

IV.I.19 Complex Hydride Systems – a New Frontier for Future Energy Applications

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Program Scope

Hydrogen storage is one of the enabling materials technologies required to assure a successful future transition from fossil to hydrogen-based fuel. The scope of the multidisciplinary effort, which draws on considerable experimental and modeling experience and expertise at the Ames Laboratory and Virginia Commonwealth University, is to achieve a fundamental understanding of the relationships between the chemical composition, bonding, structure, microstructure, properties and performance of hydrogen-rich solids. The specific objectives of this project are to address relevant issues, which have the potential to advance basic materials science of novel hydrides and open up possibilities for their future practical use.

- Synthesize an array of novel non-transition metal-based complex hydrides where the metal, metalloid or nonmetal atom is coordinated by two to six hydrogen atoms by means of solvent-free, mechanochemical technique starting from several parent light-element hydrides.
- Fully characterize the products using state-of-the-art experimental techniques.
- Create a knowledge base relating composition, structure and properties of various classes of complex hydrides by investigating the effects of varying stoichiometry and processing history on their crystal and microscopic structure, chemical, thermodynamic and physical properties.
- Extend and refine the current understanding of the mechanisms of the solid-state transformations occurring in a few model hydrides, which is in a rudimentary state, by examining the effects of various chemical and structural modifications and processing strategies on the structure-property relationships, and dehydrogenation and hydrogenation behavior of novel non-transition metal-based complex hydrides. Special emphasis is placed on bridging lengths scales ranging from a few tenths of a nanometer (a single interatomic

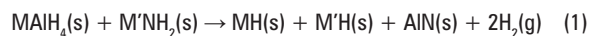
distance) to microns (a single grain) and centimeters (assemblies of multiple particles varying in size, shape and structure) in order to fully explore the potential of novel solids.

- Integrate experiment with modeling and first principles theory to provide a fundamental understanding of the nature of hydrogen bonding, the structure and stability of the complex hydride phases, the effect of dopants and catalysts, temperature, and pressure in altering the nature of hydrogen-metal bond, and the role of nanostructuring on the absorption and desorption properties of hydrogen. In addition to explaining the experimental data, the theory will be used to guide experiments in search of desirable chemical composition, preparation and processing strategy, atomic scale structure and microstructure, and the nature of the substituting element(s) – all related to resultant cyclic hydrogenation and dehydrogenation properties of complex hydrides.

Recent Progress

Mechanochemically and thermochemically-induced transformations have been studied in various systems containing complex metal hydrides such as NaAlH_4 (total hydrogen content 7.4 wt%) and LiAlH_4 (10.5%), amides NaNH_2 (5.1%) and LiNH_2 (8.7%), binary metal hydrides CaH_2 (4.8%), MgH_2 (7.7%), and LiH (12.5%). Several previously unknown mechanochemical and thermochemical reactions have been discovered.

Transformations in MAlH_4 - MNH_2 systems (where $\text{M} = \text{Li}$ or Na) have been characterized using the X-ray powder diffraction, ^{27}Al , ^7Li and ^{23}Na solid state nuclear magnetic resonance (NMR) spectroscopy, transmission electron microscopy (TEM), pressure-composition-temperature (PCT) measurements and residual gas analysis (RGA). The overall mechanochemical transformations in these systems proceed as follows:



yielding from 4.3 to 6.6 wt% of hydrogen. The actual transformation mechanisms include multiple stages and intermediaries, such as Li_3AlH_6 , $\text{Na}_2\text{LiAlH}_6$, $\text{Na}_{3-x}\text{Li}_x\text{AlH}_6$ and Na_3AlH_6 . The solid state NMR analysis and TEM were used to establish the nature of the final reaction products present as a few micron size conglomerates of much smaller, 20-50 nm particles.

