

COMMUNICATION

***In situ* high pressure NMR study of the direct synthesis of LiAlH₄†**

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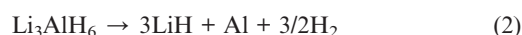
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²⁷Al and ⁷Li wide-line NMR spectroscopy incorporating a high pressure NMR apparatus has allowed the first *in situ* study of the solvent mediated, direct synthesis of an alanate, thus overcoming the dearth of analytical techniques available to study phenomena occurring in a pressurised slurry. In contrast to the decomposition reaction, the elucidated hydrogenation pathway does not proceed through the hexahydride intermediate.

The practical utilisation of hydrogen as an energy carrier awaits the development of high-capacity, hydrogen storage materials that can be recharged under moderate conditions. A viable on-board hydrogen carrier must have: high gravimetric and volumetric hydrogen capacities; thermodynamic properties that are within rather stringent limits; and dehydrogenation and rehydrogenation kinetics that allow hydrogen cycling at moderate temperatures and pressures.^{1,2} Although no directly reversible hydrogen material has yet met all of these criteria, a great deal of progress as have been made towards harnessing the high storage capacity, relatively low desorption temperatures, and comparative ease of hydrogenation of sodium alanate (NaAlH₄) and lithium alanate (LiAlH₄).³

It is well established that the dehydrogenation of both undoped and Ti-doped LiAlH₄ (Al(Ti)) proceeds *via* Li₃AlH₆ as an intermediate before decomposition into LiH and Al as seen in eqn (1) and (2).^{4–7}



The *in situ* decomposition of LiAlH₄ has been studied previously by DSC,^{7,8} X-ray and neutron diffraction measurements⁹ and NMR spectroscopy.¹⁰ The direct re-hydrogenation of LiH and Al to LiAlH₄ is challenging as the reaction in eqn (1) is exothermic (−10 kJ mol^{−1}) in the molten uncatalysed system,⁸ where the dehydrogenation occurs following melting and weakly endothermic (+1 kJ mol^{−1}) in the Ti-containing system, where the dehydrogenation occurs in the solid state.¹¹ However, in the 1960's Clasen and Ashby *et al.* found that the formation of a THF adduct circumvents the unfavourable thermodynamics associated with the formation of the unsolvated alanate. Clasen,¹² was first to observe the formation of a small amount of solvated LiAlH₄ from the reaction of LiH and activated Al in THF at 350 bar H₂ pressure at a temperature of 393 K according to eqn (3):



While Ashby *et al.*¹³ found that THF solvated LiAlH₄ could be obtained in 96% yield following 5 h or reaction at 393 K under 340 bar of H₂.

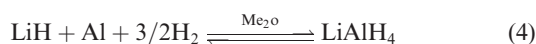
More recently, Wang *et al.* reported the utilisation of high pressure ball-milling to form crystalline LiAlH₄ with a desolvation step following the reaction.¹⁴ Graetz *et al.* subsequently demonstrated the reversibility of this material using PCT isotherms (eqn (3)).¹⁵ Hydrogenation was reported to occur at room temperature and 13 bar H₂ forming the LiAlH₄·4THF adduct from a THF slurry of LiH and Al(Ti), with the removal of the adduct at 333 K *in vacuo* to form crystalline LiAlH₄. In a final development, the complication of a requisite side process to remove the adduct prior to dehydrogenation was eliminated by Liu *et al.* who reported a remarkably mild and simple process to generate LiAlH₄ from the dehydrogenation products (eqn (4)).¹⁶

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† Electronic supplementary information (ESI) available: Preparation and diffraction patterns of LiAlH₄ materials, XRD instrument configuration, NMR spectroscopy acquisition parameters, ²⁷Al NMR spectrum of empty high pressure cell and ²⁷Al and ⁷Li NMR spectra of commercial LiAlH₄ in THF. See DOI: 10.1039/c3ta10239d



Dimethyl ether, Me_2O which is a liquid at room temperature under 100 bar of pressure, was employed as the solvent. The hydrogenation reaction occurs according to eqn (4) over 24 h, requiring only 100 ppm of Ti additive. When the H_2 overpressure is vented, the Me_2O is also eliminated leaving only Ti-containing LiAlH_4 . This material has been shown to release 7 wt% H_2 from 353 to 453 K, with kinetics that would allow its utilisation as a hydrogen storage material for onboard PEM fuel cell applications, and it has been repeatedly cycled through hydrogenation and dehydrogenation up to five times.¹⁷

Solvent mediated hydrogenations of $\text{Al}(\text{Ti})$ and LiH to LiAlH_4 occur readily at ambient temperatures.^{15–17} Graetz *et al.* proposed that it does not involve Li_3AlH_6 as an intermediate but rather involves “THF associated” intermediates.¹⁵ By contrast, the solid state hydrogenation of $\text{Al}(\text{Ti})$ and NaH requires heating to at least 400 K,³ and thus quite likely proceeds by a very different pathway. However, it has proven difficult to test this hypothesis. Liu *et al.* conducted *ex situ* XRD analysis to determine the intermediates present during Me_2O assisted hydrogenation. The products were removed from the reaction after 4 h, while 24 h are required for optimal yield. They determined that Li_3AlH_6 was not an intermediate as only LiH , Al and LiAlH_4 were identified.¹⁸

