

IV.H.11 Complex Hydrides – A New Frontier for Future Energy

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Objectives

- Examine and compare mechanical and thermal energy-driven phase transformations in model complex hydrides at and away from thermodynamic equilibrium to enable their future use.
- Establish the nature and structure of the products and intermediaries using high resolution solid-state nuclear magnetic resonance (NMR), electron microscopy, as well as first principles theory and modeling.
- Provide a fundamental understanding of the nature of hydrogen bonding and formation, structure, and stability of the model systems, the effects of mechanical energy, temperature, and pressure in controlling the nature of hydrogen-metal bonds.
- Identify events critical to achieving reversibility of hydrogen in model systems under mild conditions.

Technical Barriers

- Substantial progress is required to reduce the energy cost associated with reversible and safe hydrogen storage using metal hydrides.
- Current understanding of the mechanisms of solid-state transformations must be extended from a few known hydrides to complex hydride-hydrogen systems.
- Predictive tools should be developed to guide the discovery of materials at the atomic scale and the processing strategies for controlling the nano-, meso- and microscopic structures.

Abstract

Limited reserves of fossil fuels and the environmental impacts of their consumption drive the demand for alternative sources of energy. Although hydrogen has the highest gravimetric energy density of all fuels, its energy-related applications require safe and efficient storage media. Significant progress in relevant materials science is needed to enable the use of hydrogen in mobile applications, especially in transportation. We seek solids mimicking the structure of methane and ammonia, where several hydrogen atoms encapsulate a single carbon or nitrogen atom forming neutral CH_4 and NH_3 molecules, as opposed to conventional metal hydrides where a single hydrogen atom is encapsulated by several metal atoms. Mechanochemistry and thermochemistry coupled with advanced characterization, theory, modeling, and simulations are utilized to understand composition-structure-processing-property relationships in complex materials consisting of various light-metal hydride compounds and their derivatives.

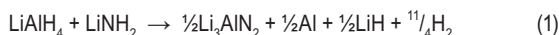
Our approach is to: (1) use different forms of energy (mechanical and thermal) to activate complex hydride materials, examine (non)equilibrium thermodynamics involved, study kinetics of (de)hydrogenation, and prepare new solid systems with hydrogen contents exceeding 10 wt%; (2) carry out state-of-the-art characterization of the structure, chemical, thermodynamic, and physical properties of the prepared complex hydrides in amorphous, nanocrystalline and crystalline forms to expand our current understanding of the mechanisms of solid-state hydrogenation-dehydrogenation, and (3) couple the experiments with the first principles theory.

Progress Report

In recent studies, we built upon our early experiments, in which we pioneered the idea of destabilizing TiCl_4 - LiAlH_4 [1-3] and alanate-amide systems [8] using mechanochemical processing (ball milling), to study the mechanisms of dehydrogenation in $M\text{NH}_2$ - CaH_2 ($M=\text{Li}$ or Na) [9] and $2M\text{NH}_2$ - 3MgH_2 ($M=\text{Li}$ or Na) [10,11]. Moreover, we demonstrated that mechanisms of mechanochemical transformations in some of these systems are different from those induced by temperature [11,12], carried out exploratory studies of direct mechanochemical hydrogenation of Al and magnesium diboride as well as dehydrogenation of ammonia borane [13], and showed that solid-state NMR is an invaluable tool in characterization of both the mechanochemical [3,8,11,14] and thermochemical [12,13,15] processes that occur in complex hydrides. As a result, we established that mechanochemistry adds a new dimension

to well-known destabilization by chemical substitutions. From density functional theory (DFT) methods, including simulated annealing and nudge-elastic band techniques, we are currently investigating the thermodynamics and kinetic barriers for materials directly relevant to our experiments, namely, (1) vacancy-mediated formation of alane (AlH_3) complexes, which may interact with other metallic elements, e.g., Li, and (2) the effects of particle size on (de)hydrogenation of MgH_2 , relevant to ball-milling [16]. In previous work, theory has detailed the issues with reversibility of H-storage reactions [4-6], e.g., LiBH_4 and $M(\text{BH}_4)_2$ with $M=\text{Ca, Mg}$, especially avoiding thermodynamically very stable $\text{MB}_{12}\text{H}_{12}$ intermediates. A brief, selected summary of our progress is given below.

Transformations of the LiAlH_4 - LiNH_2 and MNH_2 - MgH_2 ($M=\text{Li}$ or Na) Systems. To establish differences between the mechanochemical and thermochemical events occurring in the same system, we carried out a detailed study of the mechanism of thermal decomposition of (1:1) LiAlH_4 - LiNH_2 system using pressure-composition-temperature analysis, solid-state NMR, X-ray diffraction (XRD), and residual gas analysis [12]. Figure 1 illustrates the evolution of hydrogen during heating of the 1:1 mixture of LiAlH_4 and LiNH_2 from 25 to 390°C. Rapid desorption initiates at ~140°C and a total of ~9 wt% of pure hydrogen is released. To obtain insights into the chemical transformations occurring during the thermal treatment, the mixture was held at selected temperatures (see open circles in Figure 1) until the hydrogen release ceased. Subsequently, the samples were analyzed by XRD and solid-state NMR (Figure 2) providing coherent information about the intermediates and products. The major transformations detailed in this study result in the following overall reaction:



The final products in Eq. 1 are different than in the mechanochemical process, where LiAlH_4 and LiNH_2 react with one another [8]. Thermochemical transformation of the LiAlH_4 - LiNH_2 system is initiated by the decomposition of LiAlH_4 , and further release of hydrogen is determined by the presence and the concentration of LiNH_2 [12].

