Center for Hydrogen Storage Research at Delaware State University

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Project ID #
STP 24

Overview

Timeline

- Start – June 1, 2006
- Finish – May 30, 2009
- 66% complete

Budget

- Total project funding
  - DOE $990 K
  - DSU $247.5 K
- Funding received in FY 06
  - $875.6 K
- Funding for FY08
  - $361.9 K

Barriers

- Barriers addressed
  - Weight and Volume
  - Durability
  - Refueling Time
  - Hydrogen Capacity and Reversibility

Partners

- Interactions/ collaborations
  - Georgia Tech
  - University of Pittsburgh
  - University of Delaware
  - Air Liquide

Objectives

Overall	Establish a Center for Hydrogen Storage Research at Delaware State University for the preparation and characterization of selected complex metal hydrides and the determination their suitability for hydrogen storage.
2006	Develop methods for the synthesis, characterization, and modeling of complex hydrides using $LiBH_4/MgH_2$ as a model system.
2007	Identify the most promising types of complex hydrides destabilized hydrides and demonstrate the optimum temperature/pressure range and sorption kinetics of the hydrides under a variety of conditions. Determine their cyclic stability and develop improved sorption catalysts.
2008	Extend the studies to include other complex hydrides, that have greater hydrogen storage potential than the destabilized hydrides such as ternary borohydride systems. Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures.

Milestones

Year	
2006	Milestone: The methods and procedures to be used for testing and characterizing complex hydrides using $NaAlH_4$ as a model system were completed.
2007	Go/No-Go decision: It was decided that most of the effort should be expended on studying the borohydride systems for hydrogen storage instead of the alanates.
2008	.Milestone: It was discovered that the $CaH_2/LiBH_4$ system could reversibly absorb and release approximately 9 weight percent hydrogen. It was also found that certain ternary mixtures could release hydrogen at significantly lower temperatures.

Approach

- Task 1 – Preparation and characterization of the $LiBH_4/CaH_4$ system
  - Synthesis of new materials by mechanical alloying using ball milling
  - Determine thermal stability using thermal gravimetric analyses (TGA)
  - Use XRD to determine phase purity and crystal structure
  - Use PCI analyses to determine thermodynamic stability

- Task 2 – Find catalysts for making the hydriding faster and reversible

- Task 3 - Kinetic modeling study
  - Determine kinetic rate curves
  - Perform modeling to gain understanding of the mechanism

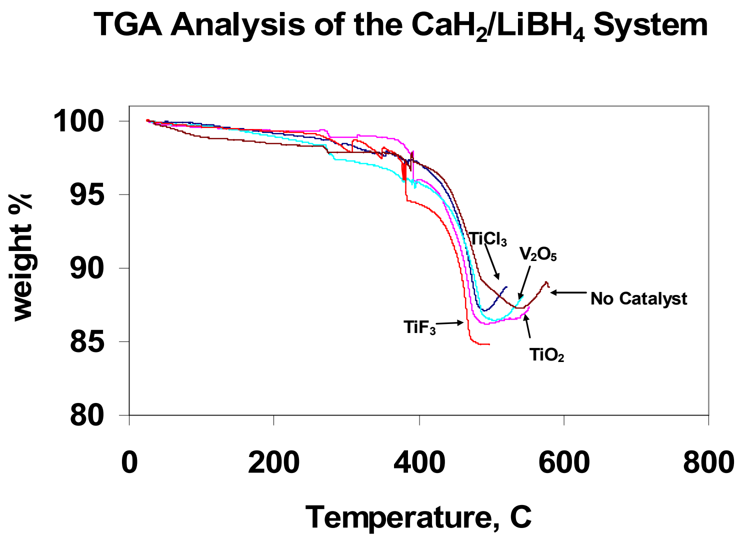
- Task 4 – Study other classes of promising hydrogen storage materials
  - Study ternary systems such as the $LiBH_4/CaH_4/LiNH_2$ system to determine if reaction temperatures can be lowered.

Technical Accomplishments/ Progress/Results

- Have completed the analyses on the $LiBH_4/CaH_2$ system using TGA, TPD and PCI analyses. Have found that this system can reversible store 9 weight percent hydrogen.
- Have done some kinetic modeling studies on the $NaAlH_4$ and $LiBH_4/CaH_2$ systems. Have identified the likely rate-controlling process.
- Have identified a ternary hydride system, $CaH_2/LiBH_4/LiNH_2$, that releases hydrogen at a significantly lower temperature than the binary $CaH_2/LiBH_4$ mixture.

