

Supporting Information

Solvent-free Mechanochemical Synthesis of Alane, AlH_3 : Effect of Pressure on the Reaction Pathway

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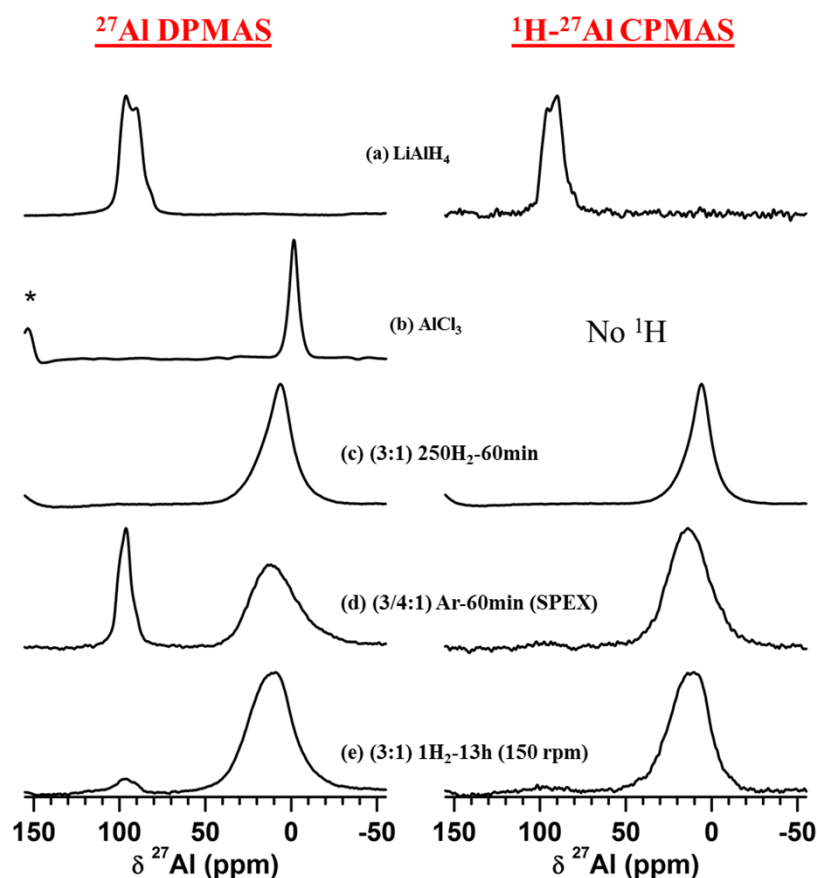


Fig. S1: (Left) ^{27}Al DPMAS and (right) $^{27}\text{Al}\{^1\text{H}\}$ CPMAS spectra of (a) pristine LiAlH_4 , (b) pristine AlCl_3 , (c) $3\text{LiAlH}_4:1\text{AlCl}_3$ mixture ball-milled under standard conditions, (d) $0.75\text{LiAlH}_4:1\text{AlCl}_3$ mixture ball-milled in an Ar atmosphere at near-ambient pressure in a SPEX Mill for 60 min (e) $3\text{LiAlH}_4:1\text{AlCl}_3$ mixture ball-milled under 1 bar hydrogen atmosphere. The spectra were normalized to constant height. $B_0 = 9.4$ T. The DPMAS spectra were obtained using $\nu_{\text{RF}}^{\text{Al}} = 125$ kHz, $\nu_{\text{RF}}^{\text{H}} = 64$ kHz for TPPM ^1H decoupling, and $\tau_{\text{RD}} = 1$ s. The CPMAS spectra were obtained using $\nu_{\text{RF}}^{\text{Al}} = 48$ kHz, $\nu_{\text{RF}}^{\text{H}} = 64$ kHz for cross-polarization and TPPM ^1H decoupling, and $\tau_{\text{RD}} = 10$ s. The asterisks denote the MAS sidebands.

