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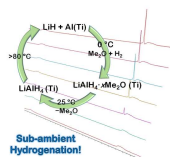
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ACCEPTED MANUSCRIPT

Regeneration of LiAlH_4 at sub-ambient temperatures studied by multinuclear NMR spectroscopy

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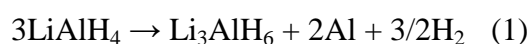
Abstract

Lithium aluminium hydride (LiAlH_4) has long been identified as a viable hydrogen storage material, due to its high attainable theoretical gravimetric hydrogen capacity of 7.9 wt%. The main impediment to its viability for technical application is its limitation for regeneration. Recently, solvent-mediated regeneration has been achieved at room temperature using dimethyl-ether, Me_2O , although the reaction pathway has not been determined. This *in situ* multinuclear NMR spectroscopy study (^{27}Al and ^7Li) has confirmed that the Me_2O -mediated, direct synthesis of LiAlH_4 occurs by a one-step process in which $\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$ is formed, and does not involve Li_3AlH_6 or any other intermediates. Hydrogenation has been shown to occur below ambient temperatures (at 0°C) for the first time, and the importance of solvate adducts formed during the process is demonstrated.

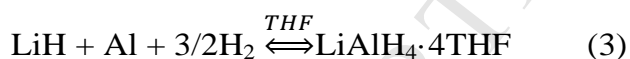
Keywords: Lithium alanate, NMR spectroscopy, rehydrogenation, solvent mediated synthesis, hydrogen storage.

1. Introduction

Lithium alanate (LiAlH_4) contains an attainable theoretical gravimetric hydrogen capacity of 7.9 wt% and has great potential as a viable hydrogen storage material [1, 2]. Combined with low levels (ca. 100 ppm) of TiCl_3 additive, LiAlH_4 dehydrogenates at temperatures as low as 80 °C, releasing over 7 wt% H_2 (Eqs. 1 and 2) [3-6] with kinetics suitable for on-board PEM fuel cell applications. It is well established that the dehydrogenation of both uncatalysed and Ti-catalysed LiAlH_4 [$\text{Al}(\text{Ti})$] proceeds via Li_3AlH_6 as an intermediate, before subsequent decomposition into LiH and Al as described in Eqs. 1 and 2 [7-10].

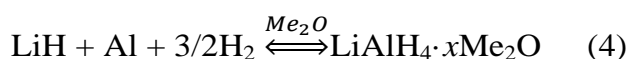


Until recently, the main impediment to the adoption of LiAlH_4 in technical applications was the difficulty in rehydrogenating the $\text{LiH} + \text{Al}$ products in Eq. 2. LiAlH_4 is thermodynamically impossible to recharge by direct hydrogenation in the solid state, and accordingly no attempts of its synthesis at high pressures, similar to that of the synthesis of AlH_3 at above 2.5 GPa [11], have been reported. On the contrary, a solution route was demonstrated by Clasen and Ashby in the 1960s: $\text{LiH} + \text{Al}$ in THF (tetrahydrofuran) or diglyme solvent reacted with 350 bar H_2 at 120 °C producing a solvated LiAlH_4 adduct according to Eq. 3 [12, 13].



Graetz and co-workers demonstrated that addition of TiCl_3 dopant to the dehydrogenated material, to form [$\text{Al}(\text{Ti})$] vastly improved the kinetics, making hydrogenation possible at room temperature and 13 bar H_2 [14, 15], to form the $\text{LiAlH}_4 \cdot 4\text{THF}$ adduct from a THF slurry of LiH and $\text{Al}(\text{Ti})$ or through mechanochemical activation in THF solvent [16]. However, removal of the bound solvent to leave crystalline LiAlH_4 is only feasible *in vacuo* at temperatures in excess of 60 °C, at which temperatures the Ti catalyst encourages release of hydrogen. Replacement of the THF solvent by the more volatile Et_2O , was also explored, but the removal of Ti and unreacted Al and LiH by filtration before the metathesis step necessitated re-milling of the product [14, 16, 17]. The challenge of solvent removal from the activated product was solved by Liu et al., who reported a remarkably mild

and simple process to generate LiAlH_4 from the dehydrogenation products (Eq. 4) [3]. Dimethyl ether, Me_2O , which boils at $-24\text{ }^\circ\text{C}$ under ambient pressure, was employed as the solvent. The hydrogenation reaction occurs according to Eq. 4, requiring only 100 ppm of Ti additive. The volatile Me_2O solvent vents naturally with the excess hydrogen pressure used in the reaction to leave dry, crystalline Ti-catalysed LiAlH_4 .