Accomplishments

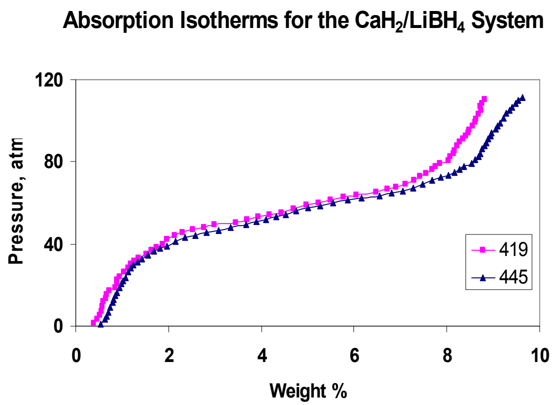
Thermal Analysis of the $CaH_2/LiBH_4$ System

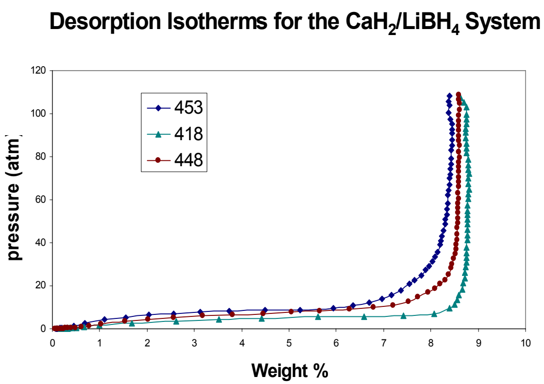


- A comparison was made of the desorption temperatures with 4 different additives. The graphs show that the desorption temperatures are in the order TiF_3 < TiO_2, ≤$TiCl_3$ <V_2O_5.
- None of these additives produce a lower temperature than 400 C.

Accomplishments

PCI Analysis of the $LiBH_4/CaH_2$ System





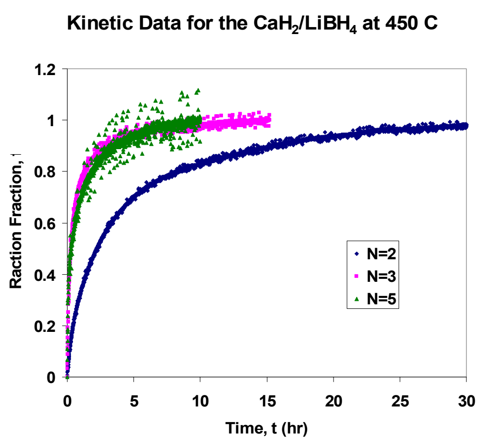
- Hydrogen is released from the $LiBH_4/CaH_2$ system via the reaction:

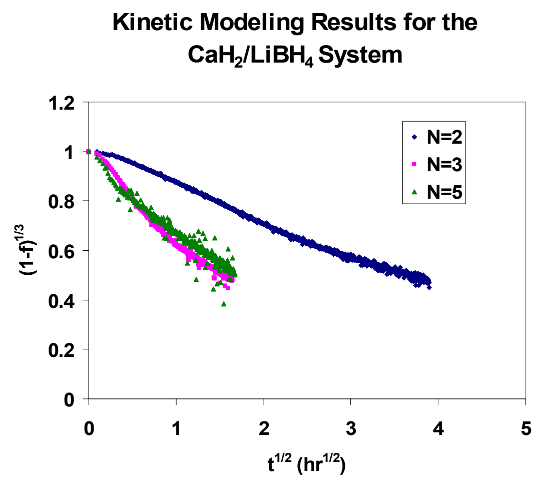
$$6\ LiBH_4 + CaH_2 \rightarrow 6\ LiH + CaB_6 + 10\ H_2$$

- The isotherms show that a single plateau is present and that about 9 weight percent hydrogen can be reversibly absorbed and released in the 400 – 450 C range. The enthalpy of desorption is about 67 kJ/mole H_2.

