCl_3 to LiBH_4 (for example) does not result in a totally reversible complex hydride system. The mechanism of the reactions between complex hydrides and additives is still unknown⁷ and it remains uncertain why TiCl_3 catalyzes the hydrogen sorption reaction in alanates but does not produce the same effect in borohydrides.

The catalytic effect of TiCl_3 doping in alanates has been accurately studied yielding various explanations, mainly reporting Ti as a spillover and/or nucleation center. In the first case, Ti dissociates the hydrogen molecule producing two hydrogen atoms which are subsequently chemisorbed by the alanate, or it recombines two H atoms, forming molecular hydrogen. In these models, Ti acts on the surface, lowering the activation energy for breaking and forming the H–H bond. The dissociated hydrogen atoms diffuse to and from the Ti site

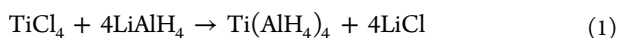
resulting in the dehydrogenation and hydrogenation of the system.^{8–12} More complicated models suggest that Ti acts as a promoter of mobile hydrogen containing species or vacancies.^{13–18} Interestingly, it was found that many other transition metals do not give rise to the same effects when used to dope NaAlH_4 as TiCl_3 .¹⁹ Kinetically, the rate limiting step of the hydrogen absorption/release from doped alanates is not identified to be the hydrogen molecule dissociation/recombination.²⁰ Therefore Ti cannot exclusively be a dissociation center. In the second case, Ti doping consists of finely dispersed nanoparticles in the bulk alanate. These models suggest that during the decomposition of NaAlH_4 , Ti particles are the centers for nucleation and growth of the decomposed phases. Ti creates defects, refines the grains, and provides an easy path for hydrogen to diffuse.^{21–23}

A different approach to add Ti to alanate systems is by metathesis;²⁴ Ti chlorides react with alanates inducing cation–anion exchange. A metathesis reaction is a chemical process that produces new Ti-containing species. Therefore Ti cannot strictly be considered as a catalyst in this case, and the use of the terminology “doping” is not accurate. For alanates in solution, the following meta-reaction is known²⁵

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The enthalpy of formation of LiCl^{26-28} (Table 1) drives the reaction and favors the Ti–Li substitution. However, this

Table 1. Enthalpy of Formation for the Reactants and Products of the Metathesis Reactions

compound	ΔH kJ/mol	reference
TiCl_4	−804	27
LiAlH_4	−115	35
LiCl	−409	27
TiCl_3	−721	27
LiBH_4	−195	36
$\text{Ti}(\text{BH}_4)_3$	−23	36

reaction is only allowed at very low temperature, since the metathesis product decomposes at -85°C . In the solid phase, a metathesis between TiCl_3 and NaAlH_4 might be possible. Although $\text{Ti}(\text{AlH}_x)_y$ species have been theoretically predicted,^{29,30} no experimental evidence for their formation has been reported to date.

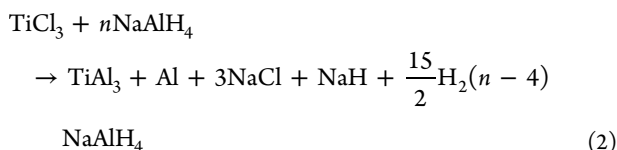
Compared to the thoroughly investigated doped alanates, little is known about the effect of TiCl_3 addition to borohydrides. Several studies^{31,32} report a catalytic activity of additives in LiBH_4 , however the result of doping LiBH_4 with TiCl_3 is not the formation of a totally reversible hydrogen storage system.³³ It has been found that the metathesis approach destabilizes borohydrides³¹ and it is a proven way to synthesize new compounds.³⁴ The explanation for the effect of TiCl_3 addition in borohydrides is still missing as well as the reason why borohydrides does not reversible store hydrogen in presence of TiCl_3 .

In this work, we specifically address the effects of TiCl_3 addition to NaAlH_4 and LiBH_4 , as examples for alanates and borohydrides, identifying similarities and differences between the two systems. Spectroscopic measurements highlight the impact metathesis reaction products have on the kinetics of the decomposition of borohydrides. Specifically, the addition of TiCl_3 to borohydrides results in the formation of volatile $\text{Ti}(\text{BH}_4)_3$. The analogous compound, $\text{Ti}(\text{AlH}_4)_3$, has not been detected. H–D exchange measurements show that $\text{Ti}(\text{BH}_4)_3$ is extremely reactive and unstable. Its formation and decomposition is an irreversible process. We identify in this species the key to achieve the reversibility of borohydrides.

MATERIALS AND METHODS

Materials. For alanates, we investigated both NaAlH_4 and LiAlH_4 , however, the similarities of the experimental results and the higher decomposition temperature of NaAlH_4 (closer to the one of LiBH_4) made us restrict the presentation to NaAlH_4 .