The pathway for the THF-mediated hydrogenation of $\text{Al}(\text{Ti})$ and LiH to form LiAlH_4 was postulated to occur directly in a single step, which does not include Li_3AlH_6 but rather involves the formation of “THF associated” intermediates, most likely $\text{LiAlH}_4 \cdot 4\text{THF}$ [14]. This pathway was demonstrated recently in an *in situ* study using multinuclear NMR spectroscopy [18]. The Me_2O -mediated reaction is anticipated to follow the same pathway. By contrast, the solid-state hydrogenation of $\text{Al}(\text{Ti})$ and NaH requires temperatures in excess of $100\text{ }^\circ\text{C}$, and involves the clear formation of Na_3AlH_6 in an intermediate step [19, 20].

Here we report a study of the Me_2O -mediated hydrogenation of $\text{Al}(\text{Ti})$ and LiH to LiAlH_4 by *in situ* ^{27}Al and ^7Li NMR spectroscopy at sub-ambient temperatures to determine the intimate reaction pathway.

2. Experimental

Commercial LiAlH_4 powder (Sigma Aldrich, 95 %) was purified by soxhlet extraction with diethylether and its purity then confirmed by powder XRD. Purified LiAlH_4 was ball milled with 0.5 mol% TiCl_3 (Sigma Aldrich, 99.99 %) in a Fritsch Pulverisette 7 Planetary Micro Mill employing tempered steel vials and balls in an Ar atmosphere. A ball to powder ratio of 20:1 was employed, with a milling time of 2 h at a speed of 300 rpm. The milled powder was then dehydrogenated at $150\text{ }^\circ\text{C}$ *in vacuo* on a Schlenk line for 16 h. All further manipulations were carried out in an Innovations Technologies glove box filled with purified Ar ($<1\text{ ppm O}_2, \text{H}_2\text{O}$) to avoid contamination.

Powder X-ray diffraction (PXD) patterns were collected using a Rigaku MiniFlex II diffractometer with a $\text{Cu } K\alpha$ radiation source. Samples for XRD analysis were

mounted in hermetically sealed sample holders. The Be cover resulted in extraneous diffraction peaks ($2\theta = 45.8, 50.9, 52.8, 70.1$ and 84.7°). The data were analysed using MDI Jade V.9.0 software.

All NMR spectra were collected on a Varian Unity Inova 400 MHz (9.4 T) spectrometer equipped with a Varian 5 mm 400 MHz Switchable Liquids probe operating at 155.4, 104.2 and 399.96 MHz for ^7Li , ^{27}Al , and ^1H respectively. Temperature calibration for the NMR was resolved using an ethylene glycol standard. Single pulse excitation with a pulse width of 4 μs , acquisition time of 15 ms, and relaxation delay of 10.0 s was used for the ^{27}Al nuclei. *In situ* data were collected utilising a pre-acquisition delay array collecting 30 scans per FID, amounting to 10 min per FID. A solid echo pulse sequence with an initial pulse width of 6.0 μs , echo delay time of 0 s, 90° observe pulse of 6.2 μs , tau1 and tau 2 were set to 25 μs , an acquisition time of 15 ms, and relaxation delay of 5.0 s was used for the ^7Li nuclei. The ssecho sequence was used as this experiment provided higher quality data than single pulse excitation. *In situ* data were collected utilising a pre-acquisition delay array, collecting 120 scans per FID, amounting to 10 min per FID. A pre-acquisition delay of 10 mins was utilised for longer scans for both nuclei measured, resulting in one scan every 20 minutes, in order to obtain a workable size file. For the ^1H nuclei an s2pul sequence was used with an acquisition time of 0.5 s, pulse width of 5 μs , relaxation delay of 2 s, with 64 scans collected per FID. External standards of 1.1 mol/L $\text{Al}(\text{NO}_3)_3$ in D_2O and 1.0 mol/L LiCl in D_2O were used to reference the ^{27}Al and ^7Li NMR spectra, respectively.

