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Ti-Doped $LiAlH_4$ for Hydrogen Storage: Synthesis, Catalyst Loading and Cycling Performance

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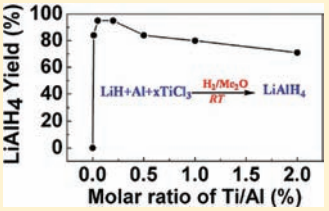
Supporting Information

ABSTRACT: The direct synthesis of $LiAlH_4$ from commercially available LiH and Al powders in the presence of $TiCl_3$ and Me_2O has been achieved for the first time. The effects of $TiCl_3$ loadings (Ti/Al = 0, 0.01, 0.05, 0.2, 0.5, 1.0 and 2.0%) and various other additives ($TiCl_3/Al_2O_3$, metallic Ti, Nb_2O_5, and $NbCl_5$) on the formation and stability of $LiAlH_4$ have been systematically investigated. The yield of $LiAlH_4$ initially increases, and then decreases, with increasing $TiCl_3$ loadings. LiH + Al → $LiAlH_4$ yields above 95% were obtained when the molar ratios of Ti/Al were 0.05 and 0.2%. In the presence of a very tiny amount of $TiCl_3$ (Ti/Al = 0.01%), $LiAlH_4$ is still generated, but the yield is lower. In the complete absence of $TiCl_3$, $LiAlH_4$ does not form. Addition of metallic Ti, Nb_2O_5, and $NbCl_5$ to commercial LiH and Al does not result in the formation of $LiAlH_4$. Preliminary tests show that $TiCl_3$-doped $LiAlH_4$ can be cycled, making it a suitable candidate for hydrogen storage.



1. INTRODUCTION

Safe and efficient hydrogen storage technology is one of the key technical barriers to the widespread commercialization of hydrogen-fueled vehicles.[1−3] Among the current hydrogen storage technologies, complex metal hydrides have received a lot of attention due to their high gravimetric H_2 capacity.[4−6] $LiAlH_4$ has a theoretical hydrogen storage capacity of 7.9 wt % and starts to desorb hydrogen close to room temperature in the presence of suitable catalysts, making it a potential hydrogen storage medium for future hydrogen-fueled vehicles.[7,8] However, the irreversibility of the dehydrogenation reactions of $LiAlH_4$ under practical conditions restricts its application as a suitable hydrogen storage medium. For example, rehydrogenation of LiH + Al to $LiAlH_4$ requires extremely high hydrogen pressures, in excess of 10 kbar.[9]

$LiAlH_4$ was first prepared through a reaction between LiH and $AlCl_3$ in ether solution (eq R1).[10] Later, a metathesis reaction was also successfully applied to synthesize $LiAlH_4$ (eq R2).[11] If $LiAlH_4$ is to be used as a hydrogen storage medium, neither of these routes will be suitable for practical regeneration of the dehydrogenated material (i.e., LiH + Al).

$$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl \quad (R1)$$

$$NaAlH_4 + LiCl \rightarrow LiAlH_4 + NaCl \quad (R2)$$

Direct synthesis of $LiAlH_4$ from its dehydrogenated products (LiH and Al) under moderate conditions is crucial if $LiAlH_4$ is to become a practical hydrogen storage material. In the 1960s, Ashby et al. reported the synthesis of $LiAlH_4$ from a mixture of LiH and activated Al in THF or diglyme solvent under 350 bar H_2 at 120 °C.[12] More recently, Wang et al. regenerated $LiAlH_4$ from a mixture of LiH and Al through high-pressure and high-energy ball-milling in the presence of THF and catalyst.[13,14] In the latter study, the five-step physical and chemical pathway for rehydrogenation of $LiAlH_4$ required separation of catalyst in each cycle, and also the removal of THF by heating under vacuum over an extended period of time. In another study, Graetz et al. demonstrated a modified route to regenerate $LiAlH_4$ through an initial hydrogenation of Ti-catalyzed Al and LiH in THF to form the adduct $LiAlH_4 \cdot 4THF$, and subsequent desolvation to recover $LiAlH_4$.[15] In this method, ethereal AlH_3 was first prepared through a reaction between $LiAlH_4$ and $AlCl_3$ in Et_2O. With the addition of $TiCl_3$, the ethereal solution of AlH_3 was dried and decomposed to obtain Ti-catalyzed Al under vacuum. The methods employing THF as the reaction medium all require a separate step for removal of the THF. It usually takes 4−6 h to remove THF completely at 60 °C under reduced pressure. Besides the efficiency and cost of these methods, it is also not easy to avoid the decomposition of Ti-doped $LiAlH_4$ during THF removal. Our group has reported a much simpler and energy-efficient single-stage regeneration procedure for Ti-doped $LiAlH_4$.[16] In this method, a mixture of LiH and Al from the decomposition of $TiCl_3$-catalyzed $LiAlH_4$ was rehydrogenated to form $LiAlH_4$ in the presence of volatile Me_2O at room temperature. Dry Ti-doped $LiAlH_4$ powder was obtained directly after a cautious release of H_2 and excess Me_2O. The use of Me_2O not only delivers a high yield of $LiAlH_4$ but also avoids the time-consuming drying process.