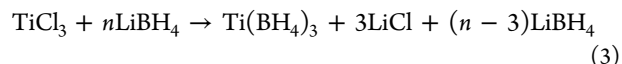
Concerning alanates, we studied the following reaction:



TiCl_3 -doped alanates decompose into solid products (NaCl , TiAl_3 , Al) and hydrogen.⁶ Evidence of Ti–Al compounds confirm the presence of Ti in the sample after the decomposition of the initial complex hydride.¹⁴ Independent of the molar percentage of the TiCl_3 additive, the

dehydrogenated alanate reabsorbs hydrogen to form the alanate again. Because of the small amount of additive required to catalyze the reaction (2–3 mol %), this is considered doping.

Concerning borohydrides, we studied the following metathesis reaction



The stability of LiCl (as in Table 1) with respect to TiCl_3 drives the reaction and induces the formation of a Ti-containing product: $\text{Ti}(\text{BH}_4)_3$. Ti is consumed in this metathesis reaction and therefore it cannot be considered a catalyst. The formation of $\text{Ti}(\text{BH}_4)_3$ enables to investigate an interesting material for hydrogen storage since this complex hydride stores 13 mass % of hydrogen. The decomposition path of the metathesis and metathesis products provides insight into the interaction between Ti atoms and borohydrides.

Methods. LiBH_4 , NaAlH_4 , TiCl_3 , and TiCl_4 were purchased from SigmaAldrich Fine Chemicals. The metatheses were carried out by ball-milling of NaAlH_4 or LiBH_4 and TiCl_3 using a Spex mill, as described in eqs 2 and 3, or simply mixing the powders with TiCl_4 , as in eq 5.

Mass spectrometry measurements were performed with a Pfeiffer 402 spectrometer. Samples were studied by monitoring the emitted species from a heated sample in UHV environment, whose base pressure remained below 10^{-9} mbar.

The weight and the gas emitted from the decomposition of the samples were studied in a combined apparatus consisting of a thermogravimetric balance (TG), by Rubotherm, and an infrared (IR) gas analyzer, Bruker Alpha spectrometer equipped with a 8 cm gas cell at a resolution of 0.9 cm^{-1} . The experimental setup and its advantages are described in detail elsewhere.^{50,51} Every sample was inserted into the balance and heated up (heating ramp was $1^\circ\text{C}/\text{min}$), while the real time analysis of the emitted gas species as a function of time or temperature was provided by the IR spectrometer. The desorption of each sample took place in a 250 ml/min flow of hydrogen (or deuterium, when indicated) at 1 bar, which transported the emitted gas from the sample to the IR-cell.

The vibrational properties of the $\text{Ti}(\text{BH}_4)_3$ molecule were calculated by density functional theory and the plane-wave pseudopotential method as implemented in the Gaussian code.^{52,53} Pseudopotentials were of the optimized norm-conserving variety with a plane-wave cutoff of 720 eV as an isolated molecule in a cell of 780 Å^3 . Calculations were performed under the PBE approximation to exchange and correlation.⁵⁴ Pseudopotential errors in the frequencies were estimated at no more than 1% from a comparison of alternative pseudopotentials.

RESULTS AND DISCUSSION

Spectroscopic and thermogravimetric measurements were performed to study the different effect of TiCl_3 addition to NaAlH_4 and LiBH_4 .

Mass Spectrometry. To analyze the processes that take place at the surface the samples, we performed mass spectroscopy (MS) in ultrahigh vacuum. In ultrahigh vacuum the species that are formed at the surface of the samples are released and the MS collects the signal of the species themselves and their fragments. In Figure 1, the collected spectra for Ti-doped NaAlH_4 of eq 2 and Ti-added LiBH_4 of eq 3 are presented.

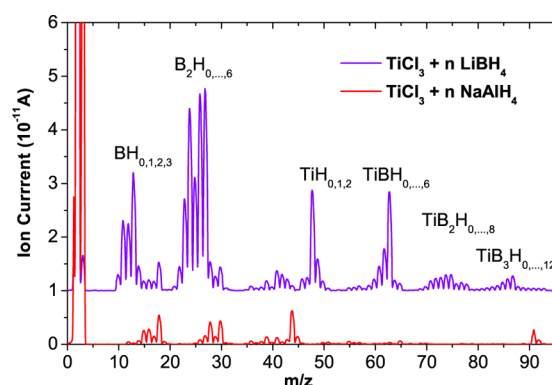


Figure 1. Mass spectrometry spectra of Ti-added NaAlH₄ and LiBH₄. Only the borohydride showed the formation of Ti-containing species.