The powder samples were packed in a Daedalus Innovations 5 mm High Pressure 1.5 kBar NMR cell (ca. 10 mg). The addition of Me_2O to the NMR tube was achieved by cooling the tube to -40°C , while under vacuum, after which the liquid was condensed on to the solid. The NMR tube was kept at -40°C , before being allowed to equilibrate to 0°C after insertion into the spectrometer and tethered to a H_2 /vacuum manifold.

3. Results and Discussion

The samples for this *in situ* hydrogenation study were carefully prepared to ensure the highest purity of material. Not only is NMR spectroscopy a highly sensitive technique but many species may have very similar chemical shifts, as such any impurities or hydrogen containing species may hinder the initial observation of formation of LiAlH_4 . In addition, it is not possible to spin the high pressure cell during data collection and as such resonances may have the tendency to be broad. As a result, the as received LiAlH_4 was initially purified before the addition of TiCl_3 (0.5 mol.%).

Dehydrogenation of the milled LiAlH_4 powder was then achieved by heating at $150\text{ }^\circ\text{C}$ *in vacuo* for 16 h. PXD (powder X-ray diffraction) analysis of the material at each stage ensured purity and confirmed that the dehydrogenated mixture consisted of only LiH and Al (Fig. 1).

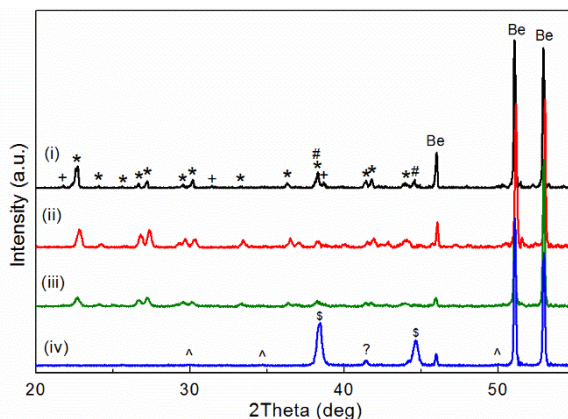


Fig. 1. XRD patterns of (i) as received LiAlH_4 , (ii) purified LiAlH_4 , (iii) LiAlH_4 with 0.5 mol% TiCl_3 , (iv) Dehydrogenated material $[\text{Al}(\text{Ti})]$. * = LiAlH_4 ; + = Li_3AlH_6 ; # = Al ; \$ = $\text{Al}(\text{Ti})/\text{LiH}$; ^ = LiCl ; ? = unknown; Be = beryllium from sample holder. λ = $\text{Cu K}\alpha$.

The high-pressure NMR tube (Daedalus Innovations) was filled with ca. 10 mg of the dehydrogenated material, followed by introduction of a sufficient amount (ca. 0.5 mL) of Me_2O to slurry the solid and fill the 0.64 mL cavity. Introduction of Me_2O into the NMR tube was achieved by cooling the tube to $-40\text{ }^\circ\text{C}$ under vacuum and condensing the solvent onto the solid. The limited volume of the tube only accommodated sufficient Me_2O to permit a low level of conversion to LiAlH_4 , restricting the amount of solid in the experiment to levels below those required for XRD analysis of the products.

In order to maintain the pressure over the sample at 100 bar during hydrogenation, a 3 m length of stainless-steel tubing connected the NMR tube to a gas-handling manifold. Inclusion of this extra volume made it difficult to maintain the Me_2O in the liquid phase. Accordingly, the NMR tube was cooled to $-40\text{ }^\circ\text{C}$, before being allowed at equilibrate at $0\text{ }^\circ\text{C}$ after insertion into the sample chamber of the spectrometer. The static, wide-line ^{27}Al NMR spectrum of the mixture prior to hydrogen charging is seen as the $t = 0$ trace in Fig. 2. The spectrum contains the following features: a large broad resonance at 1640 ppm characteristic of metallic Al [21]; and a second broad

resonance at 59 ppm resulting from alumina impurities in the zirconia NMR tube. A spectrum of the empty NMR cell is available in Ref. [18].