In the work reported here, we have eliminated the initial dehydrogenation process of Ti-doped $LiAlH_4$ and directly synthesized the

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doped material directly from commercially available LiH and Al powders, in the presence of a $TiCl_3$-derived catalyst and Me_2O. The effects of $TiCl_3$ loadings (Ti/Al = 0, 0.01, 0.05, 0.2, 0.5, 1.0, and 2.0 mol %) and of other catalysts ($TiCl_3/Al_2O_3$, metallic Ti, Nb_2O_5, and $NbCl_5$) on the formation of $LiAlH_4$ have been systematically investigated. In addition, a preliminary study of the cycling performance of Ti-doped $LiAlH_4$ and of Ti/Al_2O_3-doped $LiAlH_4$ is presented.

2. EXPERIMENTAL METHODS

LiH (Aldrich, 95%), Al powder (Alfa Aesar, ~325 mesh, 99.97%), $TiCl_3$ (Aldrich, 99.999%), Ti (Aldrich, ~325 mesh, 99.98%), $NbCl_5$ (Aldrich, 99.9%), Nb_2O_5 (Aldrich, ~325 mesh, 99.9%), and Al_2O_3 (BDH, type 60/E) were used as received. All materials and samples were handled in a nitrogen-filled glovebox. LiH/Al/catalyst (catalyst = 0.2 mol % Ti, $NbCl_5$ or 0.1 mol % Nb_2O_5) and LiH/Al/$TiCl_3$ with various concentrations of $TiCl_3$ (molar ratio of Ti/Al = 0, 0.01, 0.05, 0.2, 0.5, 1.0, and 2.0%) were each mixed by ball-milling. In a typical experiment, a 5 g mixture of the powders was loaded in a 250 mL stainless steel milling vessel containing five stainless steel balls (about 162 g). The powder mixtures were mechanically milled at room temperature in a nitrogen atmosphere at a rotational speed of 300 rpm for 12 h using a Retsch PM 100 planetary ball-mill. After every 15 min of milling, there was a 30 s pause, and the rotation was automatically reversed. Ti/Al_2O_3 catalyst was prepared by milling $TiCl_3$ and Al_2O_3 in a 1:4 mol ratio. Activation of the catalyst was carried out under an initial hydrogen pressure of 100 bar. The supported catalyst was heated to 200 °C at a ramping rate of 2 °C min^{-1}, and held at that temperature for 12 h using a PCTPro-2000 Sieverts-type instrument manufactured by HyEnergy LLC. The LiH/Al/$TiCl_3/Al_2O_3$ (0.05 mol % $TiCl_3$) mixture was recovered from the PCT vessel and ball-milled again.

Hydrogenation reactions in Me_2O (Air Liquide Canada Inc., chemically pure) were carried out in a 500 mL stainless steel stirred reactor (Parr Instruments). In a typical procedure, the reactor was loaded in a glovebox with 650 mg of the ball-milled LiH/Al/catalyst mixture. The reactor was sealed, removed from the glovebox, and connected to a Me_2O cylinder. Approximately 55 g of Me_2O was then transferred to the reactor. Next, H_2 gas (100 bar) was added to the reactor. After 24 h of stirring at ambient temperature the reaction was stopped, and H_2 and Me_2O were vented immediately.

