Supplementary Material (ESI) for Chemical Communications

Temporal and Spatial Imaging of Hydrogen Storage Materials: Watching Solvent and Hydrogen Desorption from Aluminium Hydride by Transmission Electron Microscopy†

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Synthesis of α-AlH_3

The original synthesis of pure alane was reported by Brower et al. in 1976 from the reaction between $LiAlH_4$ and $AlCl_3$ in ether, forming an alane-etherate. This complex can then be desolvated to produce at least six polymorphs.[1]

$$3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl\downarrow$$

Since this preparation was reported, many papers reference samples produced by the Dow Chemical Co. in the 1970's. Graetz and Reilly published a synthesis for α-AlH_3 in 2005,[2] which follows the original method of Brower et al.

Reagents

All reagents and solvents were handled and stored under inert conditions (N_2 or Ar), employing Schlenk vessels and/or dry boxes to avoid contact with moisture and air. The $AlCl_3$ used was *ReagentPlus*®, anhydrous, granular, ≥99.9% (Sigma-Aldrich). The $LiAlH_4$ was reagent grade, 95%, powder (Aldrich); this was purified by dissolution in and recrystallisation from ether (Et2O). The Et2O was dried using a Grubbs solvent system, then sparged with Ar gas and stored in a Schlenk vessel prior to use.

Procedure

$AlCl_3$ (2.66g; 20 mmol) is dissolved in Et_2O (100 mL), and this solution is added to a solution of $LiAlH_4$ (3.04g; 80 mmol) in Et_2O (300 mL). The resulting mixture is stirred for several minutes. The $LiAlH_4$ may not always dissolve completely. A light grey precipitate of LiCl starts to appear soon after mixing the two solutions. This is removed by filtration, along with remaining $LiAlH_4$. The Et_2O is then removed in vacuo to leave $AlH_3.nEt_2O$ as a white solid. This is ground to a fine powder and baked in vacuo at 70 °C for 6 hours. Care must be taken at this stage to prevent the fine powder being sucked from the vessel. The resulting light grey powder is then washed with Et_2O and dried in vacuo, leaving ca. 2.5 g of α-AlH_3.

SADP Ring Measurements:

Although the ring measurements do not match the theoretical values exactly, they are all within ~2% of these values. It is extremely difficult to locate the exact centre of the SADP, hence there is an unavoidable experimental error associated with measuring the ring distances.

Figure 2 Ring Measurements

Ring Radius (Å)	Al (Å)
2.317	2.338
1.986	2.024
1.492	1.431
1.211	1.221

Figure 3 Ring Measurements

Ring Radius (Å)	Al (Å)
2.357	2.338
2.067	2.024
1.454	1.431
1.236	1.221

Figure 4 Ring Measurements

Ring Radius (Å)	Al (Å)	α-AlH_3 (Å)
N/A		5.6
3.202		3.28
2.359	2.338	2.29
2.067	2.024	2.12
1.612		1.635/1.61/1.6/1.57
1.394	1.431	
1.272	1.221	

It is difficult to assign the rings at 2.359 and 2.067 Å to either Al or α-AlH_3. They likely contain contributions from both.