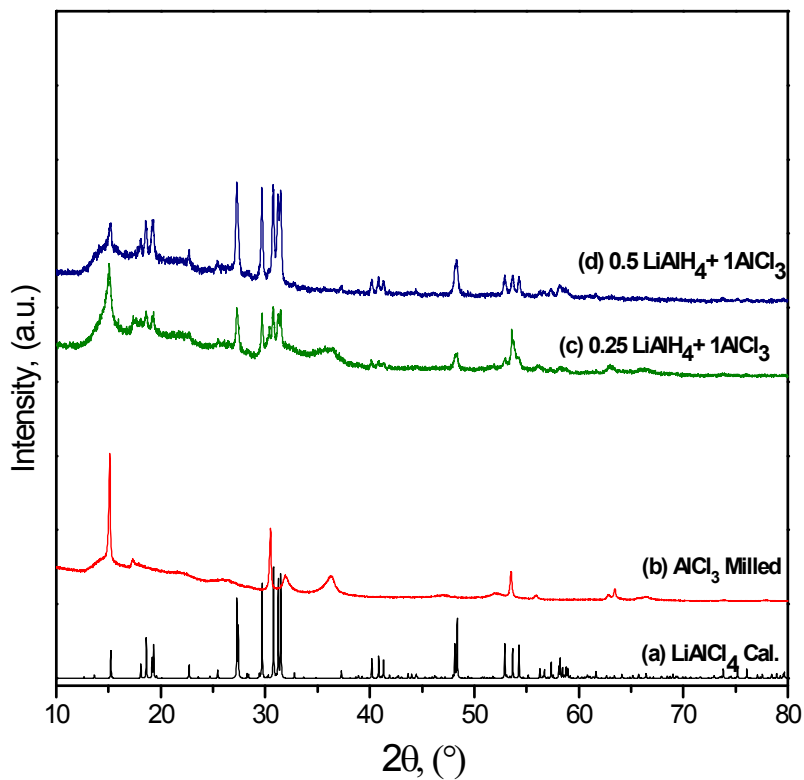
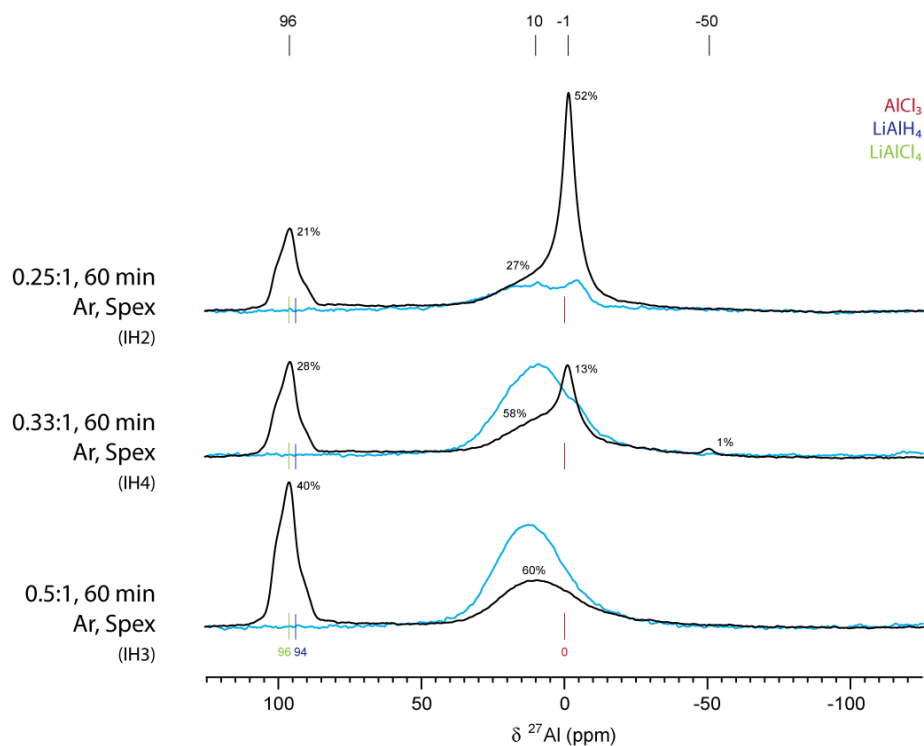


Fig S2. (top) ^{27}Al DPMAS spectra (black) obtained for samples $x\text{LiAlH}_4:\text{AlCl}_3$ ($x=0.25, 0.33$ and 0.5) shown together with their respective $^{27}\text{Al}\{^1\text{H}\}$ CPMAS spectra (blue). Shift positions of the relevant reference compounds are indicated by short, color-coded lines given along the baseline of each spectrum,