Powder X-ray diffraction (XRD) was performed on a Rigaku MiniFlex II diffractometer with a Cu Kα radiation source. Samples for XRD analysis were mounted on a PVC plastic disk and covered with parafilm to protect the material from contact with air or moisture during the experiments. The parafilm resulted in two diffraction peaks (2θ = 21.6 and 24°). Thermogravimetric analysis was performed on a TGA Q50 series thermogravimetric analyzer. In a typical procedure, approximately 8 mg of sample was loaded in an Al crucible in a nitrogen-filled glovebox. The sample was heated to 300 °C at a ramping rate of 2 °C/min under a N_2 flow rate of 120 mL/min. Decomposition kinetics plots were obtained using a commercial PCTPro-2000 Sieverts-type instrument produced by HyEnergy LLC. In a typical experiment, approximately 350 mg of sample was loaded into a sample holder in a nitrogen-filled glovebox. The sample holder was then attached to the PCT instrument without exposing the sample to air. The sample was heated at a ramping rate of 2 °C/min to 250 °C and then held at this temperature for 30 min.

In addition, the morphology and elemental analysis of the samples were studied by transmission electron microscopy (JEOL 2011 Scanning TEM).

3. RESULTS AND DISCUSSION

3.1. Effect of $TiCl_3$ Loadings on the Formation and Stability of $LiAlH_4$. Previously, we reported the regeneration of

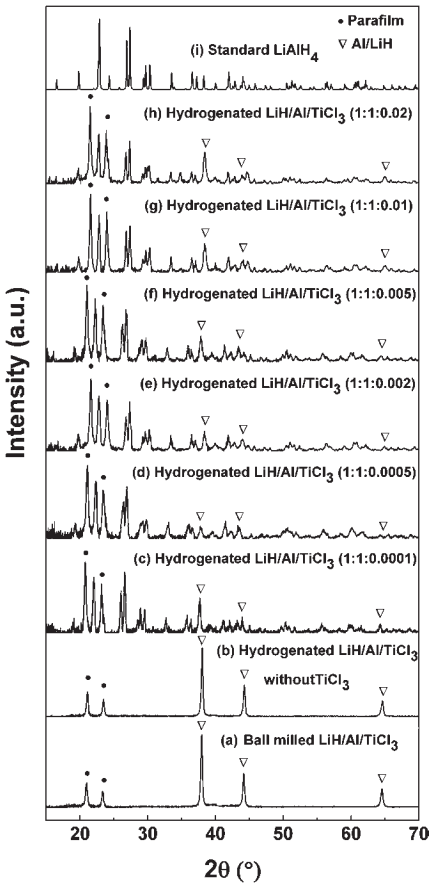

Figure 1. XRD patterns of ball-milled LiH/Al/$TiCl_3$ and hydrogenated samples with various $TiCl_3$ loadings: (a) ball-milled LiH/Al/$TiCl_3$ (1:1:0.002); (b) hydrogenated LiH/Al/$TiCl_3$ (1:1:0) without $TiCl_3$; (c) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.0001); (d) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.0005); (e) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.002); (f) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.005); (g) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.01); (h) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.02); (i) standard $LiAlH_4$ from ICDD. $LiAlH_4$ formed after the hydrogenation of ball-milled LiH/Al/$TiCl_3$, but no $LiAlH_4$ formed without the addition of $TiCl_3$.

Ti-doped $LiAlH_4$ in Me_2O at room temperature.[16] In this earlier study, $LiAlH_4$ was first doped with $TiCl_3$ and then decomposed to LiH and Al, followed by rehydrogenation in Me_2O. In the subsequent work reported here, we have avoided this rehydrogenation approach. Instead, commercially available LiH and Al (1:1) were directly doped using different amounts of $TiCl_3$ (molar ratio of Ti/Al = 0, 0.01, 0.05, 0.2, 0.5, 1.0, and 2.0%) by ball-milling and then hydrogenated at room temperature in Me_2O. It is notable that much lower amounts of $TiCl_3$ dopant are reported here. Figure 1 shows XRD patterns for ball-milled LiH/Al/$TiCl_3$ (1:1:0.002) and the hydrogenated samples with various $TiCl_3$ loadings. It is evident that these Ti-doped LiH/Al samples have been directly hydrogenated to $LiAlH_4$. The relative intensity of unreacted LiH/Al peaks decreases with decreasing amounts of $TiCl_3$ down to Ti/Al = 0.2%, indicating that lower $TiCl_3$ loading favors the formation of $LiAlH_4$ and increases its stability, in accordance with the catalyst activating both hydrogen uptake and release. However, when the $TiCl_3$ content was further lowered to 0.01% (Ti/Al), $LiAlH_4$ formed but the intensity of unreacted LiH/Al peaks increased slightly. The yield of $LiAlH_4$ as