Figure 5 Ring Measurements

Ring Radius (Å)	Al (Å)
2.352	2.338
2.045	2.024
1.460	1.431
1.232	1.221

Figure S1. Proposed intermediate α-AlH_3 phase as identified by SADP

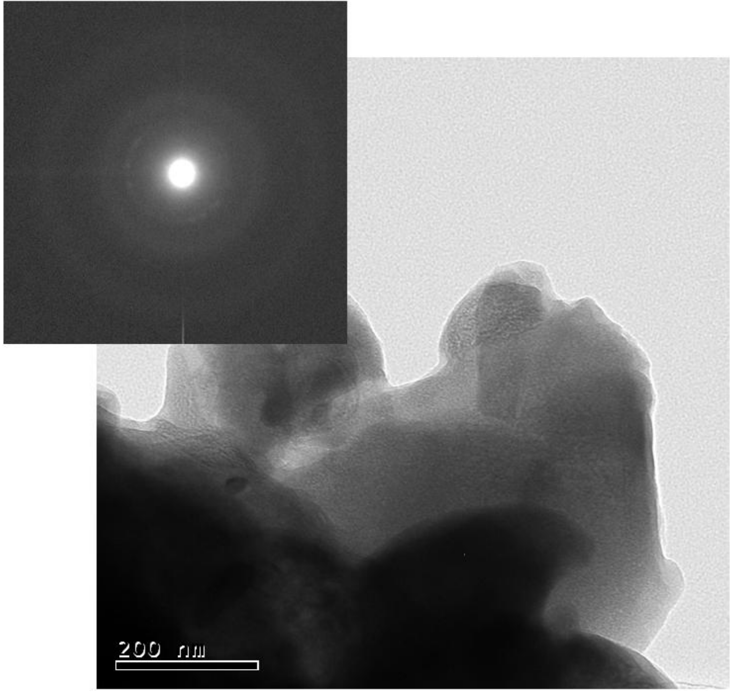

Figure S1- TEM image and SADP (inset) of proposed intermediate α-AlH_3 phase

Figure S1 shows a TEM image of what we believe is the intermediate α-AlH_3 phase corresponding to the process $AlH_3.nEt_2O$ → α-AlH_3 → Al. The SADP is faint; however there is a ring at 3.211 Å, indicative of the presence of α-AlH_3. There are rings at 2.34 and 1.235 Å, which no doubt correspond to a combination of contributions from both Al and α-AlH_3.

Figure S1 Ring Measurements

Ring Radius (Å)	Al (Å)	α-AlH_3 (Å)
N/A		5.6
3.211		3.28
2.340	2.338	2.29
Too faint	2.024	2.12
Too faint		1.635/1.61/1.6/1.57
Too faint	1.431	
1.235	1.221	

XRD Pattern of synthesised α-AlH_3.

Figure S2 shows the XRD pattern of the as prepared α-AlH_3 sample. The peaks near 21 and 24° arise from the parafilm used to cover the samples and prevent exposure to the atmosphere during XRD measurements. The XRD pattern for parafilm is superimposed on the α-AlH_3 pattern for comparison (arbitrarily scaled intensity). The unidentified peaks could be from aluminum or other alane phases (e.g.: ξ). The main constituent, however, is α-AlH_3.

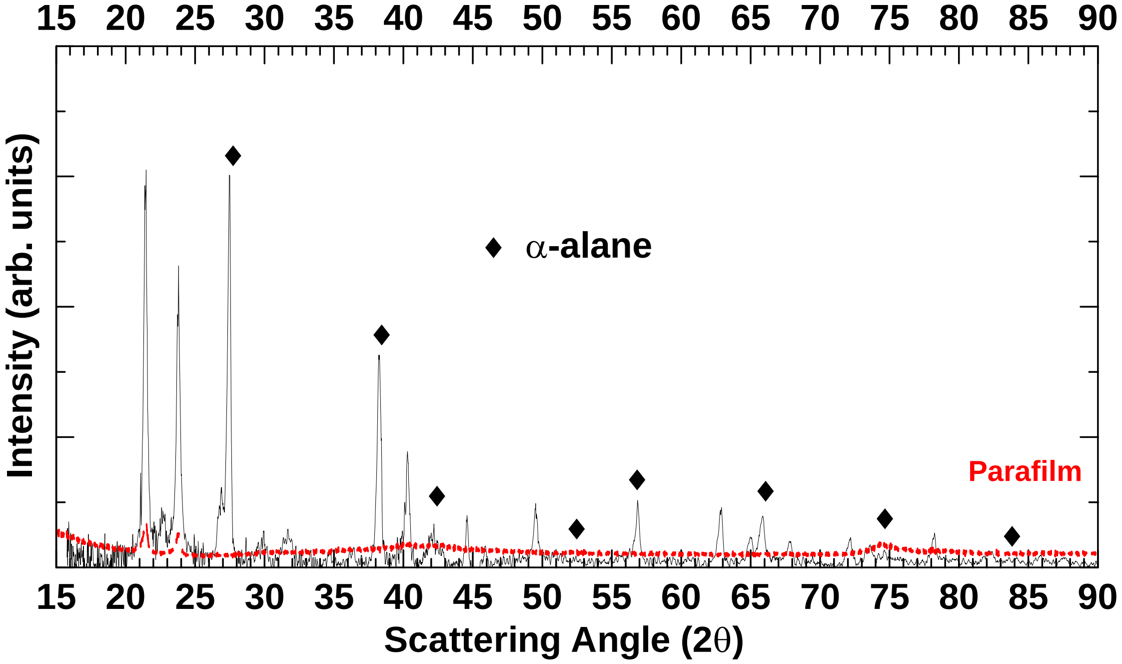

Figure S2 - XRD pattern of the as prepared α-AlH_3

References

1. F. M Brower, N. E. Matzek, P. F. Reigler, H. W. Rinn, C. B. Roberts, D. L. Schmidt, J. A. Snover and K. Terada K. *J. Am. Chem. Soc.*, 1976, **98**, 2450.
2. J. Graetz and J. Reilly, *J. Phys. Chem.*, 2005, **109**, 22181.