

## *In situ* high pressure NMR study of the direct synthesis of NaAlH<sub>4</sub>

Cite this: DOI: 10.1039/c3cp50777g

Received 21st February 2013,  
Accepted 27th February 2013

DOI: 10.1039/c3cp50777g

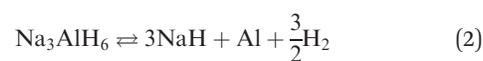
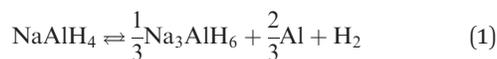
www.rsc.org/pccp

Terry D. Humphries,<sup>a</sup> Derek Birkmire,<sup>b</sup> Bjørn C. Hauback,<sup>a</sup> G. Sean McGrady<sup>c</sup> and Craig M. Jensen<sup>\*b</sup>

The direct synthesis of NaAlH<sub>4</sub> has been studied, for the first time, by *in situ* <sup>27</sup>Al and <sup>23</sup>Na wide-line NMR spectroscopy using high pressure NMR apparatus. Na<sub>3</sub>AlH<sub>6</sub> formation is observed within two minutes of hydrogenation addition, while NaAlH<sub>4</sub> is detected after a total of four minutes. This indicates the formation of the hexahydride does not proceed to completion before the formation of the tetrahydride ensues.

The practical utilization 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 fall within rather stringent limits; and dehydrogenation and rehydrogenation kinetics that allow hydrogen cycling at moderate temperatures and pressures.<sup>1,2</sup> One of the most important breakthroughs in the development of hydrogen storage materials in the past 20 years was provided by Bogdanović and Schwickardi, whose pioneering studies demonstrated that addition of selected titanium compounds to NaAlH<sub>4</sub> results in enhanced kinetics and reversibility under moderate conditions in the solid state.<sup>3</sup> These studies were prompted by earlier reports from Wiberg *et al.*, who observed that titanium compounds catalyze the dehydrogenation of complex aluminum hydrides in solution.<sup>4</sup> The enigmatic extension of this catalytic effect to the solid state has been the inspiration for over 260 publications on Ti-enhanced NaAlH<sub>4</sub> alone, and it is safe to estimate that it prompted an equal number of studies of the effect of Ti additives on the dehydrogenation kinetics of other complex hydrides.<sup>5</sup>

Ashby and Kobetz demonstrated that the dehydrogenation of NaAlH<sub>4</sub> to NaH and Al occurs *via* two distinct reactions, as shown in eqn (1) and (2).<sup>6</sup> This work established that eqn (2) has a significantly higher activation energy, as it occurs at higher temperatures than eqn (1). Dehydrogenation *via* two discrete pathways was also observed for Ti-enhanced NaAlH<sub>4</sub>, despite the dramatic lowering of the activation energy for both of the dehydrogenation reactions.<sup>3,7</sup> This stepwise pathway has been confirmed for Ti-enhanced NaAlH<sub>4</sub> by a number of *in situ* XRD,<sup>8,9</sup> TEM<sup>10</sup> and NMR studies<sup>11</sup> of the dehydrogenation reaction. It has long been assumed that the rehydrogenation of NaH and Ti-enhanced Al (Al\*) proceeds through the microscopic reverse of the two step dehydrogenation process (eqn (1) and (2)), entailing the complete conversion of NaH to Na<sub>3</sub>AlH<sub>6</sub> before there is any significant formation of NaAlH<sub>4</sub>. However, there is little experimental evidence in support of this received wisdom. The formation of Na<sub>3</sub>AlH<sub>6</sub> by mechanochemical activation of NaH and Al with a mischmetal nanocatalyst under 3 bar hydrogen pressure has been described in an *ex situ* XRD study,<sup>12</sup> but no *in situ* studies of the complete process progressing to NaAlH<sub>4</sub> have been reported. In a parallel study, *in situ* high pressure <sup>27</sup>Al and <sup>7</sup>Li NMR measurements of the THF-mediated hydrogenation of LiH and Al\* to LiAlH<sub>4</sub> have revealed this process to occur in a single step without any Li<sub>3</sub>AlH<sub>6</sub> intermediate.<sup>13</sup> Here we report a similar measurements of the high pressure hydrogenation of NaH and Al\* to NaAlH<sub>4</sub> utilizing <sup>27</sup>Al and <sup>23</sup>Na NMR spectroscopy, which represent the first *in situ* studies of the hydrogenation of Al\* and NaH to NaAlH<sub>4</sub>.