For the alanate (red spectrum), the visible peaks corresponded to hydrogen ($m/z = 2$) and Al ($m/z = 26, 27$). The remaining peaks in the spectrum occurred due to background impurities, such as THF and water, and were visible in all measurements. These results are in good agreement with spectra from the literature for Ti-doped NaAlH₄.³⁷ When the doped sample was heated, no Ti-containing species were detected during the decomposition of NaAlH₄. This indicates that during the alanate decomposition, no intermediate Ti-species are generated at the sample surface, or if intermediate Ti-species are formed, they are so unstable that they immediately decompose, making them not detectable by MS.

For the borohydride (purple spectrum), at room temperature MS peaks from hydrogen ($m/z = 2$) and from diborane ($m/z = 10, \dots, 13, 22, \dots, 28$) were detected. The other peaks were assigned to Ti-containing species and fragments, specifically

- $m/z = 40, 49, 50$ from TiH_{0,1,2};
- $m/z = 59, \dots, 65$ from TiBH_{0,\dots,6};
- $m/z = 70, \dots, 78$ from TiB₂H_{0,\dots,6};
- $m/z = 81, \dots, 93$ from TiB₃H_{0,\dots,12}.

These results indicate that Ti is consumed during the reaction and the product of the metathesis are Ti(BH_x)_y. Because of the nature of MS, we infer that Ti(BH_x)_y are formed at the surface of the sample.

Thermogravimetric Balance. To analyze the processes that take place in the bulk and lead to the emission of gaseous species, we performed thermogravimetric measurements (TG). We analyzed the evolution of the Ti-added complex hydrides, as in eqs 2 and 3. The sample was inserted into a gravimetric balance and heated in hydrogen flow: the mass loss due to the emission of gaseous species was measured. Figure 2 shows the TG data, that is, the mass loss as a function of temperature for both Ti-containing systems.

For the alanate (red curve), the addition of TiCl₃ catalyzed the decomposition reaction of NaAlH₄. The mass loss of approximately 4 mass % is in agreement with hydrogen release from NaAlH₄.

For the borohydride, pure LiBH₄ decomposes into LiH, B and hydrogen above 300 °C, with the mass loss corresponding to hydrogen release of around 14 mass%.³⁸ The addition of TiCl₃ to LiBH₄ made the decomposition reaction of TiCl₃ + LiBH₄ start at room temperature (purple line in figure 2). The mass loss (higher than 14 mass %) could not only be ascribed to hydrogen emission from LiBH₄ but rather also occurred due

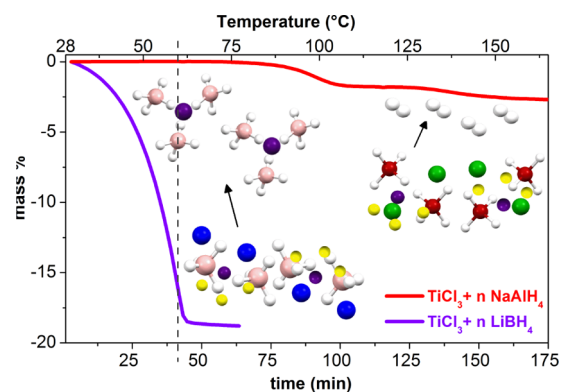


Figure 2. TG measurements of the complex hydrides with the addition of TiCl₃ in hydrogen gas flow, as indicated. Color code for the schematic illustration of the emitted species: Ti, purple; Cl, yellow; Li, blue; B, pink; Al, red; Na, green; and H, gray.

to formation and emission of volatile Ti(BH_x)_y compounds and diborane, in agreement with MS measurements.

A quantitative study of the influence of additive concentration to the kinetics of LiBH₄ was then performed, as in the top panel of Figure 3. Up to 100 °C, the mass loss of the TiCl₃ added LiBH₄ scaled linearly with the amount of TiCl₃ added (1, 0.5, and 0.1 mol %), as shown in the inset. In this inset, the correlation between the theoretical mass loss due to Ti(BH₄)₃