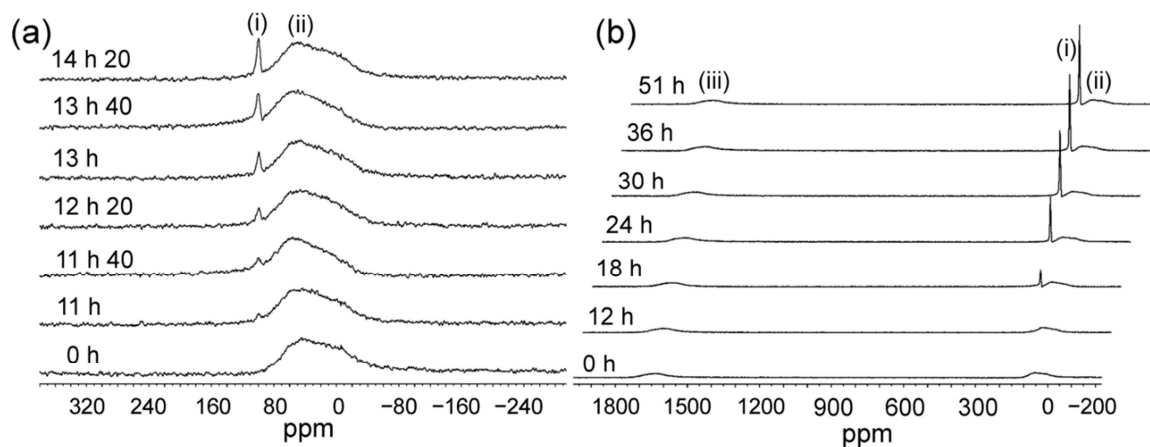


Fig. 2. Hydrogenation of LiAlH_4 in Me_2O monitored by ^{27}Al NMR spectroscopy. (a) $t = 0$ -14 h; (b) $t = 0$ -51 h. (0°C , 95 bar H_2). (i) LiAlH_4 (99.8 ppm); (ii) Al contained in NMR cell (59 ppm); (iii) Al powder (1640 ppm).

After equilibration at 0°C , the sample was charged with 95 bar of hydrogen, and the valve on the tank was left open to maintain a constant pressure. As shown in Fig. 2a, after ca. 11 h a sharp resonance was observable at 99.8 ppm. This feature continued to intensify over the 51 h of the experiment. The narrow resonance is most easily understood as arising from a solubilised product, in contrast to the two other broad Al resonances seen in Fig. 2b that are clearly associated with solid species. This conclusion accords with previous results obtained by ^{27}Al NMR studies on the production of LiAlH_4 in tetrahydrofuran (THF) solvent, where the nearly insoluble LiH and Al were shown to react with H_2 to form a soluble THF species (Eq. 3), with an associated chemical shift of 103 ppm [18], revealing a quintet structure resulting from the coupling of the ^{27}Al nucleus to the four equivalent hydrogens of the $[\text{AlH}_4]^-$ anion, ($^1J_{\text{H-Al}} = 168$ Hz) (Fig. 3). A quintet is also observed upon dissolution of LiAlH_4 in Me_2O , albeit with $^1J_{\text{H-Al}} = 183$ Hz. The increase in chemical shift from 99.8 ppm ($\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$) to 103 ppm ($\text{LiAlH}_4 \cdot x\text{THF}$) is also an indication of the decrease in stability of the $\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$ complex compared to the THF analogue with the increased electron density afforded by the THF ligand stabilising the complex compared to Me_2O [22]. This accords with observations made during the reversible hydrogenation studies of LiAlH_4 by Graetz et al [14, 15] and Liu et al [3]. Hydrogenation of $[\text{Al}(\text{Ti})]$ in THF yields a sticky residue [14], whereas hydrogenation

in Me₂O yields a dry powder reflecting the stronger solvent binding exhibited by THF [3].