In other studies, several mixed systems containing Mg have been investigated. Examination of thermochemical transformations in (2:3) MNH_2 - MgH_2 system ($M = \text{Li}$ or Na) indicated the following overall reactions [10]:



The 2NaNH_2 - 3MgH_2 system can be partially rehydrogenated in 190 bar hydrogen at 395°C with formation of the MgNH imide. Similarly, mechanochemical transformations during ball milling of sodium amide (NaNH_2) with MgH_2 in 2:3 and 2:1 molar ratios have

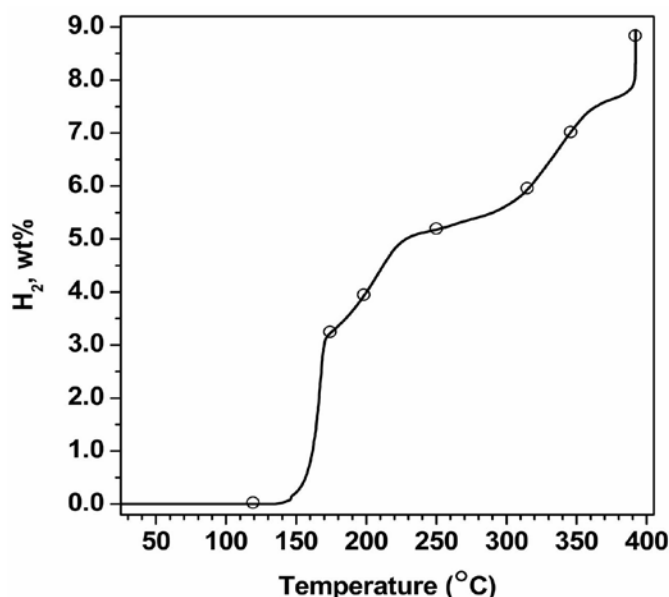
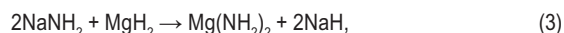


FIGURE 1. Temperature programmed decomposition of the 1:1 LiAlH_4 - LiNH_2 mixture with a heating rate of 1°C/min

been studied using XRD and solid-state NMR [11]. The mechanochemical processing of the 2NaNH_2 - 3MgH_2 system yields the same final products as the thermochemical reaction (see Eq. 2 with $M=\text{Na}$) via a different pathway, which involves the formation of MgNH [11]. However, the mechanochemical transformation of the 2NaNH_2 - MgH_2 system proceeds without any hydrogen release:



Our studies also revealed a possibility that some mechanochemical reactions, which appear to be solid-state processes, may occur in a liquid phase via the formation of low-melting eutectics [14].

Ammonia Borane-Based Materials. The mechanism of thermochemical dehydrogenation of the 1:3 mixture of Li_3AlH_6 and NH_3BH_3 (AB) has been studied by the extensive use of solid-state NMR and theoretical calculations. The activation energy for the dehydrogenation is lower than for pristine AB (110 kJ mol⁻¹ vs. 184 kJ mol⁻¹) [13]. The major hydrogen release from the mixture occurs at 60°C and 72°C, which compares favorably with pristine AB and related hydrogen storage materials, such as lithium amidoborane (LiNH_2BH_3 , LiAB). Based on the reported chemical reaction between lithium hydride (LiH) and AB [7], we expected the thermal treatment of Li_3AlH_6 -3AB to proceed via the formation of lithium amidoborane (LiNH_2BH_3 ; LiAB) through the reaction $\text{Li}_3\text{AlH}_6 + 3\text{AB} = 3\text{LiAB} + \text{Al} + 9/2 \text{H}_2$. However, the solid-state NMR measurements and calculations showed that the mixture decomposes via the formation of a different intermediate phase with improved dehydrogenation properties as compared to pristine AB.