while those given in black at the top of the figure correspond to the approximate shift observed for the samples of interest. A percentage represents the integrated area of the DPMAS signal. Note also, that an absolute intensity scale has been maintained within the set of DPMAS spectra, as well as within the set of CPMAS spectra. The ^{27}Al spectra were obtained using a 400-MHz Agilent DD2 spectrometer equipped with a 3.2-mm Otsuka double resonance probe at a frequency of 104.2 MHz and a ^1H frequency of 400.0 MHz. For ^{27}Al DPMAS: $\nu_{\text{RF}}(^{27}\text{Al}) = 125$ kHz during excitation (used in conjunction with a flip angle of 11°); $\nu_{\text{RF}}(^1\text{H}) = 64$ kHz during TPPM decoupling; $\tau_{\text{RD}} = 1$ s; NS = 256; $\nu_{\text{R}} = 16$ kHz. For $^{27}\text{Al}\{^1\text{H}\}$ CPMAS: $\nu_{\text{RF}}(^1\text{H}) = 100$ kHz during excitation and 64 kHz during CP and TPPM decoupling; $\nu_{\text{RF}}(^{27}\text{Al}) = 48$ kHz during CP; $\tau_{\text{CP}} = 0.2$ ms; $\tau_{\text{RD}} = 60$ s; NS = 512; $\nu_{\text{R}} = 16$ kHz. (bottom) Corresponding x-ray diffraction patterns for samples with $x = 0.25$ and 0.5 along with the experimental and calculated patterns for AlCl_3 and LiAlCl_4 respectively. All the reactions were performed in a SPEX ball mill under Ar for 60 minutes.

In the ^{27}Al DPMAS spectra above (Figure S2 top, black), at least three different ^{27}Al sites are observed: i) the high-frequency peak centered at ca. 96 ppm, ii) the broad signal centered at ca. 10 ppm, and iii) the narrow peak occurring at approximately -1 ppm. The latter appears to correspond with AlCl_3 based on its highly symmetrical lineshape and a previously obtained reference spectrum. The broad resonance corresponds to a $^{27}\text{Al}^{\text{VI}}$ species, which, based on the Gaussian-like peak shape, is subjected to a highly disordered environment. The high-frequency peak (ca. 96 ppm) in the DPMAS spectra may arise either from LiAlH_4 , LiAlCl_4 , or a mixture of the two since there is only a very small shift difference between these species. However, from the CPMAS spectra (blue line) it is clear that the observed signal arise from LiAlCl_4 since there is no evidence of a proton-containing species. Other features to note from the CPMAS data are: i) the difference in the region of the Al^{VI} signal observed in the 0.25:1 sample relative those in the 0.33 and 0.5:1 spectra; it is quite evident from the peak shape that the former shows at least two Al^{VI} sites, ii) the small left-shift in the CPMAS spectrum of the 0.33:1 sample associated with the Al^{VI} resonance, which is consistent with there being more than one Al^{VI} environment, Also, the appearance of a small signal near -50 ppm (~1% of spectral area) in the 0.33:1 DPMAS spectrum is noted. As this signal is not observed in the 0.25 or 0.5:1 samples, this small peak suggests the presence of an additional, though minor, species in the 0.33 sample.

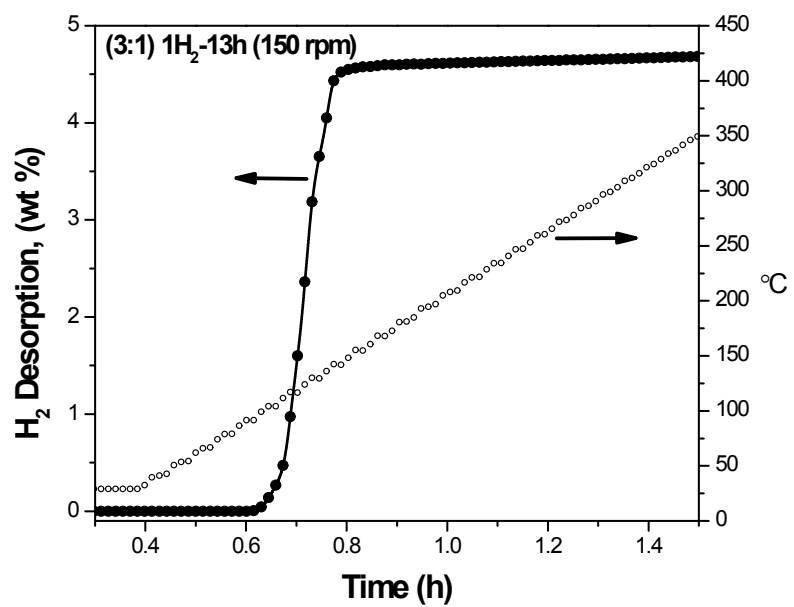


Fig. S3: Desorption curve obtained during heating of products obtained from reaction of $3\text{LiAlH}_4 + 1\text{AlCl}_3$ at *150 rpm*