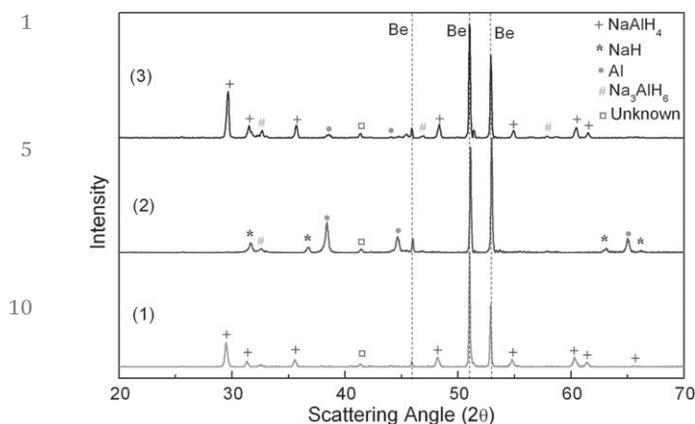


Samples for the *in situ* hydrogenation study were prepared by dehydrogenation of NaAlH<sub>4</sub> with 2 mol% TiCl<sub>3</sub> additive by heating at 423 K *in vacuo* on a Schlenk line for 24 h. XRD analysis (data collected on a Rigaku MiniFlex II diffractometer

<sup>a</sup> Department of Physics, Institute for Energy Technology, P.O. Box 40, NO-2027, Kjeller, Norway. E-mail: terry.humphries@ife.no; Fax: +47 63 81 09 20; Tel: +47 63 80 61 81

<sup>b</sup> Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822-2275, USA. E-mail: jensen@hawaii.edu; Fax: +1 808 956 5908; Tel: +1 808 956 2769

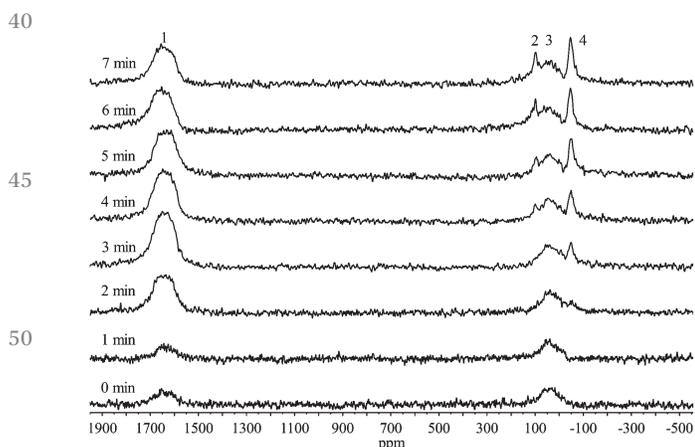
<sup>c</sup> Department of Chemistry, University of New Brunswick, P.O. Box 4400, Fredericton NB E3B 5A3, Canada. E-mail: smcgrady@unb.ca; Fax: +1 506 453 4981; Tel: +1 506 452 6340



**Fig. 1** Powder X-ray diffraction pattern of (1) NaAlH<sub>4</sub> (2 mol% TiCl<sub>3</sub>), (2) NaH/Al\* (2 mol% TiCl<sub>3</sub>) and (3) Rehydrogenated NaH/Al\* (2 mol% TiCl<sub>3</sub>). Be peaks arise from the hermetic sample holder.

and analyzed using MDI Jade V.9.0 software), confirmed that the product mixture consisted of only NaH and Al, as illustrated in Fig. 1. A sample of the dehydrogenated material was loaded in a glove box into a high pressure NMR tube (Daedalus Innovations). Single pulse excitation with a pulse width of 4  $\mu$ s, acquisition time of 15 ms and relaxation delay of 10.0 s was used for the <sup>27</sup>Al nuclei. *In situ* data were collected by adding up 30 scans, amounting to  $\sim$ 5 min per FID. The static, wide-line <sup>27</sup>Al NMR spectrum (Varian 400 MHz NMR (9.4 T); <sup>27</sup>Al at 104.227 MHz), of the mixture prior to hydrogen charging is seen as the  $t = 0$  trace in Fig. 2. The spectrum contained the following features: a large broad resonance at a chemical shift of 1640 ppm that is characteristic of Al; a second broad resonance at 59 ppm that is due to the alumina impurity in the zirconia NMR tube; and very small, sharp resonance which is easily assigned to Na<sub>3</sub>AlH<sub>6</sub> from its chemical shift of  $-45$  ppm.<sup>7,14</sup>