In situ powder X-ray diffraction has been the predominant method of choice to study the dehydrogenation of candidate hydrogen storage materials in recent years. This is largely due to the high sensitivity of XRD and its ability to identify and quantify distinct phases and provide structures of the reaction products and intermediates. *In situ* NMR spectroscopy has also proven valuable for the identification of the dehydrogenation pathway of many hydrides.^{10,19} However, until recently apparatus has restricted the ability to study hydrogenation reactions by NMR to only modest pressures of H_2 . High pressure NMR spectroscopy experiments were originally conducted in pressurised borosilicate, quartz, Vespel or sapphire tubes but these are meticulous to handle.²⁰ The theoretical maximum pressures these tubes can withstand are 61 bar for borosilicate, 434 bar for quartz and 492 bar for sapphire, although Erlach has demonstrated that they can handle 2 kbar before perishing. More recently, alumina-toughened zirconia (AZO) tubes (Daedalus Innovations), have been introduced which are capable of withstanding pressures of up to 2.5 kbar (Fig. 1).²¹

To date, the products of hydrogenation of LiAlH_4 have only been characterised by *ex situ* powder XRD measurements owing to the requirement of a solvent during the process.^{14–16} We here report studies of the THF mediated hydrogenation of $\text{Al}(\text{Ti})$ and LiH to LiAlH_4 utilising high pressure ^{27}Al and ^7Li NMR spectroscopy: the first *in situ* study of the hydrogenation of a complex hydride to date.

Material for the *in situ* hydrogenation study was prepared by dehydrogenation of LiAlH_4 previously doped with 0.5 mol% TiCl_3 by heating at 423 K *in vacuo* for 16 h (Experimental details are in the ESI†). XRD analysis confirmed that the product mixture consisted of only LiH and Al (instrument details and



Fig. 1 Alumina-toughened zirconia high pressure NMR sample tube (Daedalus Innovations).

XRD patterns are in the ESI†). The high pressure NMR tube (Daedalus Innovations) was filled to a height of 2 cm with a sample of the dehydrogenated material followed by introduction of a sufficient amount (~ 0.5 mL) of dry, deoxygenated tetrahydrofuran (THF) to slurry the solid and fill the 0.64 mL cavity. The static ^{27}Al NMR spectrum (Varian 400 MHz NMR (9.4 T), ^{27}Al at 104.227 MHz, acquisition details are in the ESI†), of the mixture prior to hydrogen charging is seen as the $t = 0$ trace in Fig. 2. A broad peak is observed for Al at the characteristic chemical shift of 1640 ppm (ref. 22) while the second broad upfield resonance is assigned as alumina impurity in the zirconia NMR tube. The sample was heated to 313 K and charged with 35 bar of hydrogen, the tank being left open to allow constant pressure. As shown in Fig. 2, after 20 min, a sharp resonance was observable at 103 ppm. This feature was seen to continue to intensify over the 920 min experiment. This narrow peak is most easily understood as arising from a solution species, in contrast to the two other broad Al resonances seen in Fig. 2 that are clearly associated with solid species. This conclusion supports the suggestion by Graetz *et al.* that during the course of the reaction, insoluble LiH and Al react with H_2 to form a soluble THF species that is stabilised by four THF solvate

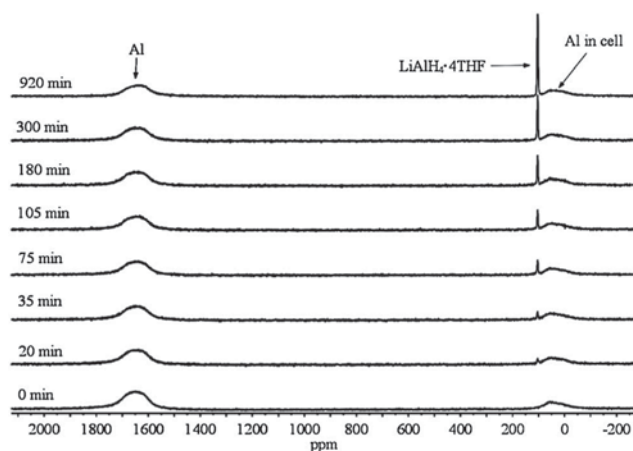


Fig. 2 Hydrogenation of LiH and $\text{Al}(\text{Ti})$ in THF observed by ^{27}Al NMR spectroscopy.