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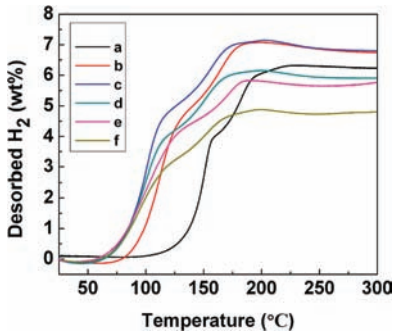

Figure 2. Temperature-programmed desorption (TPD) curves measured by TGA: (a) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.0001); (b) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.0005); (c) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.002); (d) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.005); (e) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.01); (f) hydrogenated LiH/Al/$TiCl_3$ (1:1:0.02).

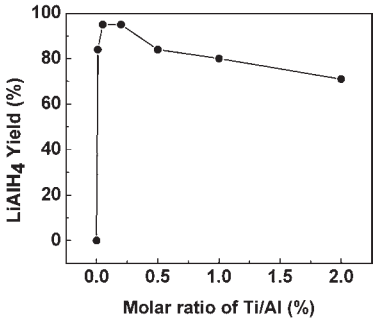

Figure 3. Dependence of $LiAlH_4$ yield on the loading of $TiCl_3$ (molar ratio of Ti/Al).

a function of $TiCl_3$ loadings is discussed below. Undoped LiH/Al (Figure 1b) could not be hydrogenated to $LiAlH_4$, indicating that a very small but nonzero amount of $TiCl_3$ is necessary for the formation of $LiAlH_4$. It should be pointed out that the diffraction peaks of LiH are difficult to discern (Figure 1a) on account of the low atomic numbers of the elements, because LiH becomes amorphous after ball-milling, and/or because its peaks overlap with those of Al.[13,14]

Figure 2 shows temperature-programmed desorption (TPD) curves of hydrogenated samples with various $TiCl_3$ loadings. The TPD curves were derived from TGA data. The maximum amounts of desorbed H_2 for LiH/Al/xTiCl$_3$ (x = 0.0001, 0.0005, 0.002, 0.005, 0.01, and 0.02) were 6.3, 7.1, 7.1, 6.2, 5.8, and 4.9 wt %, respectively. Considering the purity of LiH (95%) and the maximum hydrogen content of $LiAlH_4$ (7.5 wt %, 95% purity), the yields of $LiAlH_4$ were calculated to be 84, 95, 95, 84, 80, and 71%, respectively. The dependence of the $LiAlH_4$ yield on the loading of $TiCl_3$ is presented in Figure 3. The yield of $LiAlH_4$ tends to increase with decreasing $TiCl_3$ loading down to x = 0.002, and then decreases as x drops to 0.0001, in agreement with XRD analysis. The results also indicate that the $TiCl_3$-derived catalyst acts in both directions: it promotes the conversion of LiH/Al to $LiAlH_4$, and it activates the decomposition of $LiAlH_4$ to Li_3AlH_6 or LiH/Al. Under the current reaction conditions (room temperature and 100 bar H_2), a low Ti/Al proportion of 0.05−0.2% provides the optimum balance between conversion to $LiAlH_4$ and stability of $LiAlH_4$, resulting in a high yield. However, $LiAlH_4$ did not form at all when LiH/Al was ball-milled

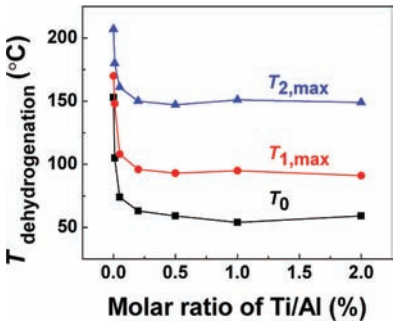

Figure 4. Dependence of dehydrogenation temperature on the loading of $TiCl_3$ (molar ratio of Ti/Al). T_0, $T_{1,max}$, and $T_{2,max}$ represent the onset dehydrogenation temperature, the dehydrogenation temperature at the maximum desorption rate during the first-stage dehydrogenation, and the dehydrogenation temperature at the maximum desorption rate during the second-stage dehydrogenation, respectively.