After establishing the  $t = 0$  benchmark, the sample was heated to 393 K and charged with 138 bar of hydrogen. Fig. 2 illustrates the progress of hydrogenation as monitored by <sup>27</sup>Al spectroscopy over a 15.5 h period. In accordance with the

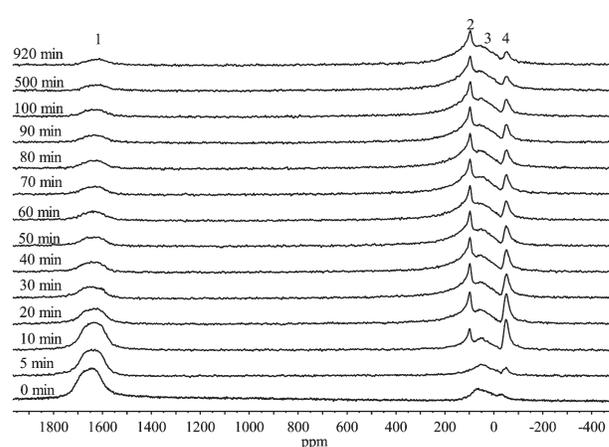


**Fig. 2** Hydrogenation of NaH/Al\* observed by <sup>27</sup>Al NMR spectroscopy. FIDs were collected every 5 min. 1 Al powder (1640 ppm); 2 NaAlH<sub>4</sub> (103 ppm); 3 Al contained in NMR cell (59 ppm); 4 Na<sub>3</sub>AlH<sub>6</sub> ( $-45$  ppm).

reverse of eqn (2), the resonance intensity for Na<sub>3</sub>AlH<sub>6</sub> increases rapidly upon addition of H<sub>2</sub> until it reaches a maximum at  $\sim$ 30 min, after which it begins to diminish. After *ca.* 10 min, the distinctive resonance for NaAlH<sub>4</sub> is clearly visible at 103 ppm.<sup>7,14</sup> The relative intensity of this resonance continues to increase with time. However, the spectrum obtained after 920 min shows that the reaction has not gone to completion, as resonances corresponding to Al and Na<sub>3</sub>AlH<sub>6</sub> are still observed. This accords with previous reports that the NaAlH<sub>4</sub> obtained from the hydrogenation of stoichiometric amounts NaH and Al\* contains significant amounts of residual Al and Na<sub>3</sub>AlH<sub>6</sub> owing to the formation of an Al<sub>0.85</sub>Ti<sub>0.15</sub> solid solution.<sup>15,16</sup> Accurate quantification of the Al species present in the reaction mixtures is not feasible as Al in the probe contributes (albeit minimally) to the intensity of the Al metal resonance. Moreover, the resonance for alumina contained in the tube (3) overlaps with the alanate peaks. The data obtained does however allow the qualitative identification of all Al species present in the reaction mixture and clearly demonstrates that significant amounts of NaAlH<sub>4</sub> are formed before full conversion of NaH to Na<sub>3</sub>AlH<sub>6</sub>.

The <sup>27</sup>Al NMR spectra shown in Fig. 2 were each collected over a period of 5 min to ensure a decent signal-to-noise ratio. However, this study revealed that hydrogenation occurs more rapidly than expected. In order to ascertain how early NaAlH<sub>4</sub> appears in the hydrogenation process, a separate experiment was conducted with 1 min scans for the first 7 min of the hydrogenation process. As seen in Fig. 3, Na<sub>3</sub>AlH<sub>6</sub> is detectable after 2 min and NaAlH<sub>4</sub> appears within 4 min, clearly demonstrating that only minimal conversion to Na<sub>3</sub>AlH<sub>6</sub> occurs prior to formation of NaAlH<sub>4</sub>. The experimental conditions of this hydrogenation study are very comparable to others in the literature.