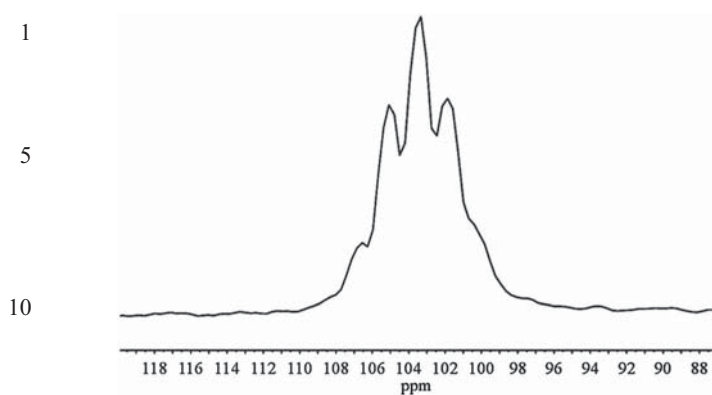


Fig. 3 Expansion of the $\text{LiAlH}_4 \cdot x\text{THF}$ peak in the ^{27}Al NMR spectrum after 920 min of hydrogenation.

molecules (eqn (1)).¹⁵ The identification of the product is easily established as an expanded view of the NMR resonance associated with the dissolved hydrogenated product (Fig. 3) is clearly a quintet resulting from the coupling of the ^{27}Al nucleus to the four equivalent hydrogens of the $[\text{AlH}_4]^-$ anion. Further verification is provided by our observation of $^1J_{\text{H-Al}}$ coupling constant of 168 Hz which is in good agreement with the 170 Hz value reported by Lefebvre and Conway for LiAlH_4 in 0.4 M THF solution.²³ The 103 ppm chemical shift of the product is identical to that observed by Wiench *et al.*⁶ for pure LiAlH_4 , and very close to the 98 ppm measured by Lefebvre and Conway²³ of 0.4 M LiAlH_4 in THF. Due to the low capacity of the NMR tube and the required amount of LiH and Al required to obtain spectra with reasonable sign-to-noise within 3 min, it was possible to add only 0.6 mL of THF to the tube. This was only a sufficient amount of THF to achieve a low conversion to LiAlH_4 . The volumetric limitation of the NMR tube also restricted the material in the experiment to an amount below that which is required for XRD analysis.

A complementary *in situ* hydrogenation study of a slurry of LiH and Al(Ti) in THF was conducted in which the reaction was monitored by static ^7Li NMR spectroscopy (Varian 400 MHz NMR (9.4 T), ^7Li at 155.455 MHz, acquisition details are in the

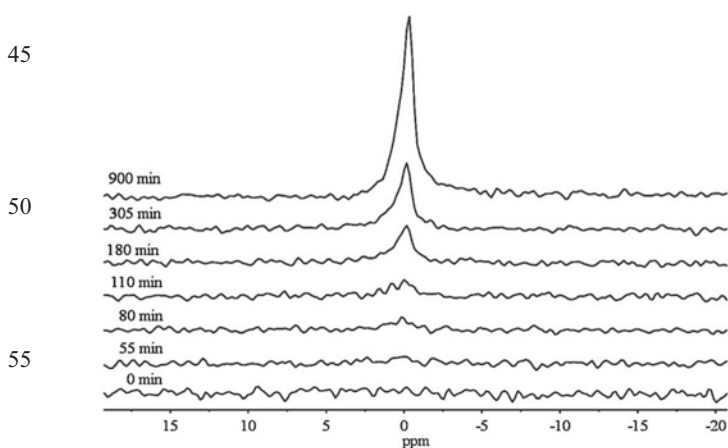


Fig. 4 Hydrogenation of LiH and Al(Ti) in THF observed by ^7Li NMR spectroscopy.

ESI†). The results of this study are depicted in Fig. 4. Under these experimental conditions the ^7Li nucleus has a much lower NMR sensitivity than ^{27}Al and thus sufficient signal intensity could not be obtained to observe the very broad signal for solid LiH from the 60 scans applied during data acquisition. Likewise the observation of a ^7Li signal for the highly mobile, dissolved product also required a significantly longer time than for the corresponding ^{27}Al experiment. However, a product peak appeared at -0.3 ppm after 55 min at 313 K under 35 bar of hydrogen pressure. This chemical shift is indicative of solvated Li^+ and closely matches the -0.2 ppm shift observed for LiAlH_4 in HMPA solution.^{24,25} The signal continued to grow in intensity over the course of the experiment. The appearance of only one resonance throughout the course of the experiment confirms the conclusion reached from the ^{27}Al namely, $\text{LiAlH}_4 \cdot x\text{THF}$ is formed directly in a solvent-mediated reaction and does not proceed through Li_3AlH_6 or any other intermediates. The oxophilicity of the hard Li^+ results in a strong interaction with the basic THF 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 eqn (5) that is known to occur in the solid state.²⁶ This circumvention of Li_3AlH_6 as an intermediate in hydrogenation is a key to the low energy process that occurs during solvent mediated, direct synthesis of alanates.



In conclusion, this study has confirmed that the THF-mediated, direct synthesis of LiAlH_4 occurs by a one step process in which $\text{LiAlH}_4 \cdot x\text{THF}$ is formed and does not involve Li_3AlH_6 or any other intermediates. This study is the first *in situ* NMR spectroscopic investigation of the hydrogenation of the direct synthesis of a complex hydride and the first *in situ* study of hydrogenation in a pressurised slurry. This high pressure NMR technique thus opens the door to mechanistic studies of a wide variety of systems that undergo reversible hydrogenation and thus may provide invaluable insights of use in the development of advanced, solid state hydrogen storage systems.

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