without $TiCl_3$, indicating the crucial role of tiny amounts of Ti in the formation of $LiAlH_4$. $TiCl_3$ shows a high catalytic efficiency in this system, and the loadings of $TiCl_3$ used in this study were much lower than those used in the previously reported THF-based synthesis of $LiAlH_4$,[15] or of the widely studied $NaAlH_4$ system,[17] where 2 mol % Ti is typically used. In this study, high $TiCl_3$ loadings (Ti/Al > 0.5%) result in a significant decrease in the yield, because $LiAlH_4$ is less thermodynamically stable than its Na congener, and higher $TiCl_3$ loadings promote decomposition of $LiAlH_4$. A two-stage decomposition of Ti-doped $LiAlH_4$ can be clearly observed in Figure 2, in agreement with previous studies.[7,18]

Figure 4 shows the dependence of dehydrogenation temperature on the loading of $TiCl_3$ (molar ratio of Ti/Al). T_0 represents the onset dehydrogenation temperature, $T_{1,\ max}$ represents the dehydrogenation temperature at the maximum desorption rate on the first stage of dehydrogenation, and $T_{2,max}$ represents the dehydrogenation temperature at the maximum desorption rate on the second stage of dehydrogenation. T_0, $T_{1,max}$, and $T_{2,max}$ each show a significant decrease with increasing $TiCl_3$ loading (Ti/Al < 0.2%). When Ti/Al is above 0.2%, the dehydrogenation temperature changes slightly, indicating that a small amount of $TiCl_3$ greatly decreases the dehydrogenation temperature of $LiAlH_4$ and an excess of $TiCl_3$ might aggregate to form some "Ti-rich" areas (clusters) during the venting of H_2 and Me_2O. The activity of the Ti catalyst will be degraded by the formation of Ti clusters.

To investigate the formation of "Ti-rich" clusters, a TEM study was performed on a rehydrogenated LiH/Al/$TiCl_3$ (1:1:0.005) sample. Figure S1 shows an EDAX pattern measured for this sample, with the corresponding TEM image inset. This particle was chosen for its high Ti content. According to energy-dispersive X-ray (EDX) analysis, the composition of this particle is ~96% Ti and 4% Al, strongly suggesting that the Ti aggregates during cycling. This aggregation may explain the falloff in cycling performance. After each de-/rehydrogenation cycle, the Ti catalyst agglomerates into large particles with low surface area, that are not necessarily in contact with the majority of the $LiAlH_4$/LiH/Al sample.

3.2. Dehydrogenation Kinetics of Synthesized Ti-Doped $LiAlH_4$. The decomposition kinetics of Ti-doped $LiAlH_4$ was investigated by means of a Sieverts-type apparatus. As shown in Figure S2, as-received $LiAlH_4$ can release 7.5 wt % H. The

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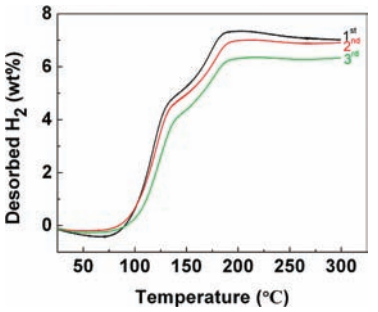

Figure 5. Cycling performance of $TiCl_3$-catalyzed $LiAlH_4$ as measured by TGA. The amount of H_2 desorbed in the first, second, and third cycles is 7.3, 7.0, and 6.4 wt %, respectively.

desorbed hydrogen contents for the hydrogenated LiH/Al/xTiCl$_3$ (x = 0.0005 and 0.005) are 7.1 and 6.1 wt %, respectively, in excellent agreement with the TGA data reported in Figure 2. From the slope of the curves, the two-stage decomposition of as-received and synthesized Ti-doped $LiAlH_4$ can be clearly observed. Compared to as-received $LiAlH_4$, the onset decomposition temperature for Ti-doped $LiAlH_4$ is significantly lowered, to around 80 °C. The onset temperature for hydrogenated LiH/Al/$TiCl_3$ (1:1:0.005) was lower than that for hydrogenated LiH/Al/$TiCl_3$ (1:1:0.0005), demonstrating that the dehydrogenation temperature of $TiCl_3$-catalyzed $LiAlH_4$ decreases with increasing $TiCl_3$ concentration. However, it should be noted that the dehydrogenation temperature did not significantly change when a certain loading level of $TiCl_3$ (Ti/Al > 0.2%) was reached (as discussed above).