Recently, experimental evidence has been obtained in support of the hypothesis that the hydrogenation process is initiated by the surface formation of intermediate AlH<sub>x</sub> ( $x = 2, 3$ ) species.<sup>8,17</sup> Hwang *et al.* have reported chemical shifts of 5.8, 21.5, and 10.9/36.0 ppm for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -AlH<sub>3</sub> respectively.<sup>18</sup> Our study is not able to explore this possibility, as the broad resonance at 59 ppm associated with the alumina of the NMR cell will likely



**Fig. 3** Hydrogenation of NaH/Al\* observed by <sup>27</sup>Al NMR spectroscopy. FIDs were collected every 1 min. 1 Al powder (1640 ppm); 2 NaAlH<sub>4</sub> (103 ppm); 3 Al contained in NMR cell (59 ppm); 4 Na<sub>3</sub>AlH<sub>6</sub> ( $-45$  ppm).

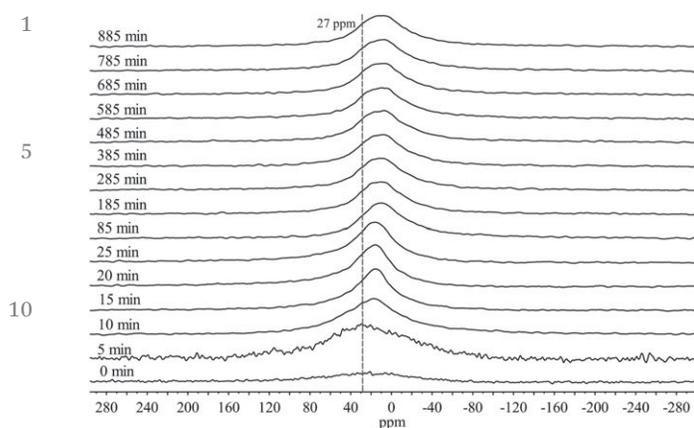


Fig. 4 Hydrogenation of NaH/Al\* observed by  $^{23}\text{Na}$  NMR spectroscopy. FIDs were collected every 5 min.

obscure any resonances arising from a relatively low concentration of alane species forming on the particle surfaces. Another limitation of this study is that wide-line NMR spectroscopy does not allow for fine details to be observed; hence it is not possible to distinguish Al metal from Al present in an  $\text{Al}_{0.85}\text{Ti}_{0.15}$  solid solution or other Al–Ti phases.<sup>15,16</sup> We note also that the mobile “ $\text{AlH}_3$ ” intermediate reported at 109 ppm in a recent *in situ* dehydrogenation study of  $\text{NaAlH}_4$  was not evident throughout our studies.<sup>19</sup>

We have studied the hydrogenation process in parallel by *in situ*  $^{23}\text{Na}$  NMR spectroscopy (Varian 400 MHz NMR (9.4 T),  $^{23}\text{Na}$  at 104.227 MHz). A solid echo pulse sequence with an initial pulse width of 6.0  $\mu\text{s}$ , 90° observe pulse of 6.2  $\mu\text{s}$ , an acquisition time of 15 ms and relaxation delay of 5.0 s was used for the  $^{23}\text{Na}$  nuclei. *In situ* data was collected by adding up 60 scans, amounting to  $\sim 5$  min per FID. The spectrum illustrated in Fig. 4 measured at  $t = 0$  min contains only a very broad feature centered at ca. 16 ppm and almost indiscernible from the base line, which is attributed to NaH.<sup>7</sup> Due to the large line widths and the low sensitivity of the  $^{23}\text{Na}$  nucleus, the 6 mol% NaCl arising from the generation of the active Ti species is not observed. After 5 min of hydrogenation, a sharper, downfield resonance arises at 27 ppm, previously reported to be  $\text{Na}_3\text{AlH}_6$ .<sup>7</sup> A discrete resonance for  $\text{NaAlH}_4$  at  $-10.2$  ppm,<sup>7</sup> was not observed on account of the breadth of the resonance and its overlap with the equally broad feature arising from  $\text{Na}_3\text{AlH}_6$ . However, the contribution of signal from  $\text{NaAlH}_4$  from the composite feature gradually increases, causing the peak maximum to shift to lower frequency, reaching  $\sim 10$  ppm after 885 min.