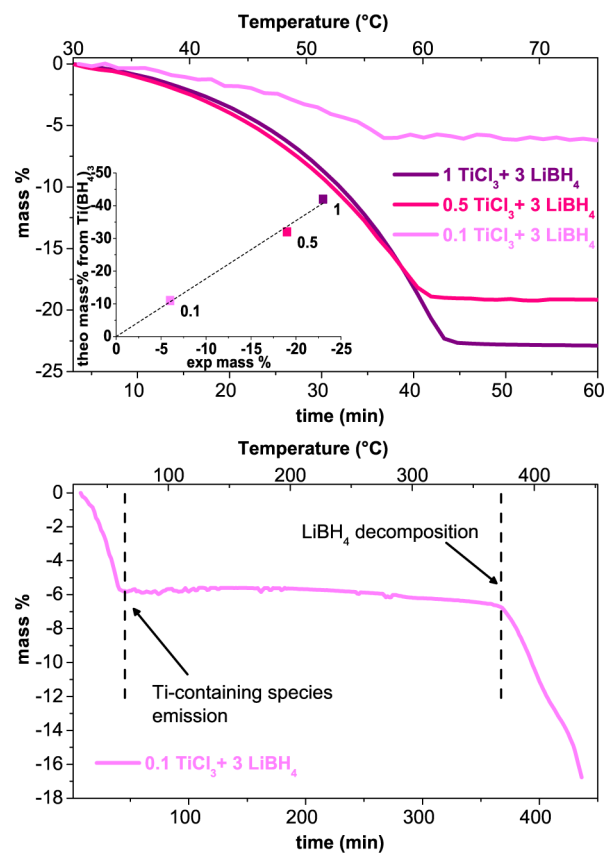


Figure 3. TG measurements in 1 bar hydrogen gas flow of TiCl₃ + n LiBH₄. Top panel: quantitative study revealing the influence of TiCl₃ concentration to the emission of Ti(BH₄)₃. In the inset, the correlation between the additive concentration and the registered mass loss. Bottom panel: full decomposition reaction of LiBH₄ with 0.1 mol % TiCl₃ addition.

emission and the experimentally detected mass loss is presented. The experimental data collected as a function of additive concentration sit on a line intercepting the origin. This indicates that all the added Ti was consumed during the decomposition reaction. This means that the turnover number of the additive is 1 and that it cannot be considered a catalyst. To be mentioned, the slope of the curve is smaller than 1 because of the gas loss during the loading of the samples inside the balance. To decompose the excess of LiBH_4 in the sample with the lowest additive concentration, the sample temperature had to be above 300°C , as expected for pure LiBH_4 , bottom panel of Figure 3. The addition of TiCl_3 to LiBH_4 leads to formation of a metastable volatile phase that is proportional to the TiCl_3 content. Neither TiCl_3 nor $\text{Ti}(\text{BH}_x)_y$ affect the dehydrogenation kinetics of LiBH_4 ; they do not catalyze hydrogen desorption reaction in LiBH_4 , as in the bottom panel of Figure 3.

The $\text{TiCl}_3 + \text{LiBH}_4$ metathesis is extremely vigorous; at room temperature, 1 bar hydrogen pressure, the spontaneous mass loss due to the emission of $\text{Ti}(\text{BH}_x)_y$ was completed within 5 h.

XRD analysis (not shown) on the solid residue of the reaction shows that LiCl was the main solid product; LiCl is the only crystalline product if the stoichiometry of the reactants was $1 \text{ TiCl}_3 + 3 \text{ LiBH}_4$. TiH_2 was not detected in the sample residue. We cannot exclude the presence of nano Ti-species in the residue, which might have an impact on the reactions of LiBH_4 .³⁹ A similar effect has been shown in alanates, as discussed in the introductions.^{21–23} In the presented system, Ti–H species, revealed by the MS analysis, are decomposition products of volatile $\text{Ti}(\text{BH}_x)_y$.

The gray dashed line in Figure 2 indicates the temperature (60°C) which corresponds to the IR gas analysis, presented below in Figure 4.

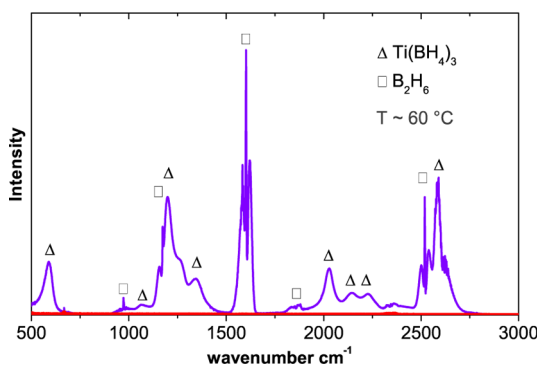


Figure 4. IR spectra of the samples with TiCl_3 in hydrogen flow at 60°C ; no volatile species are detected in the case of Ti-doped NaAlH_4 (red line), while Ti-added LiBH_4 emits $\text{Ti}(\text{BH}_4)_3$ and diborane (purple line^{42,43}).

Infrared Spectroscopy. Many complex hydrides are known to decompose and emit volatile boron- and hydrogen-containing species,⁴⁰ for example, diborane. The analysis of these gaseous species is complementary to solid-state investigations and gives important information for identifying the decomposition reaction pathway. To complete the gas evolution analysis of the Ti-added complex hydrides, as in eqs 2 and 3, an infrared spectrometer (IR) was connected to the TG, providing simultaneous analyses. The gaseous species emitted by the samples in the TG were carried to the IR spectrometer by the gas flow. A real-time identification of the emitted gas

species from the samples in the TG as a function of time and sample temperature was provided by the IR spectrometer. Figure 4 presents the IR spectra of the gaseous products emitted from the samples at 60°C .