3.3. Hydrogenation−Dehydrogenation Cycling Performance of Ti-Doped $LiAlH_4$. About 1 g of Ti-doped $LiAlH_4$ that was prepared from the hydrogenation of LiH/Al/$TiCl_3$ (1:1:0.0005) was first dehydrogenated at 120 °C under a dynamic vacuum. Ball-milling was performed on the sample before each successive rehydrogenation in order to ensure proper dispersion of the catalyst, which may have agglomerated as a result of the dehydrogenation procedure (as discussed above). The dehydrogenated sample was rehydrogenated under the same conditions as the initial synthesis of $LiAlH_4$. The hydrogen capacity of the rehydrogenated sample was measured by TGA. The remaining sample was decomposed at 120 °C under dynamic vacuum for a second and third time and rehydrogenated under the same conditions. Figure 5 reports the amount of desorbed H_2 obtained from these three cycles: 7.3, 7.0, and 6.4 wt %, respectively, indicating the potential of $TiCl_3$-doped $LiAlH_4$ as a rechargeable hydrogen storage system. However, it was noted that the temperature for hydrogen release increased slightly with successive cycles; this may be attributed to gradual loss in catalytic activity or degradation of the active catalyst species, which is present only in very low amounts.

3.4. Effects of Al_2O_3-Supported Ti on the Hydrogen Storage Performance of $LiAlH_4$. In an attempt to investigate further the cycling performance of $TiCl_3$-doped $LiAlH_4$, $TiCl_3$ was deposited on an Al_2O_3 support. It was anticipated that this support may help to maintain a uniform distribution of the catalyst upon cycling, eliminating the need for ball-milling before successive rehydrogenation procedures, and improving the cyclic performance. The supported catalyst Ti/Al_2O_3 was prepared in a 1:4 mol ratio and activated with hydrogen at 200 °C. The reactant mixture (LiH and Al) was then doped with 0.05 mol % of this

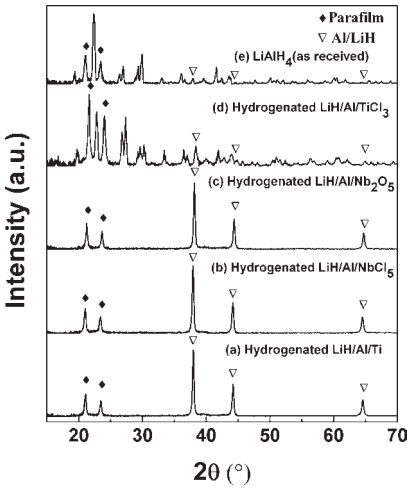

Figure 6. XRD patterns for hydrogenated samples with different additives (additive/Al = 0.2%): (a) hydrogenated LiH/Al/Ti; (b) hydrogenated LiH/Al/$NbCl_5$; (c) hydrogenated LiH/Al/Nb_2O_5; (d) hydrogenated LiH/Al/$TiCl_3$; (e) as-received $LiAlH_4$. No $LiAlH_4$ formed when metallic Ti, $NbCl_5$, or Nb_2O_5 was added in place of $TiCl_3$.

supported Ti and hydrogenated in Me_2O. This amount of catalyst was chosen because it gave the best performance in terms of yield and stability when neat $TiCl_3$ was used as a dopant (Section 3.1). A hydrogen desorption capacity of 5.9 wt % was obtained for the hydrogenated LiH/Al/$TiCl_3$/Al_2O_3 product (Figure S3). After dehydrogenation and subsequent rehydrogenation, the hydrogen capacity dropped to 4.0 wt % in the second cycle. The supported Ti/Al_2O_3 catalyst lowered the hydrogen desorption temperature, with release commencing at ca. 125 °C as opposed to 180 °C for the undoped material. Hydrogen desorption during the second cycle started at a higher temperature (140 °C) than for the first cycle (125 °C). It is possible that the Ti catalyst became detached from the support upon cycling and did not remain properly dispersed, thereby reducing its effectiveness. Hence, the cycling performance of the Ti/Al_2O_3-catalyzed material was found to be inferior to that of the straightforward Ti-doped $LiAlH_4$. Given the additional weight of the Al_2O_3 support, we conclude that there is no advantage to using a Ti catalyst in this form for the hydrogen cycling of $LiAlH_4$.

