Electronic Supplementary Information (ESI)

In Situ High Pressure NMR study of the Direct Synthesis of $LiAlH_4$

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Sample Preparation

Commercial $LiAlH_4$ powder (Sigma Aldrich, 95 %) was purified by soxhlet extraction with Et_2O and its purity then confirmed by powder XRD. Purified $LiAlH_4$ was doped 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 decomposed at 423 K *in vacuo* on a Schlenk line. All manipulations were carried out in an Innovations Technologies glove box filled with purified Ar (<1 ppm O_2, H_2O) to avoid contamination.

Powder X-ray diffraction (PXD) patterns were collected using a Rigaku MiniFlex II diffractometer with a Cu *K*α radiation source. Samples for XRD analysis were mounted in hermetically sealed sample holders. The Be cover resulted in extraneous diffraction peaks (2θ = 45.8, 50.9, 52.8, 70.1 and 84.7°). The data were analyzed using MDI Jade V.9.0 software.

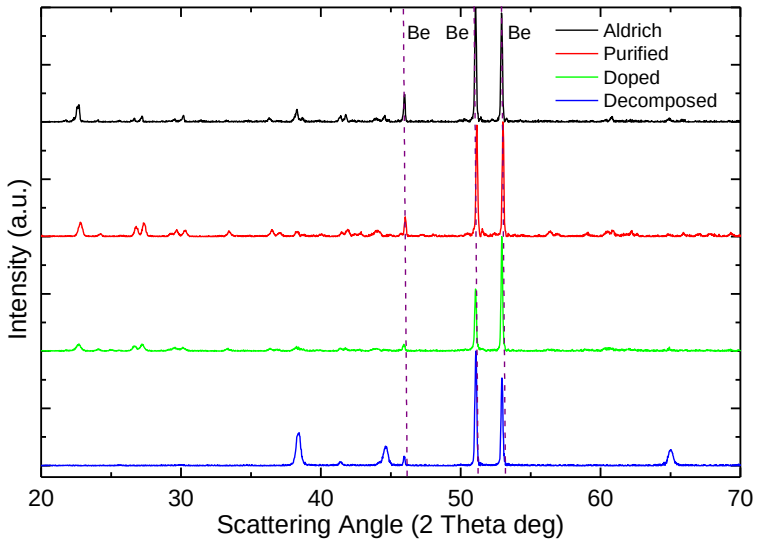

Fig. S1 XRD analysis of $LiAlH_4$ materials used in this study.

NMR Experiments

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 and 104.2 MHz for ^{7}Li and ^{27}Al respectively. Samples were packed in a Daedalus Innovations 5 mm High Pressure 1.5 kBar NMR cell in a N_2 atmosphere glovebox. The cell was loaded in the NMR under ambient conditions and tethered to a H_2/vacuum manifold. Temperature calibration 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 by adding up 30 scans, amounting to ~5 min per FID. A solid echo pulse sequence with an initial pulse width of 6.0 μs, 90° observe pulse of 6.2 μs, an acquisition time of 15 ms and relaxation delay of 5.0 s was used for the ^{7}Li nuclei. *In situ* data was collected by adding up 60 scans, amounting to ~5 min per FID.

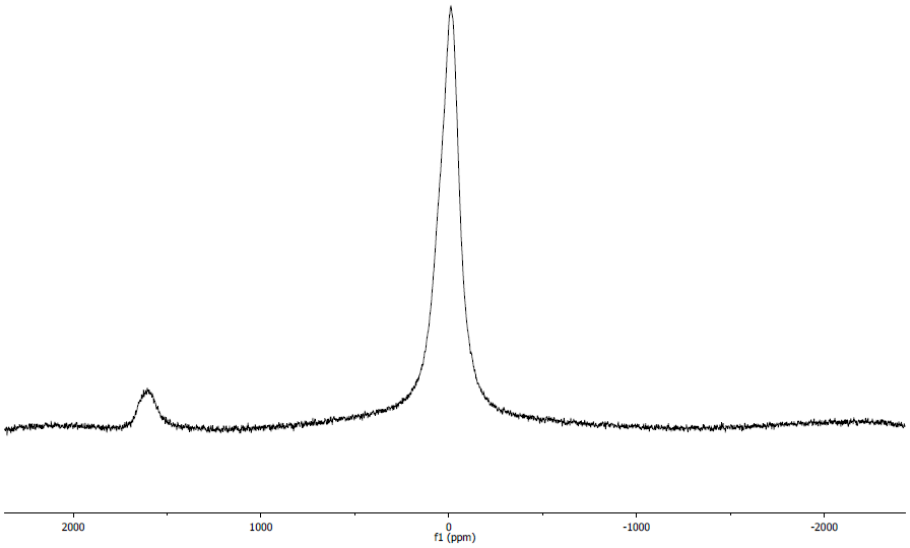

Fig. S2 ^{27}Al NMR spectrum of the empty NMR cell.