For the alanate (red spectrum), the IR analysis did not reveal the presence of any volatile species above impurity level (hydrogen is IR inactive). No Ti-containing compounds were emitted, in agreement with both the MS and TG measurements.

For the borohydride, the IR analysis (presented in purple) shows that trivalent titanium borohydride and diborane were the main emitted species. $\text{Ti}(\text{BH}_4)_3$ is formed at the surface and released as a gas. Because of the volatility of $\text{Ti}(\text{BH}_4)_3$, one of the main problems in the past was the misidentification of $\text{Ti}(\text{BH}_4)_3$ (confused with diborane);⁴¹ clearly, solid state investigations³³ were not suitable for detecting $\text{Ti}(\text{BH}_4)_3$ and the analysis of the gas phase in the study of the decomposition of complex hydrides systems is critical.

IR spectra were collected as a function of time, which is coupled to the temperature of the sample from the TG data. Since the IR analysis was performed during the whole decomposition process, it is possible to follow the evolution of the individual gaseous species. In Figure , the mass loss rates

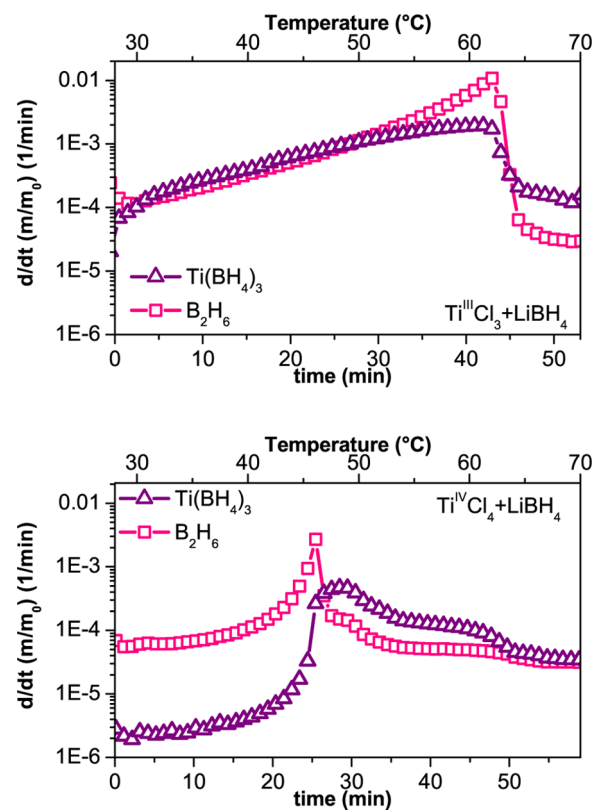


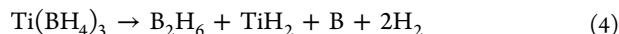
Figure 5. Mass loss rates in hydrogen flow for $\text{Ti}(\text{BH}_4)_3$ and B_2H_6 , as computed from the IR time evolution spectra, as a function of the temperature. Top: solid–solid metathesis. Bottom: liquid–solid metathesis.

of the sample due to $\text{Ti}(\text{BH}_4)_3$ and diborane emission are presented. The mass loss rates were computed from the intensity variation of the infrared absorbance signal of the selected gaseous species.

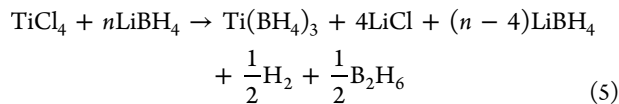
To investigate the effect of the valence state of the additive we focused on two metatheses: solid–solid via addition of

TiCl₃ (powder) to LiBH₄ or liquid–solid via addition of TiCl₄ (liquid) to LiBH₄.⁴⁴ Figure 5 presents the mass loss rates of diborane and Ti(BH₄)₃ in the two different syntheses: solid–solid in the top panel and liquid–solid in the bottom panel.

In the solid–solid synthesis, diborane emission is not predicted by eq 3. However, its IR-active vibration peaks were clearly visible. In the top panel of Figure 5, the mass loss rate due to diborane emission increased simultaneously with the IR signal of Ti(BH₄)₃ and became predominant after 50 °C. From the time evolution of the two species, we infer that diborane is a product of the decomposition of Ti(BH₄)₃. The combination of these results with the information from MS and XRD of TiH₂ are summarized in the eq 4



The reaction path for the liquid–solid synthesis is different. The emitted species above impurity level were TiCl₄, diborane and trivalent titanium borohydride. From the IR analysis in the bottom panel of Figure 5, it is shown that diborane emission occurred immediately at room temperature, while Ti(BH₄)₃ was emitted only once the sample reached 45 °C. At this temperature, Ti(BH₄)₃ suppressed the diborane emission almost completely. The remaining diborane emission resulted from the decomposition of Ti(BH₄)₃ as before. This abrupt step in the decomposition reaction path might suggest the formation of an intermediate unstable species. Tetravalent titanium borohydride has been theoretically described, but not experimentally found, because it is predicted to decompose to trivalent titanium borohydride below room temperature.⁴⁵ However, to reduce the oxidation state of Ti and form titanium borohydride trivalent, diborane emission is required, as in eq 5