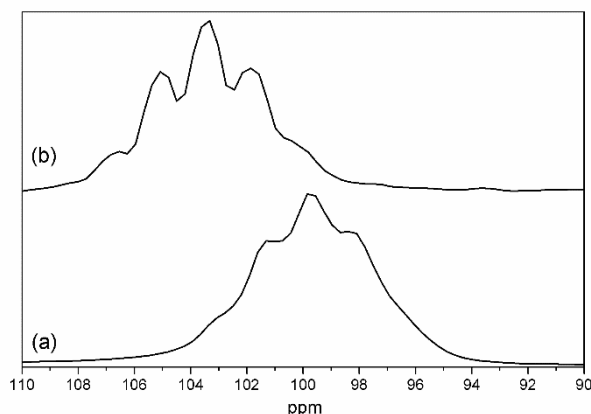


Fig. 3. Expansion of the LiAlH₄·*x*Me₂O (a) and LiAlH₄·*x*THF (b) peak in the ²⁷Al NMR spectrum after 51 h and 15 h of hydrogenation, respectively.

A complementary *in situ* study of the rehydrogenation of dehydrogenated Ti-catalysed LiAlH₄ was conducted, monitored by static ⁷Li NMR spectroscopy. The results of this study are depicted in Fig. 4. At *t* = 0, A broad resonance is observed at 0.34 ppm which is attributed to partially solvated LiH [23]. Over the first 10 h of the experiment this broad peak appears to increase in intensity, while after 12 h it begins to shift upfield, registering at 0.05 ppm. The deceptive increase in intensity is due to the formation of LiAlH₄, whose resonance is masked by the broad LiH feature until after 10 h. Full deconvolution of the two peaks is not achieved during the course of the reaction, but after 48 h the final chemical shift is measured at −0.53 ppm (Fig. 4b). This closely matches the −0.2 ppm shift observed for LiAlH₄ in hexamethylphosphoramide (HMPA) solution [24] and −0.3 ppm in THF [18]. Even so, despite the temperature effects that are often incurred, the significant upfield shift of LiAlH₄·*x*Me₂O compared to the LiAlH₄·*x*THF adduct is indicative of incremental shielding of the ⁷Li nucleus. Given the stronger coordination of Li⁺ by the THF adduct, the observed chemical shift may suggest a higher coordination number for the Me₂O adduct [25].

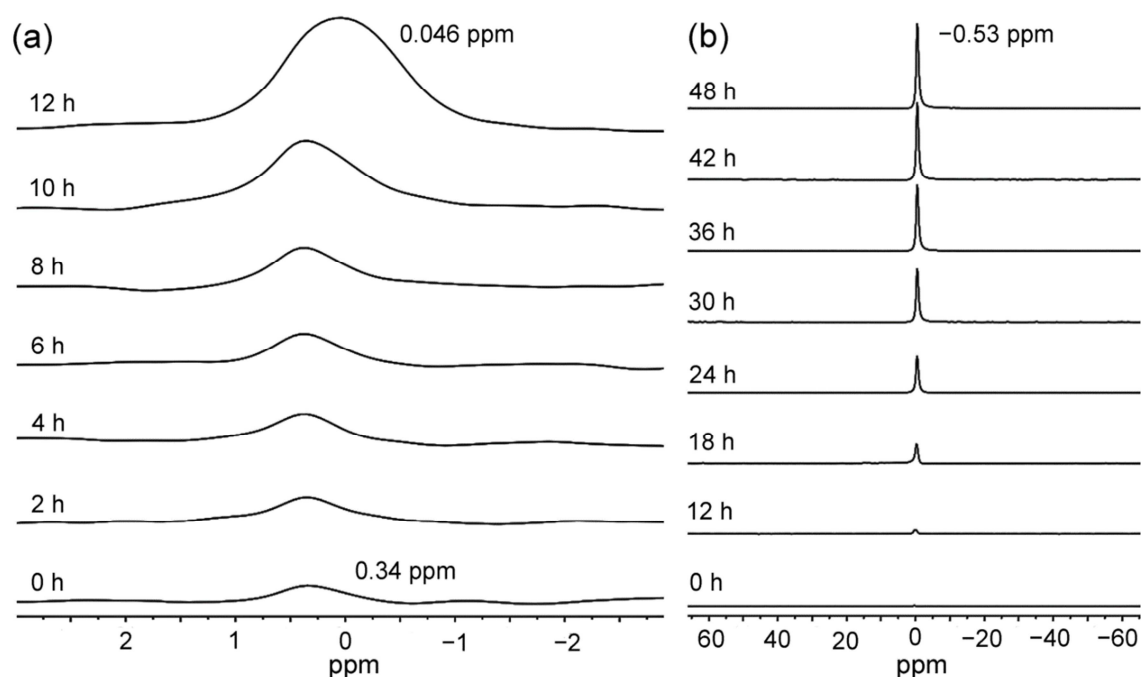


Fig. 4. Hydrogenation of LiAlH_4 in Me_2O monitored by ^7Li NMR spectroscopy. (a) $t = 0$ -12 h; (b) $t = 0$ -48 h (0°C , 95 bar H_2).