In conclusion, this  $^{27}\text{Al}$  and  $^{23}\text{Na}$  NMR spectroscopic investigation utilizing high-pressure apparatus represents the first *in situ* study of the direct synthesis of  $\text{NaAlH}_4$ . The widely held belief that this proceeds as the microscopic reverse of eqn (1) and (2) has been shown to be incorrect. A significant amount of  $\text{Na}_3\text{AlH}_6$  appears within the first 2 min of  $\text{H}_2$  addition, and the onset of  $\text{NaAlH}_4$  formation occurs after only 4 min. Thus, while there is a large difference in activation energies for the two dehydrogenation reactions (eqn (1) and (2)), the activation energies of the reverse reactions are quite similar. The presence of  $\text{H}_2$  as a reagent in the

reverse forms of eqn (1) and (2) points to a common rate-determining step in these two hydrogenation stages; namely, activation of the strong H–H bond by the Ti catalyst. This work, in tandem with our parallel study of the direct synthesis of  $\text{LiAlH}_4$  (ref. 13) demonstrates impressively how high-pressure NMR studies can shed important new light on the intimate mechanisms of a wide variety of systems that undergo reversible hydrogenation, and shows the technique to be a valuable new weapon in the armory of synthetic chemists and material scientists engaged in the development of advanced, solid state hydrogen storage systems.

## Notes and references

- S. Satyapal, J. Petrovic and G. Thomas, *Sci. Am.*, 2007, **296**, 80.
- US Department of Energy. Multi-Year Research, Development and Demonstration Plan - 2011 Interim Update, <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/storage.pdf>, (accessed 06/12/2012).
- B. Bogdanovic and M. Schwickardi, *J. Alloys Compd.*, 1997, **253**, 1.
- E. Wiberg, R. Bauer, M. Schmidt and R. Uson, *Z. Naturforsch., B: Anorg. Chem. Org. Chem. Biochem. Biophys. Biol.*, 1951, **6**, 393.
- Scifinder Web Version, Chemical Abstracts Service, P.O. Box 3012 Columbus, Ohio 43210, U.S.A., (accessed 06/29/2012).
- E. C. Ashby and P. Kobetz, *Inorg. Chem.*, 1966, **5**, 1615.
- B. Bogdanovic, M. Felderhoff, M. Germann, M. Hartel, A. Pommerin, F. Schuth, C. Weidenthaler and B. Zibrowius, *J. Alloys Compd.*, 2003, **350**, 246.
- K. J. Gross, S. Guthrie, S. Takara and G. Thomas, *J. Alloys Compd.*, 2000, **297**, 270.
- K. J. Gross, G. Sandrock and G. J. Thomas, *J. Alloys Compd.*, 2002, **330**, 691.
- S. Isobe, H. Yao, Y. Wang, H. Kawasaki, N. Hashimoto and S. Ohnuki, *Int. J. Hydrogen Energy*, 2010, **35**, 7563.
- G. Majer, E. Stanik, B. L. E. Valiente, F. Grinberg, O. Kircher and M. Fichtner, *J. Alloys Compd.*, 2005, **404–406**, 738.
- D. Pukazhselvan, M. S. L. Hudson and O. N. Srivastava, *Int. J. Hydrogen Energy*, 2012, **37**, 3697.
- T. D. Humphries, D. Birkmire, B. C. Hauback, G. S. McGrady and C. M. Jensen, *J. Mater. Chem. A*, 2013, **1**, 2974.
- M. H. W. Verkuijlen, P. J. M. van Bentum, O. Zabara, M. Fichtner and A. P. M. Kentgens, *J. Phys. Chem. C*, 2011, **115**, 13100.
- H. W. Brinks, B. C. Hauback, S. S. Srinivasan and C. M. Jensen, *J. Phys. Chem. B*, 2005, **109**, 15780.
- H. W. Brinks, C. M. Jensen, S. S. Srinivasan, B. C. Hauback, D. Blanchard and K. Murphy, *J. Alloys Compd.*, 2004, **376**, 215.
- R. T. Walters and J. H. Scogin, *J. Alloys Compd.*, 2004, **379**, 135.
- S. J. Hwang, R. C. Bowman, J. Graetz, J. J. Reilly, W. Langley and C. M. Jensen, *J. Alloys Compd.*, 2007, **446**, 290.
- T. M. Ivancic, S.-J. Hwang, R. C. Bowman Jr., D. S. Birkmire, C. M. Jensen, T. J. Udovic and M. S. Conradi, *J. Phys. Chem. Lett.*, 2010, **1**, 2412.