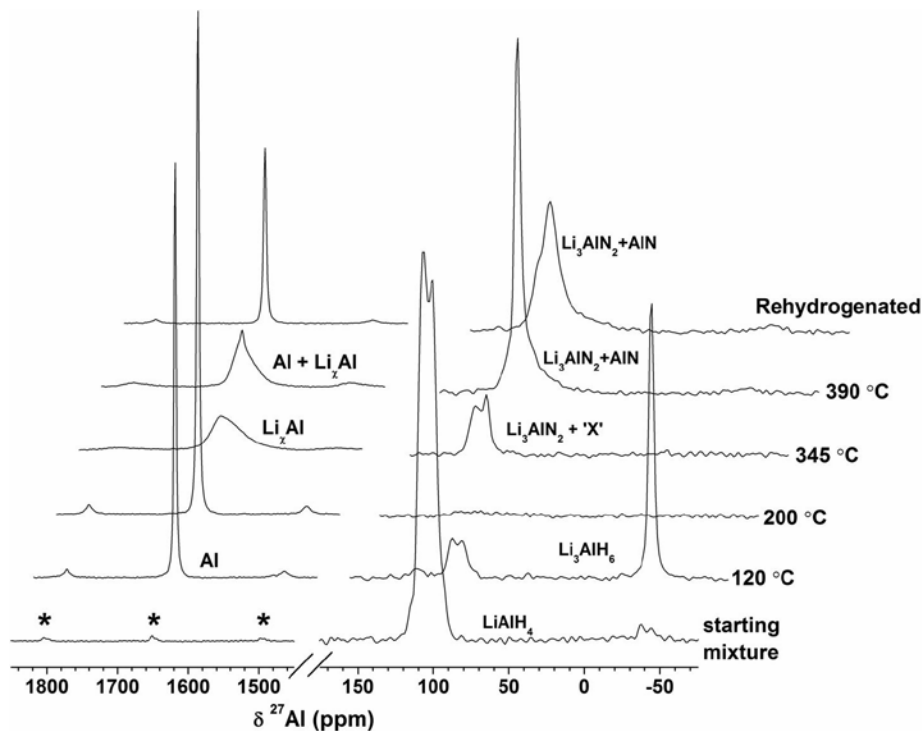


FIGURE 2. ^{27}Al magic angle spinning NMR spectra of LiAlH_4 - LiNH_2 mixture treated at various temperatures. Asterisks indicate spinning sidebands.

DFT Study of H-Desorption in Doped MgH_2 (110)

Surfaces. Using DFT nudged-elastic bands, H_2 desorption barrier with Ti-doping (Figure 3) drops by 0.41 eV (–22% change), agreeing with 0.46 eV from experiment [16]. In addition, we find that particle size alone does not affect desorption enthalpies [17], so it is a combination of dopant and non-equilibrium processing.

Vacancy-Mediated Formation of Alane. Using DFT-based molecular dynamics, we have shown that vacancy (as created by ball-milling) stabilizes alane formation on Al(111), whereas Ti-doping helps dissociate H_2 , making alane formation exothermic only with defect-dopant interactions. These results are being prepared for publication.

Future Directions

More work at fundamental level is needed to understand the structure – hydrogen storage activity relationships among promising complex hydrides and the role of nonequilibrium states in dehydrogenation and hydrogenation. Reaching our goals requires basic understanding of the mechanisms of processes occurring in a ball mill, and differences between the mechanically- and thermally-induced transformations. We will continue to rely upon integrating innovative transformations with state-of-the-art characterization and modeling that directly addresses processing effects, especially those dictated by defect-mediated mechanisms

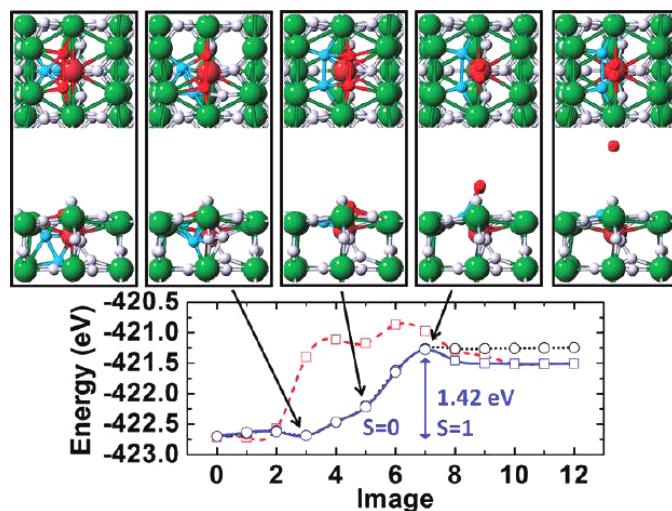


FIGURE 3. H_2 desorption path for Ti-doped MgH_2 (110) rutile surface. With Ti spin state S changes from 0 (circles) to 1 (squares) during desorption. Fixed S results are given as dashed (dotted) line.

inherent in mechanical processing. Our general objectives and strategy will remain similar as in the previous funding period while pursuing new research directions, including: (1) understanding of the direct mechanochemical synthesis of AlH_3 with high yields; (2) mechano- and thermo-chemical studies of magnesium borohydride- and aminoborane-based systems; (3) development and testing

of hybrid materials composed of complex hydrides and conventional intermetallic hydrogen absorbers; (4) use of mechanical energy to create nonequilibrium rehydrogenation pathways under low temperatures and hydrogen pressures; (5) development of improved characterization methods, such as in situ solid-state NMR spectroscopy; and (6) integration of experiments with theoretical modeling providing better understanding of thermodynamics and kinetics of (de)hydrogenation in selected model systems and guidance toward the discovery of hydrogen-containing solids that would be unattainable using synthetic and processing methods alone.

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