3.5. Effects of Metallic Ti, Nb_2O_5, and $NbCl_5$ Additives on the Formation of $LiAlH_4$. The effects of other additives (metallic Ti, Nb_2O_5, and $NbCl_5$) on the formation of $LiAlH_4$ from commercial LiH and Al were also investigated. However, under the experimental conditions described in Section 2, none of these resulted in the formation of $LiAlH_4$, as reported in Figure 6.

Extensive studies have been performed on the catalyzed $NaAlH_4$ system.[18−23] However, the details of the role of titanium halide catalysts in the improved reversibility of $NaAlH_4$ are still unclear. An initial reduction reaction was suggested, and X-ray absorption spectroscopy confirmed that reduction of the original $TiCl_3$ in fact occurs, with Ti(III) being reduced to Ti(0) when $NaAlH_4$ was ball-milled with $TiCl_3$, and remaining in this oxidation state during subsequent desorption and absorption of hydrogen.[21] The structure formed after ball-milling was close to that of metallic Ti but in a more distorted state. The formation of LiCl and the reduction of Ti(IV) were observed when $LiAlH_4$ was ball-milled with $TiCl_4$ in an early study.[24] As to the catalytic

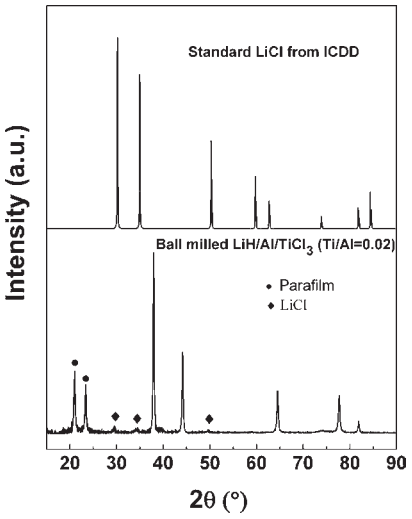

Figure 7. XRD patterns of standard LiCl from ICDD and ball-milled $LiH/Al/TiCl_3$ (1:1:0.02). LiCl was observed in the ball-milled mixture of $LiH/Al/TiCl_3$.

mechanism of our $LiH/Al/TiCl_3$ system, there might be some differences owing to the utilization of Me_2O. Interestingly, LiCl also formed after the mixture of $LiH/Al/TiCl_3$ was ball-milled (see Figure 7), and Ti(3+) might have a similar reduction in oxidation state during the ball-milling process. A detailed study of the catalytic mechanism of the conversion of LiH/Al to $LiAlH_4$ is still in progress.

4. CONCLUSIONS

In summary, we have succeeded in directly preparing Ti-doped $LiAlH_4$ from commercially available LiH and Al through the use of a $TiCl_3$ additive and Me_2O solvent. The yield of $LiAlH_4$ first increased and then decreased with increasing $TiCl_3$ content. A low percentage of $TiCl_3$ ($TiCl_3/Al$ = 0.05−0.2%) provides the optimum balance between the formation and stability of $LiAlH_4$, resulting in a high yield. However, $LiAlH_4$ did not form at all without the addition of $TiCl_3$. Furthermore, metallic Ti, Nb_2O_5, and $NbCl_5$ did not show any catalytic activity, and $LiAlH_4$ was not generated in the hydrogenation reactions. The hydrogenated $TiCl_3$-doped samples released more than 7 wt % hydrogen, with an onset dehydrogenation temperature of 80 °C. The dehydrogenated material could be cycled, with the material retaining about 6.4 wt % H capacity after three cycles. Al_2O_3-supported Ti showed some cycling ability but was deemed inferior to straightforward $TiCl_3$-doped $LiAlH_4$, which shows significant promise as a reversible, high-capacity hydrogen storage material.

■ ASSOCIATED CONTENT

Supporting Information. EDAX spectrum with TEM image inset, dehydrogenation kinetics curves measured by a Sieverts-type apparatus, and cycling performance of $TiCl_3/Al_2O_3$-catalyzed $LiAlH_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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