In agreement with our measurements. The IR analysis of the gas emitted species identified the volatile metathesis product Ti(BH₄)₃ and highlighted that the metathesis product is independent of the valence of the Ti halide. In both analyzed metatheses, trivalent titanium borohydride is the reaction product. However the valence of the Ti halide changes the reaction pathway and might, in the case of liquid–solid synthesis, involve the formation of intermediate unstable species.

Hydrogen–Deuterium Exchange. The formation of Ti(BH₄)₃ compels an investigation of the mobility of hydrogen atoms in this complex hydride. Hydrogen–deuterium exchange experiments (H–D) are a powerful tool to label atoms. Deuterium substitution can be detected by optical spectroscopy due to the isotopic shift of D-containing species in the IR spectra.

It has been reported that pure LiBH₄ in 1 bar of deuterium flow does not exchange hydrogen and deuterium below the melting point,^{46,47} while TiCl₃ doped NaAlH₄ does in the solid phase.¹³

TG and IR measurements of the metathesis shown in eq 3 under deuterium flow were performed. A heating ramp was set up to 100 °C, well before the melting point of LiBH₄ and the IR spectra were collected as a function of time and sample temperature. For comparison with the previous measurements in hydrogen flow, the top panel of Figure 6 presents the IR spectrum recorded at a sample temperature of 60 °C. The IR

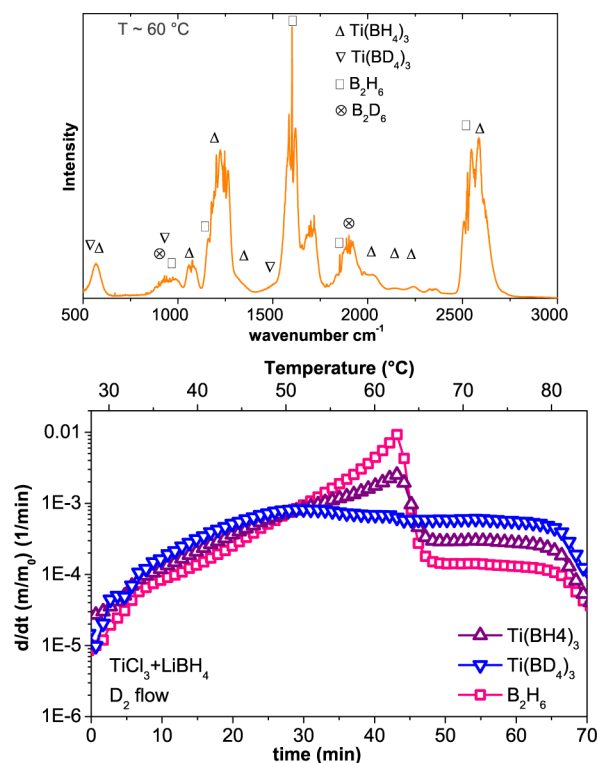


Figure 6. Top panel: IR spectra of TiCl₃+LiBH₄ exposed to 1 bar deuterium flow, at 60 °C. Bottom panel: mass loss rates in deuterium flow for Ti(BD₄)₃, Ti(BH₄)₃, and B₂H₆, as computed from the IR time evolution spectra, as a function of the temperature.

analysis of the metathesis reaction under deuterium flow shows the formation of multiple new peaks compared to the corresponding spectrum under hydrogen flow (in Figure 4): Ti(BH₄)₃ and Ti(BD₄)₃ as well as B₂H₆ and B₂D₆ were formed. The H–D exchange occurred in the gas phase, however the formation of the Ti-species at the surface can also favor the exchange at the surface. As before, the mass loss rates of the metathesis gaseous products exposed to deuterium flow were computed from the IR intensity lines. The lower panel of figure 6 shows that hydrogen was substituted by deuterium in Ti(BH₄)₃ at room temperature. The decomposition of Ti(BH₄)₃ into diborane, however, is not affected by the H–D exchange; Ti(BH₄)₃ decomposes into diborane up to 65 °C, similarly as under hydrogen flow (top panel of Figure 4).