Unlike mechanochemical reactions, thermochemical transformations in the same systems proceed differently,

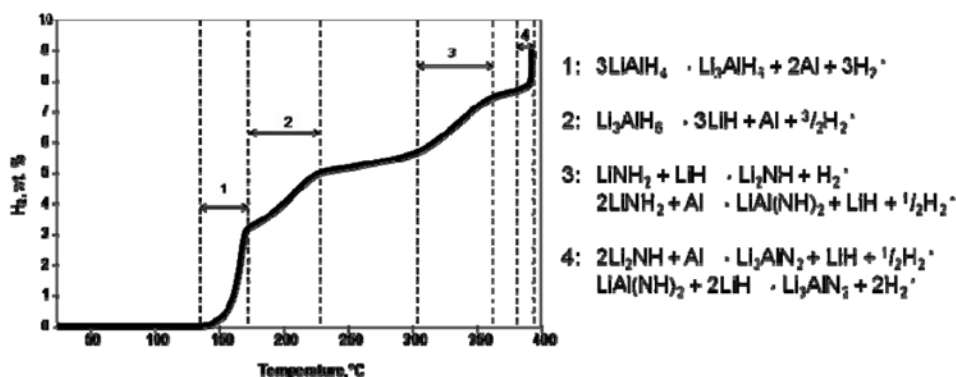
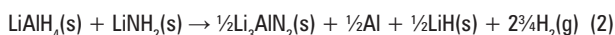


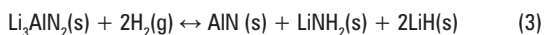
FIGURE 1. Hydrogen release during the thermal decomposition of the LiAlH_4 - LiNH_2 mixture taken in a 1:1 molar ratio.

as illustrated in Figure 1. When both M and M' are Li, the overall transformation is:

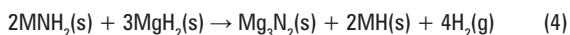


yielding a total of 9 wt% of hydrogen by weight.

The products (Equation 2) can be rehydrogenated at $P_{\text{H}_2} = 180$ bar and 275°C , and the rehydrogenation reaction is shown in Equation 3.

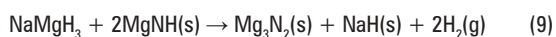
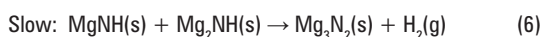
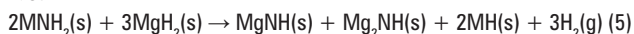


Mechanochemical reactions between alkali metal amides and magnesium hydride taken in 2:3 molar ratios have been investigated. Magnesium nitride, alkali metal hydrides and pure hydrogen form as end products after the high energy ball milling of the mixtures:



The amount of released hydrogen is 6.5 wt% for 2LiNH_2 - 3MgH_2 system and 5.1 wt% for 2NaNH_2 - 3MgH_2 system. Intermediate phases are MgNH and Mg_2NH with cubic structures analogous to CaNH and Ca_2NH . Mixed hydride NaMgH_3 was observed in a sodium system as one of the intermediates. The mechanism of the mechanochemical transformation in 2MNH_2 - 3MgH_2 systems can be described as follows:

Fast:



The final products of thermal decomposition of 2MNH_2 - 3MgH_2 mixtures are similar to the products

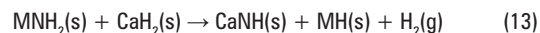
obtained via the mechanochemical route (Equation 4). The difference is only in the mechanism of the solid state transformation:



Competing reactions (Equation 8 and 12) were observed in this reaction.



Mechanochemical transformations of lithium and sodium amides with calcium hydride taken in 1:1, 1:2, 2:1 and 2:3 molar ratios, have been also investigated. Formation of calcium imide, alkali metal hydrides and gaseous hydrogen was observed for all investigated stoichiometries. In all cases, the overall mechanochemical transformations are equimolar and proceed as the following solid state reaction:



If the molar concentrations of starting materials are different from 1:1, then one of the reactants remains in excess.