The appearance of only one resonance throughout the course of the experiment confirms the conclusion reached from the ^{27}Al NMR study; namely that $\text{LiAlH}_4 \cdot x\text{-Me}_2\text{O}$ is formed directly in a solvent-mediated reaction that does not proceed through Li_3AlH_6 or any other intermediates. Wiench et al. previously showed by ^{27}Al NMR spectroscopy that the resonance for octahedral Li_3AlH_6 occurs at -30 ppm [26]. Analysis of the ^{27}Al NMR spectroscopy data shows no obvious signs of a peak at this chemical shift and no alteration to the broad resonance for the tube was observed over time. The resonance for Li_3AlH_6 by ^7Li NMR spectroscopy has yet to have been reported, but would be expected to be below 0 ppm. No additional peaks were observed to appear throughout the experiment. This result corroborates the study by Liu et al. in which Li_3AlH_6 was not observed during ex situ XRD studies during hydrogenation of $\text{LiH}/\text{Al}(\text{Ti})$ in Me_2O [5]. The oxophilicity of the hard Li^+ results in a strong interaction with the basic Me_2O donor to form a tightly solvated cation that prevents the direct ion pairing of Li^+ and $[\text{AlH}_4]^-$. This strong solvation of Li^+ and the concomitant high solubility of LiAlH_4 then prevents the reaction described in Eq. 5,

$$\text{LiAlH}_4 + 2\text{LiH} \rightarrow \text{Li}_3\text{AlH}_6 \quad (5)$$

that is known to occur in the solid state [27]. This circumvention of Li_3AlH_6 as an intermediate in the rehydrogenation is a key feature of the low energy process that occurs during solvent mediated, direct synthesis of alanates.

There is a substantial increase in the time required for LiAlH_4 to appear in the hydrogenation of LiH/Al(Ti) in Me_2O as compared with THF (11 h and 20 min, respectively). This is primarily due to the considerably lower solubility of hydrogen in Me_2O . The mole fraction solubilities of H_2 under a partial pressure of 61 bar in THF is 1.650 (20 °C) [28]; whereas its solubility on Me_2O is only 0.058 under 71 bar at 15 °C and 0.072 under 81 bar at 33 °C [29]. Hence, the reaction kinetics would not be significantly improved by increasing the temperature, although agitation would enhance dissolution. The low solubility of H_2 in Me_2O is illustrated by ^1H NMR spectroscopy in Fig. 4. The spectrum for pure Me_2O at 0 °C (Fig. 5a) has a single broad resonance at 3.2 ppm, while after 48 h the peak for dissolved H_2 at 4.3 ppm [30] is still very small in comparison (Fig. 5b). The reason for the asymmetric tailing on the Me_2O peak is due to a lack of shimming of the high pressure tube; as the sample was not deuterated it was not possible to shim. Some FID shimming was undertaken, but due to the high concentration of sample and high intensity of the peak, it was impossible to eliminate these shimming problems. The added tailing caused by the addition of H_2 (Fig. 5(b)) may be due to an increase in the heterogeneity of the sample or the dissolved gas, causing a dramatic change to the solvent dielectric properties. and altering the magnetic susceptibility of the sample in the probe.

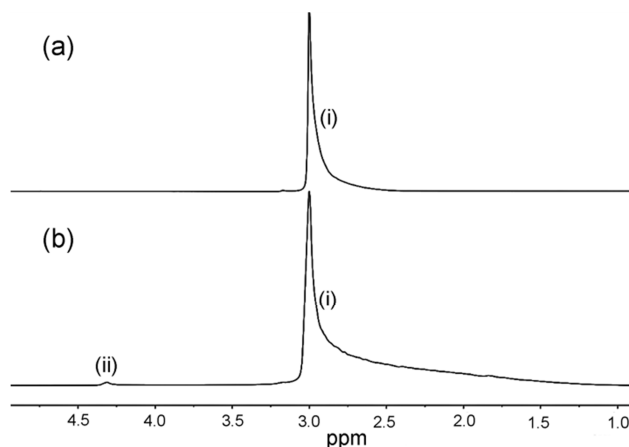


Fig. 5. Solubility of H_2 in Me_2O observed by ^1H NMR spectroscopy (0°C). (a) Before H_2 addition; (b) 48 h after H_2 addition (135 bar). (i) Me_2O (3.2 ppm); (ii) dissolved H_2 (4.3 ppm).