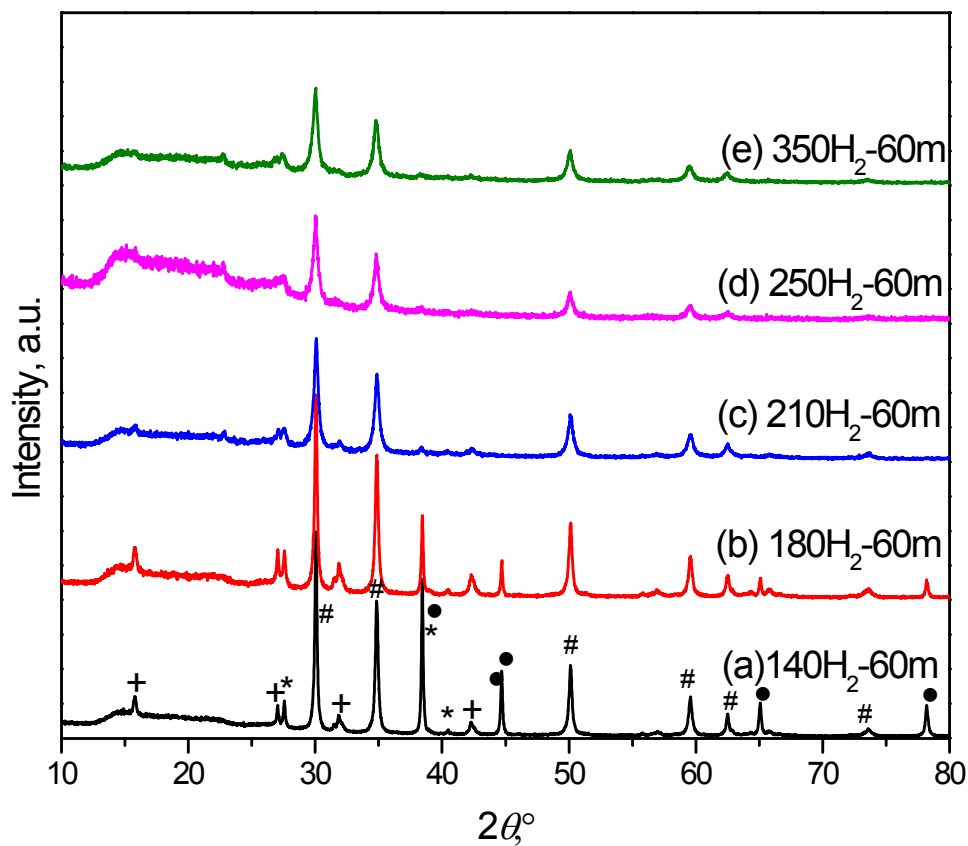


Fig. S4: X-ray diffraction patterns of the products obtained after mechanical mixing of $3\text{LiAlH}_4 + 1\text{AlCl}_3$ up to 60 min under various H_2 pressure at 230 rpm . (*) $\alpha\text{-AlH}_3$, (+) $\alpha'\text{-AlH}_3$, (#) LiCl , and (●) metallic aluminum.

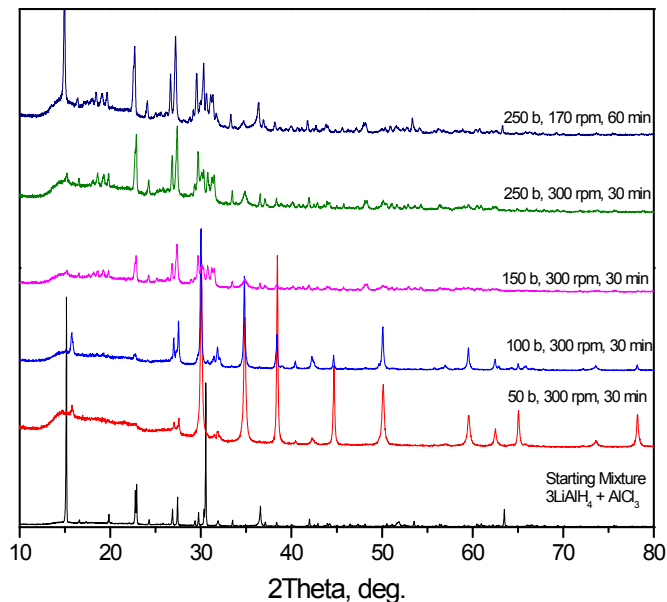


Figure S5: Reaction under Argon: Since the reaction between LiAlH_4 and AlCl_3 is stoichiometric and does not necessitate any gaseous hydrogen uptake, we also examined the reaction of LiAlH_4 and AlCl_3 under argon pressure. Initially *standard milling conditions* were employed. However, it was soon realized that milling under argon pressure between 50–200 bar in a planetary mill was not effective at 300 rpm. It was evident from the acoustic noise or lack thereof that the balls were “stuck” (spinning along with the vessels without colliding) and not generating any significant impact or shear forces.