Total energies and enthalpies of formation for different reaction products during the dehydrogenation of CaH_2 - MNH_2 mixtures were calculated (Table 1). It appears that mechanochemical processing (ball milling) can drive a system towards nonequilibrium configurations, resulting in different final products, and therefore, different mechanisms when compared to equilibrium dehydrogenation reactions induced by heating. Reduction of grain size, formation of structural defects, and ballistic diffusion are all believed to play a role in these nonequilibrium transformations.

TABLE 1. Enthalpies of formation for different reaction products during the dehydrogenation of CaH₂ and LiNH₂ (or NaNH₂) mixture.

Reactants	Path	Reaction Products	ΔE (eV)	ΔH (KJ/mol/H ₂)
CaH ₂ + LiNH ₂	1	CaH ₂ + LiNH ₂ = CaNH + LiH + H ₂	0.560	54.032
	2	CaH ₂ + 2LiNH ₂ = Li ₂ Ca(NH) ₂ + 2H ₂	1.615	77.912
	3	CaH ₂ + 2LiNH ₂ = CaNH + Li ₂ NH + 2H ₂	1.445	69.711
	4	Step. 1: CaH ₂ + 2LiNH ₂ = Ca(NH ₂) ₂ + 2LiH	-0.155	
		Step. 2A: Ca(NH ₂) ₂ + 2LiH = CaNH + Li ₂ NH + 2H ₂	1.600	77.188
		Step. 2B: Ca(NH ₂) ₂ + 2LiH = Li ₂ Ca(NH) ₂ + 2H ₂	1.770	85.390
CaH ₂ + NaNH ₂	1	CaH ₂ + NaNH ₂ = CaNH + NaH + H ₂	0.409	39.463
	2	CaH ₂ + 2NaNH ₂ = Na ₂ Ca(NH) ₂ + 2H ₂	2.056	99.187
	3	CaH ₂ + 2NaNH ₂ = CaNH + Na ₂ NH + 2H ₂	1.796	86.644
	4	Step. 1: CaH ₂ + 2NaNH ₂ = Ca(NH ₂) ₂ + 2NaH	-0.458	
		Step. 2A: Ca(NH ₂) ₂ + 2NaH = CaNH + Na ₂ NH + 2H ₂	2.254	108.739
		Step. 2B: Ca(NH ₂) ₂ + 2NaH = Na ₂ Ca(NH) ₂ + 2H ₂	2.514	121.282

Future Work

Systematic work to integrate innovative synthetic approaches with state of the art characterization and theoretical modeling will continue. Our main objectives can be summarized as follows.

- The studies of temperature induced transformations of mixed systems containing sodium alanate and sodium amide will be carried out in order to establish details of their mechanisms.
- Mechano- and thermo-chemical studies will be extended to include several new systems such as lithium and sodium borohydrides.
- The applicability and effectiveness of the mechanochemical approach as a nonequilibrium processing tool for rehydrogenation of complex hydrides under low and high hydrogen pressures and different temperatures will be thoroughly studied.
- New hybrid materials consisting of complex hydrides and intermetallic hydrogen absorbers, as well as complex hydrides supported on mesoporous carbon nanoparticles, nanotubes and fullerenes will be developed and examined.
- We will continue to employ and improve characterization methods, such as gas-volumetric analyses, PCT measurements, solid-state NMR spectroscopy, X-ray diffraction, residual gas analysis, and electron microscopy to determine to the best extent possible the structure and properties of all materials developed in this project.
- The theoretical modeling will emphasize multi-scale techniques based on density functional theory.
- As our knowledge advances, there will be an increased emphasis on integrating experiment with theory. We expect that these efforts will guide us

toward the discovery of hydrogen-containing solids that would be unattainable using conventional synthetic methods. They will also lead to a more complete understanding of both thermodynamics and kinetics of dehydrogenation and hydrogenation transformations in these materials.

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