Unfortunately, it was not possible to quantify the fraction of material that was hydrogenated during the ^{27}Al or ^7Li NMR spectroscopy experiments. The Al and LiH starting materials are insoluble (LiH is sparingly soluble), while the LiAlH_4 product is soluble; therefore accurate quantification and comparison is impossible. An external standard may allow quantification of the LiAlH_4 , although the small volume of the NMR tube (0.64 mL) does not allow for an additional capillary to be inserted and would also decrease the already miniscule quantity of Me_2O that can be added to the tube. Quantification by XRD was impossible due to the small quantity of powder added to the tube (~ 10 mg) and the difficulty of removing the powder from the tube after evaporation of the solvent. The reversibility of LiAlH_4 mediated by Me_2O solvent has been studied in depth by Liu et al., showing that cycling capacity is lost due to an increase in particle size and Ti-Al alloy phases [5].

4. Conclusions

This *in situ* multinuclear NMR study has confirmed that the Me_2O -mediated, direct synthesis of LiAlH_4 occurs by a one-step process in which $\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$ is formed, and does not involve Li_3AlH_6 or any other intermediates. Hydrogenation has been shown to occur below ambient temperatures (at 0°C) for the first time, the importance of solvate adducts formed during the process is demonstrated. These avoid the

thermodynamically preferred route via Li_3AlH_6 that is dominant in the corresponding solid-state process.

This study further promotes the practicality of LiAlH_4 as a hydrogen storage material, showing that recharging can be achieved directly at or below room temperature without the need for re-addition of catalyst or any further processing.

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Fig. 1. XRD patterns of (i) as received LiAlH_4 , (ii) purified LiAlH_4 , (iii) LiAlH_4 with 0.5 mol% TiCl_3 , (iv) Dehydrogenated material $[\text{Al}(\text{Ti})]$. * = LiAlH_4 ; + = Li_3AlH_6 ; # = Al; \$ = $\text{Al}(\text{Ti})/\text{LiH}$; ^ = LiCl ; ? = unknown; Be = beryllium from sample holder. $\lambda = \text{Cu K}\alpha$.

Fig. 2. Hydrogenation of LiAlH_4 in Me_2O monitored by ^{27}Al NMR spectroscopy. (a) $t = 0-14$ h; (b) $t = 0-51$ h. (0°C , 95 bar H_2). (i) LiAlH_4 (99.8 ppm); (ii) Al contained in NMR cell (59 ppm); (iii) Al powder (1640 ppm).

Fig. 3. Expansion of the $\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$ (a) and $\text{LiAlH}_4 \cdot x\text{THF}$ (b) peak in the ^{27}Al NMR spectrum after 51 h and 15 h of hydrogenation, respectively.

Fig. 4. Hydrogenation of LiAlH_4 in Me_2O monitored by ^7Li NMR spectroscopy. (a) $t = 0-12$ h; (b) $t = 0-48$ h (0°C , 95 bar H_2).

Fig. 5. Solubility of H_2 in Me_2O observed by ^1H NMR spectroscopy (0°C). (a) Before H_2 addition; (b) 48 h after H_2 addition (135 bar). (i) Me_2O (3.2 ppm); (ii) dissolved H_2 (4.3 ppm).

Highlights

- Regeneration of LiAlH_4 has been studied by ^{27}Al and ^7Li NMR spectroscopy
- Solvent-mediated regeneration occurs at sub-ambient temperatures using dimethyl-ether
- Direct synthesis of LiAlH_4 occurs in a one-step process without an Li_3AlH_6 intermediate
- $\text{LiAlH}_4 \cdot x\text{Me}_2\text{O}$ is identified similar to $\text{LiAlH}_4 \cdot x\text{THF}$ observed during regeneration in THF