Accomplishments

Kinetic Modeling Studies on the $LiBH_4/CaH_2$ system



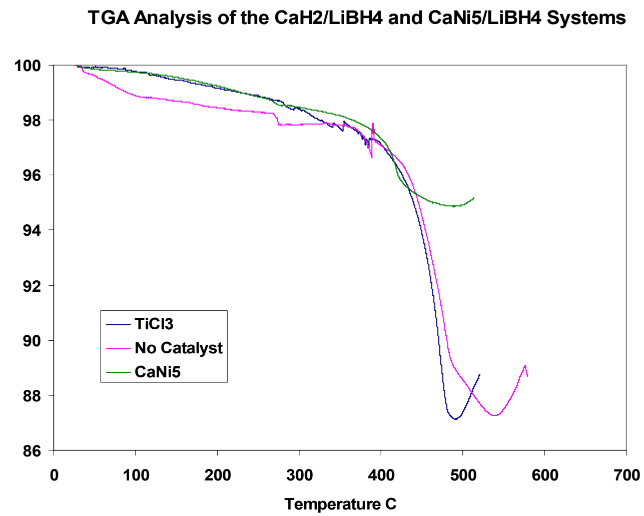


- An N-value was defined as the ratio of the plateau pressure to the applied pressure.
- The plots of reacted fraction versus time show that the rates increase with increasing N-values. Kinetic modeling was attempted with nucleation and growth, moving boundary and diffusion models. The best fit was obtained with the diffusion model according to the equation:

$$(1-f)^{1/3} = 1-(\frac{\sqrt{kt}}{R})$$

Accomplishments

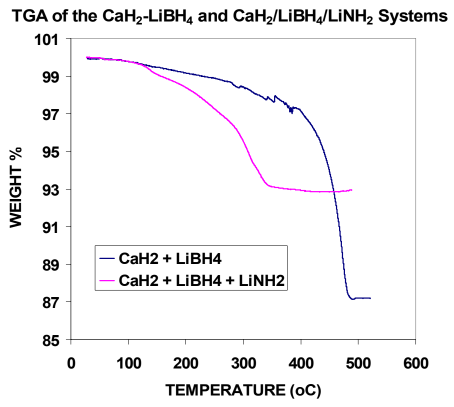
Hydrogen Storage in the $LiBH_4/CaNi_5H_4$ System

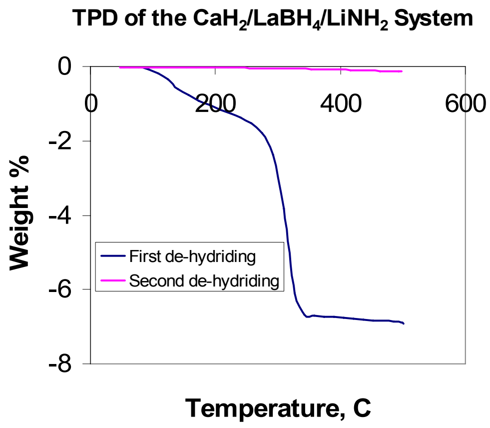


- TGA analyses were done on $CaH_2/LiBH_4$ with $TiCl_3$; $CaH_2/LiBH_4$ without $TiCl_3$; and a $CaNi_5H_4/LiBH_4$ mixture.
- The results show that all three mixtures release hydrogen at about the same temperature. Thus $CaNI_5H_4$ is not an effective dopant.
- The $CaH_2/LiBH_4$ mixture releases a lower weight percentage hydrogen due to the added weight of the nickel.

Accomplishments

Hydrogen Storage in the $LiBH_4/CaH_2/LiNH_2$ system

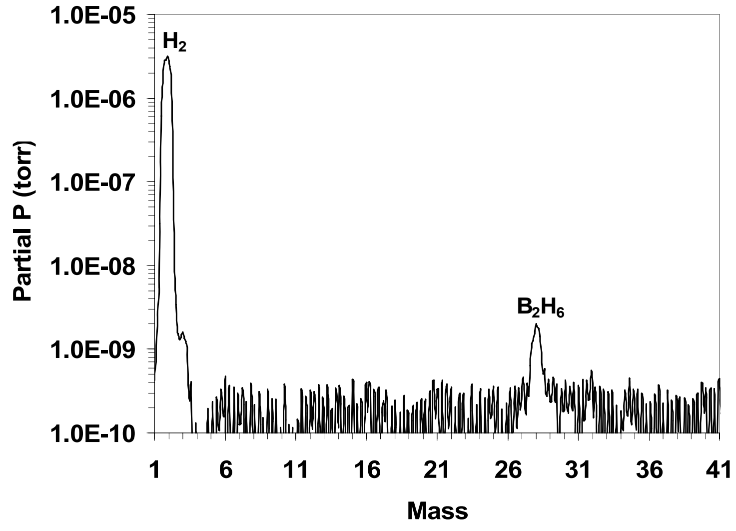




- TGA shows that the $LiBH_4/CaH_2/LiNH_2$ system releases hydrogen at about 100 C lower than the $LiBH_4/CaH_2$ system. However, the amount of hydrogen released from the ternary system is lower than the amount released from the binary system.
- TPD analysis shows that the ternary system does not absorb and release hydrogen reversibly. It initially releases about 7 weight percent hydrogen but subsequent attempts to re-hydride and release hydrogen were unsuccessful.

