DOE Hydrogen Program

Complex Hydrides for Hydrogen Storage: Studies of the $Al(BH_4)_3$ System

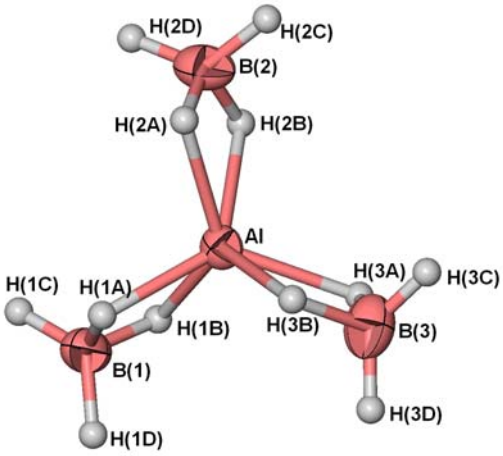
Exploring Novel Materials for Reversible Storage

Background

On-board hydrogen storage is considered to be one of the most challenging aspects for the successful transition to a hydrogen economy. Basic research is essential for identifying novel materials and processes that can provide potential breakthroughs needed to meet DOE Hydrogen Program goals, which include 6 wt.% H_2 for onboard vehicle storage. Metal hydrides are one class of materials that exhibit the potential to achieve these goals. However, a basic understanding of the physical, chemical, and mechanical properties of these materials is needed.

Technology

This effort seeks to develop the chemistry for a hydrogen storage system based on complex hydrides such as the borohydrides or the alanates of the light elements in the periodic table. ORNL is collaborating with the Metal Hydride Center of Excellence partners by developing new materials and synthetic methods for producing materials and by studying chemical reactions. The chemistry of liquid and volatile metal borohydrides such as $Al(BH_4)_3$, $Ti(BH_4)_3$, and $Zr(BH_4)_4$ is being developed.



Chemical structure of $Al(BH_4)_3$ with dual bridging Al-H- bonding

These three complexes are covalent molecular compounds with bridging M-H-B bonds. The concept for hydrogen storage is that metal boride can be transported to a heated zone containing a catalyst for hydrogen production and deposition of a spent boron containing metal solid. The application of heat and elevated hydrogen pressure in the presence of a catalyst regenerates the hydrogen storage compound, which is transported to a cool zone of the reactor.

Borohydride complexes of Al, Ti, and Zr have been shown to be precursors for the chemical vapor deposition of metal borides with the evolution of H_2 as a by-product. This work will focus on making the reaction reversible. Volatile or liquid hydrogen storage materials are anticipated to have some engineering advantages for scale-up including ease of heat and mass transfer.

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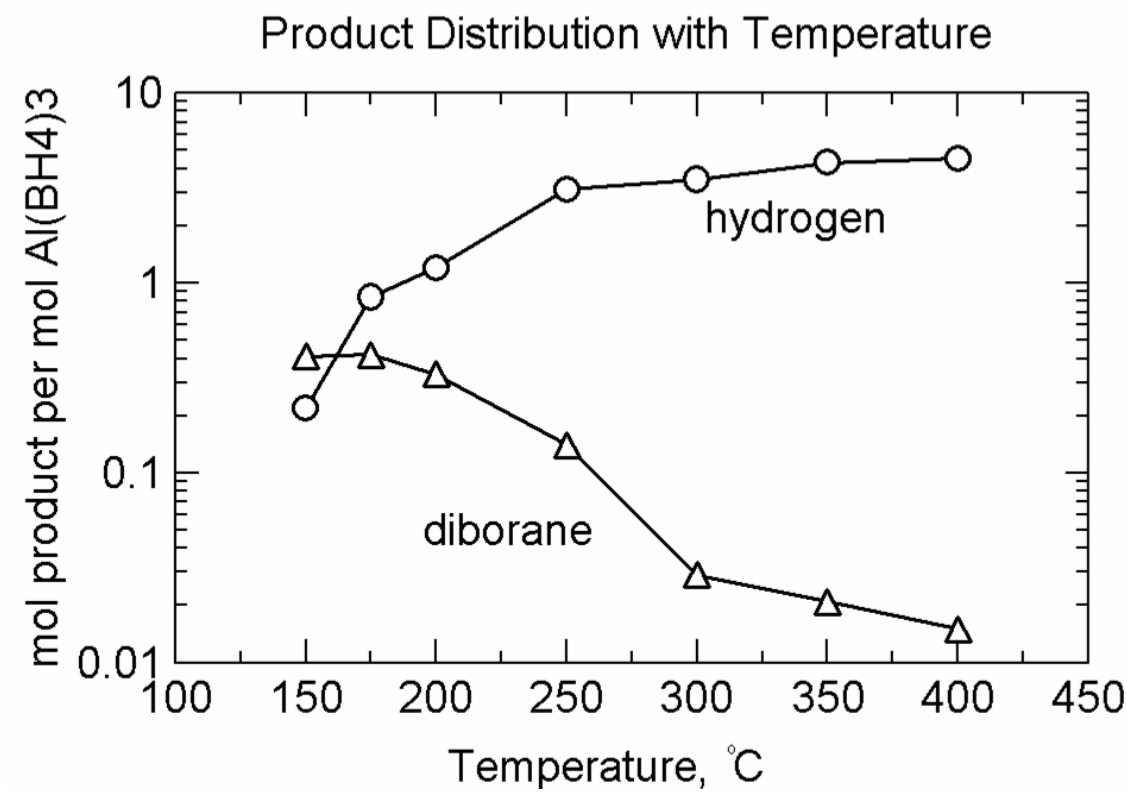
Research Results

This work has demonstrated that the thermal decomposition of $Al(BH_4)_3$ (which contains 16.8 wt. % hydrogen) at less than 200ºC leads to the reversible formation of $AlH(BH_4)_2$ and diborane (B_2H_6). At much higher temperatures (>350ºC) the amount of hydrogen evolved is close to the theoretical maximum for decomposition according to the reaction

$$Al(BH_4)_3 \rightarrow Al + 3(BH)_n + 4.5\ H_2$$

A complex diborane thermal decomposition mechanism also indicates several point of reversibility. These two mechanisms may lead to viable regeneration of metal borohydride hydrogen storage materials. Further studies of metal borohydrides (Mg, Ca, and Ti) in combination with aluminum borohydride are planned to identify materials with the most favorable hydrogen evolution and regenerative capacities.



Dehydrogenation of $Al(BH_4)_3$

Benefits

- The high hydrogen content of these materials exceeds DOE requirements
- Laboratory synthesis is straight forward, and many metal borohydrides are commercially available
- The liquid and volatile nature of these materials may aid in mass transfer in complex on-board fuel systems
- These materials can be safely handled using established methods for the development of air sensitive materials

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