The H–D exchange experiment indicates that H atoms in Ti(BH₄)₃ are extremely mobile. The high mobility of hydrogen atoms is moreover shown by the reaction time constants. Two competing processes are involved in the reaction: the decomposition of Ti(BH₄)₃ into B₂H₆ and the isotope exchange between Ti(BH₄)₃ and Ti(BD₄)₃. From the mass loss rates (Figure 6), it is possible to deduce that the competition between the processes only is significant at the beginning of the reaction, below 50 °C. The emission of Ti(BH₄)₃ is accelerated by the increasing temperature. The subsequent decomposition of Ti(BH₄)₃ into diborane becomes the predominant effect above 50 °C. However, upon analyzing the data below 50 °C, it is possible to estimate the reaction rate constants for the two competing reactions. With the assumption that the exchange and decomposition reactions are independent and of first order, the value of *k*₂ is found to be more than twice as large as that of *k*₁; exchange is more than two times faster than decomposition.

H-D exchange experiments show that $\text{Ti}(\text{BH}_4)_3$ is reactive because it exchanges its hydrogen atom easily. Its formation and decomposition is an irreversible process, which affects the decomposition reaction of TiCl_3 added LiBH_4 .

Theoretical Simulations. H-D exchange experiments gave rise to fully deuterated species, $\text{Ti}(\text{BD}_4)_3$ and B_2D_6 , and the formation of partially exchanged species. The assignment of all IR peaks (spectrum in the top panel of Figure 6) is thus severely complicated by these species. The $\text{Ti}(\text{BH}_4)_3$ molecule has three BH_4 units coordinated to the Ti atom. Three out of the four hydrogen atoms in the BH_4 unit are bridging Ti and B atoms, while the fourth hydrogen atom of the BH_4 unit points outward, away from the Ti center. Therefore there are two different sites, where hydrogen and deuterium exchange.

We calculated DTF IR spectra simulating the IR spectra for $\text{Ti}(\text{BH}_4)_3$ with an increasing number of deuterium substituting hydrogen atoms. We analyzed the simulated spectra for the different possible configurations of hydrogen and deuterium in partially exchanged species and compared them with the evolution of the IR experimental spectra in deuterium flow. The bridging H atoms between the Ti and B centers were identified as the most reactive sites, where deuterium first exchanges with hydrogen. Once these sites are deuterated, the terminal sites are also exchanged.

Taking into account the weighted distribution of equivalent configurations of partially H-D exchanged molecules, we could average all the spectra and show the resulting IR spectrum in black in Figure 7. The simulated spectrum is in agreement with

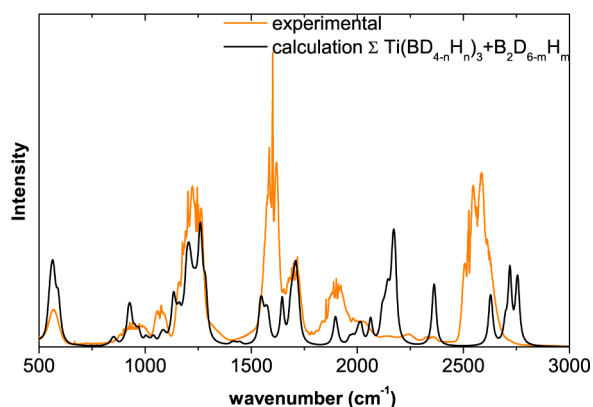


Figure 7. Experimental (as in Figure 6) and simulated IR spectra of $\text{TiCl}_3 + \text{LiBH}_4$ exposed to 1 bar deuterium flow.

the experimental results (Figure 6) and drawn for comparison (orange line in Figure 7). The simulations confirmed the formation of $\text{Ti}(\text{BD}_4)_3$, as well as that of partially exchanged species. The experimental spectrum shows a higher concentration of diborane in the emitted gas from the sample, compared to the simulated spectrum, which is due to the decomposition of $\text{Ti}(\text{BH}_4)_3$ into B_2H_6 . This process competes with the isotope exchange, as explained before, and it is not taken into account for the simulations.

Different Mechanisms. The presented results show the importance of identifying Ti-containing species in understanding the decomposition reactions of borohydrides. These investigations are fundamental to understand the differences between TiCl_3 added to borohydrides and alanates.

Evidence for the presence of Ti in the sample after the decomposition of the alanates¹⁴ is solid and our measurements are consistent with these findings. Although it remains

controversial how the Ti-species act as a catalyst, it is clear that Ti-containing species remain in the solid residue phase of the decomposed alanates and thereby enable the rehydrogenation of alanates. The active catalytic centers during the reversible dehydrogenation of NaAlH_4 are identified as Ti-containing species; TiCl_3 therefore is their precursor. The possibility of a reaction pathway involving an intermediate step, where a Ti–Al–H-containing intermediate species ($\text{Ti}(\text{AlH}_4)_4$) is formed, exists. However, if this is the case the intermediate species is extremely unstable and immediately decomposes because no evidence of this phase has been found under the presented experimental conditions.