Accomplishments

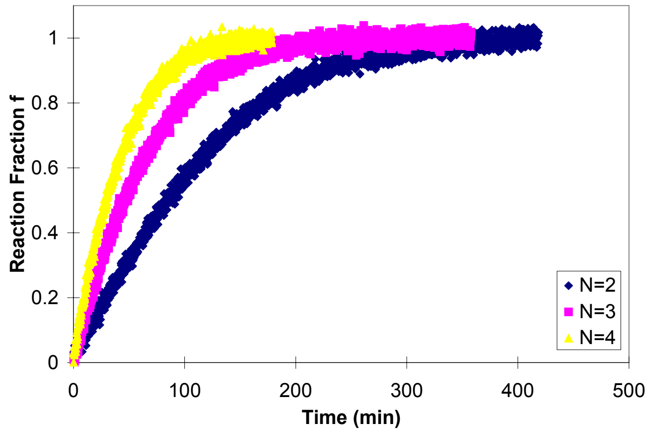
Residual gas analysis of the $LiBH_4/CaH_2/LiNH_2$ System

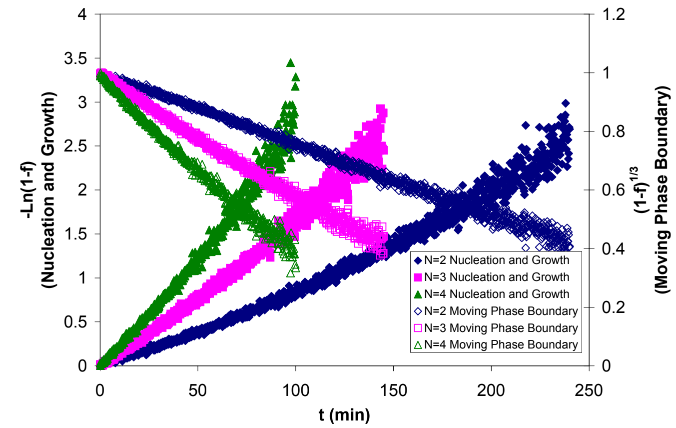


- The analysis shows that about 0.06% of the gas released from the ternary mixture is B_2H_6. There was no detectable amount of NH_3 released.

Accomplishments

Kinetic Modeling Studies on the $NaAlH_4$ system





- Absorption and desorption experiments were done at 160 C for the lower plateau and at various N-values. The results show that a moving phase boundary model is a better fit for the data at various N-values
- The moving boundary model is described according to the equation:

$$(1-f)^{1/3} = 1 - (\frac{k_2}{R})t$$

Future Work

- In the FY 08-09, the following are planned
  - Find a way to make the $LiBH_4/CaH_2/LiNH_2$ system absorb and release hydrogen reversibly
  - Preparation and thermal analysis of the other ternary systems similar to the $LiBH_4/CaH_2/LiNH_2$ system
  - Determine the cyclic stability of complex hydrides
  - Use techniques such as FTIR and NMR to further characterize and understand complex hydrides
  - Improve kinetics and lower reaction temperatures by optimizing hydrogenation catalysts

Project Summary

Relevance: The materials under consideration in this study have the potential to provide the solution to the on board hydrogen storage goals established by the DOE.

Approach: Methods such as ball milling, TGA, TPD, XRD, PCI measurements, kinetics measurements and residual gas analyses were used to synthesize and characterize hydrides.

Technical Accomplishments: Have demonstrated that $LiBH_4/CaH_2$ may be a suitable hydrogen storage material. Have developed a ternary system that has significantly lower reaction temperature. Identified a possible rate controlling process via kinetic modeling.

Proposed Future Research: Studies will be done on a variety of destabilized hydrides including ternary systems, to determine those that meet DOE's hydrogen storage goal and which have suitable kinetics and thermodynamic stability.