MECHANOCHEMICAL APPROACH TO SYNTHESIZE AMINE-AlH₃ ADDUCTS AS ENERGETIC MATERIALS

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The direct synthesis of AlH₃ from Al with H₂ requires extreme conditions beyond technical feasibility, which limits the use of AlH₃. However, this limitation can be bypassed via stabilizing nitrogen-based ligands and ball milling.^[1]

Two approaches using *triethylenediamine* (TEDA) and *hexamethylenetetramine* (HMTA) resulted in the formation of $[(TEDA) \cdot AlH_3]_n$ and $[(HMTA) \cdot AlH_3]_n$, while using quinuclidine resulted in isolated molecular complexes (quinuclidine)₂·AlH₃^[2]. The solvochemical method uses LiAlH₄ + AlCl₃ to obtain AlH₃, which is then reacted with amines at low temperature. In contrast, the mechanochemical method operates under 100 - 180 bar H₂–pressure with metallic Al powder and amines at ~RT. The crystal structures were determined from X-ray powder diffraction data (Figure 1); decomposition behavior was analyzed by TGA-DSC coupled with mass spectrometry.

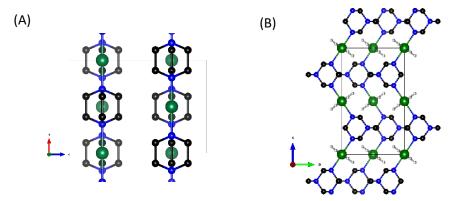


Figure 1. Packing motifs of coordination polymers [TEDA-AlH₃]_n (A) and [HMTA-AlH₃]_n (B)

Due to the high hydrogen capacity of 10.1 wt.% in AlH₃ and its easy dehydrogenation at mild conditions, AlH₃ has attracted particular attention as an energetic material, including solid propellants for rockets, promoting the specific impulse while reducing the erosion of the engine nozzles.^[3] Since AlH₃ is not stable towards oxidizers in the solid propellant mixture, adding Lewis bases to form Al-N compounds significally enhanced the stability while maintaining a desireable combustion energy.

In summary, we showed two procedures to the direct hydrogenation of Al metal in the presence of amines to obtain remarkably stable AlH₃ complexes as energetic materials for solid rocket boosters.

References

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