On the contrary, the situation is different for borohydrides, as schematically represented in Figure 8. As shown in eq 3 and

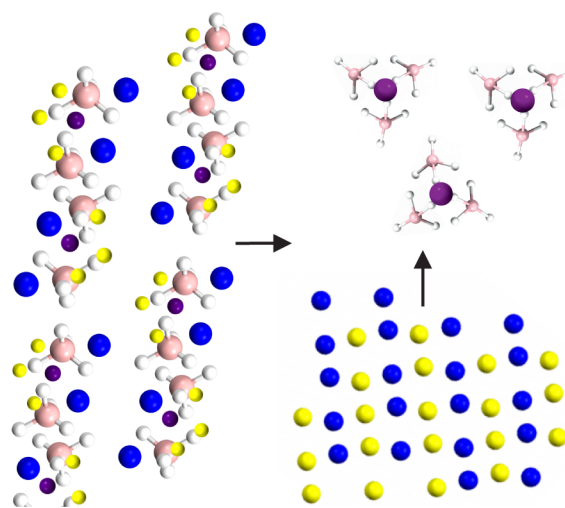


Figure 8. Schematic illustration of the effect of TiCl_3 addition in borohydrides. Volatile Ti-containing species are emitted causing Ti depletion of the system. Color code: Ti, purple; Cl, yellow; Li, blue; B, pink; and H, gray.

established by spectroscopic measurements, a volatile titanium species, $\text{Ti}(\text{BH}_4)_3$, is formed at the surface of the sample during the metathesis $\text{TiCl}_3 + \text{LiBH}_4$.^{48,49} Consequently titanium borohydride desorbs from the sample, depleting the element that is responsible for reversibility in the alanate systems. The metathesis produces $\text{Ti}(\text{BH}_4)_3$ and LiCl . $\text{Ti}(\text{BH}_4)_3$ is formed at the surface of the sample and emitted. It decomposes into TiH_2 , diborane, boron, and hydrogen. Rehydrogenation has been attempted. However these experiments did not show the formation of $\text{Ti}(\text{BH}_4)_3$.⁵⁵ The solid residue of $\text{TiCl}_3 + \text{LiBH}_4$ decomposition reaction is Ti-depleted and cannot reabsorb hydrogen. The active centers during the decomposition reaction of $\text{TiCl}_3 + \text{LiBH}_4$ are identified as Ti-containing species. $\text{Ti}(\text{BH}_4)_3$ is extremely reactive, but it is the volatile product of a complete metathesis reaction. Although we cannot exclude the catalytic effect of Ti nanoimpurities in the residue sample, our measurements show that neither $\text{Ti}(\text{BH}_4)_3$ nor TiCl_3 have a catalytic effect on LiBH_4 .

CONCLUSION

These findings disclose new perspectives for achieving reversibility of complex hydrides; the main effect of TiCl_3 addition in LiBH_4 is the formation of a new Ti-containing species, $\text{Ti}(\text{BH}_4)_3$, through metathesis. This is the fundamental difference between alanates and borohydrides.

For $\text{TiCl}_3 + \text{NaAlH}_4$, no experimental evidence has been found for the formation of an analogous Ti-containing intermediate, such as $\text{Ti}(\text{AlH}_4)_4$. Even if such an intermediate did exist, it would only be an intermediate step of the reaction, extremely unstable and immediately decomposed into solid components. Therefore, the elements Al, Na, and Ti stay in the solid phase and hydrogen is the only emitted species during the dehydrogenation reaction.

In the case of $\text{TiCl}_3 + \text{LiBH}_4$, the formation of Ti-containing species has been identified. $\text{Ti}(\text{BH}_4)_3$ is volatile, extremely reactive, and exhibits a high H mobility. The spectroscopy measurements combined with isotope exchange analyses confirm the high reactivity of $\text{Ti}(\text{BH}_4)_3$ and the fact that the compound has no impact on the dehydrogenation kinetics of LiBH_4 ; it is not a catalyst. Because of the volatility of $\text{Ti}(\text{BH}_4)_3$, the $\text{TiCl}_3 + \text{LiBH}_4$ system becomes Ti-depleted after the first desorption, preventing, under these conditions, the reversibility of the system.

Our results indicate that creating a reversible hydrogen storage system based on borohydrides can not simply be achieved with Ti additives because a metathesis reaction takes place that consumes the additive. On the contrary, a clear catalytic effect is the reason for the enhancement of hydrogen sorption kinetics in alanates. This study sheds light on the effect of the addition of Ti chlorides to complex hydrides and highlights the reasons for the different behaviors of alanates and borohydrides: catalysis or metathesis.

New prospects have emerged; the possibility of trapping or (nano)confining Ti in the borohydride systems is a real option to possibly achieve the reversibility of borohydrides. However, even if Ti is confined in the borohydride system, a metathesis reaction must be avoided. Moreover, the complementarity of the presented experimental techniques is shown to be key to thoroughly investigate spontaneous decomposing reactions.

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Notes

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