Hydrogen Storage Materials for Fuel Cell Powered Vehicles

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Project ID # ST048

Overview

Timeline

- Start – June 1, 2006
- Finish – May 30, 2013
- 50% complete

Budget

- Total project funding
  - DOE $2,417 K
  - DSU $609 K
- Funding received as of FY 09
  - $1,275 K
- Funding for FY10
  - $ 506 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
  - West Chester University

Relevance

- The objectives of this project are to:
- Identify complex hydrides that have the potential to meet DOE's goals for storage and demonstrate the optimum temperature and pressure ranges under a variety of conditions.
- Improve the sorption properties of systems that have been identified as good prospects for hydrogen storage.
- Determine the cyclic stability of new materials and develop strategies for improving reversibility.
- Perform kinetic modeling studies and develop methods for improving kinetics and lowering reaction temperatures, thereby reducing refueling time.
- Extend the studies to include other complex hydrides, that have greater hydrogen storage potential.
- Develop a viable storage system using flow, reaction kinetics and thermal modeling, followed by system design, fabrication and performance evaluation. This will be done in collaboration with the University of Delaware.

Approach

- Task 1 – Design suitable methods using MgH_2 as a model system
  - Synthesis of new materials by mechanical alloying using ball milling
  - Determine thermal stability using TGA or TPD.
  - 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 using constant pressure driving forces
  - Perform modeling to gain understanding of the mechanism

- Task 4 – Study other classes of promising hydrogen storage materials
  - Focus on the $LiBH_4/CaH_2$ system and new classes of destabilized hydride materials such as those based on $Mg(BH_4)_2$.

Approach/Milestones

Year	Milestone or Go/No-Go Decision
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, with a desorption enthalpy of 63 kJ/mol H_2. It was also found that certain ternary mixtures could release hydrogen at significantly lower temperatures but they were not reversible.

Approach/Milestones

Year	Milestone or Go/No-Go Decision
2009	Go/No-Go Decision: We decided not to continue studies on ternary borohydride systems that contain amides. We will continue to focus on other borohydride systems with reaction enthalpies predicted to be less than 50 kJ/mol H_2.
2010	Milestone: It was discovered that some destabilized $Mg(BH_4)_2$-based systems could absorb and release hydrogen reversibly starting at less than 200 ^oC. Studies on pure MgH_2 showed that a mixture of catalysts may be the most effective way to lower temperatures and increase rates.

Technical Accomplishments/ Progress/Results

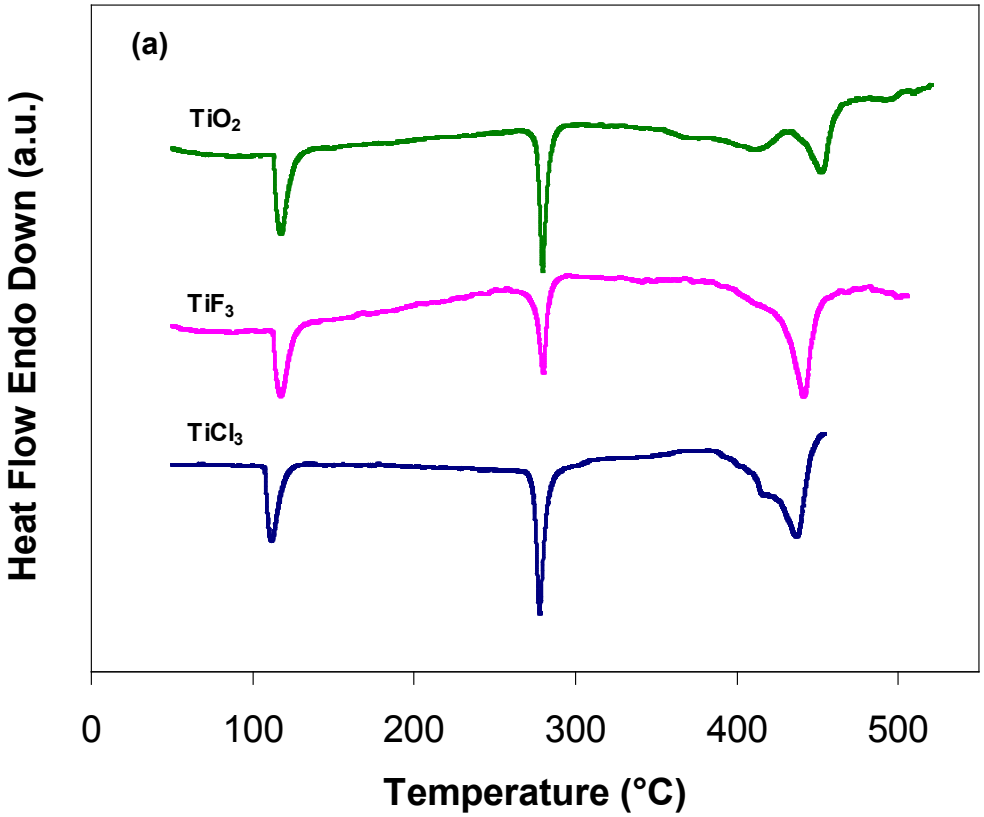
- Last year we reported that the destabilized borohydride system described by the equation:

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

  absorbed hydrogen in a reversible manner. Further studies have been done to determine the effect of various additives on the desorption temperatures and activation energy of this system. The additives studied were $TiCl_3$, TiF_3 and TiO_2. It was found that the $TiCl_3$ additive lowered the dehydrogenation temperature more than the other additives. Furthermore, higher amounts of $TiCl_3$ were more effective in reducing the desorption temperature than lesser amounts. Kissinger plots were used to determine the activation energies of the catalyzed systems. The activations energies for mixtures containing 4, 10 and 25 mol% of $TiCl_3$ were 141, 126 and 110 kJ/mol, respectively. Results are given in the following three figures.

Accomplishments

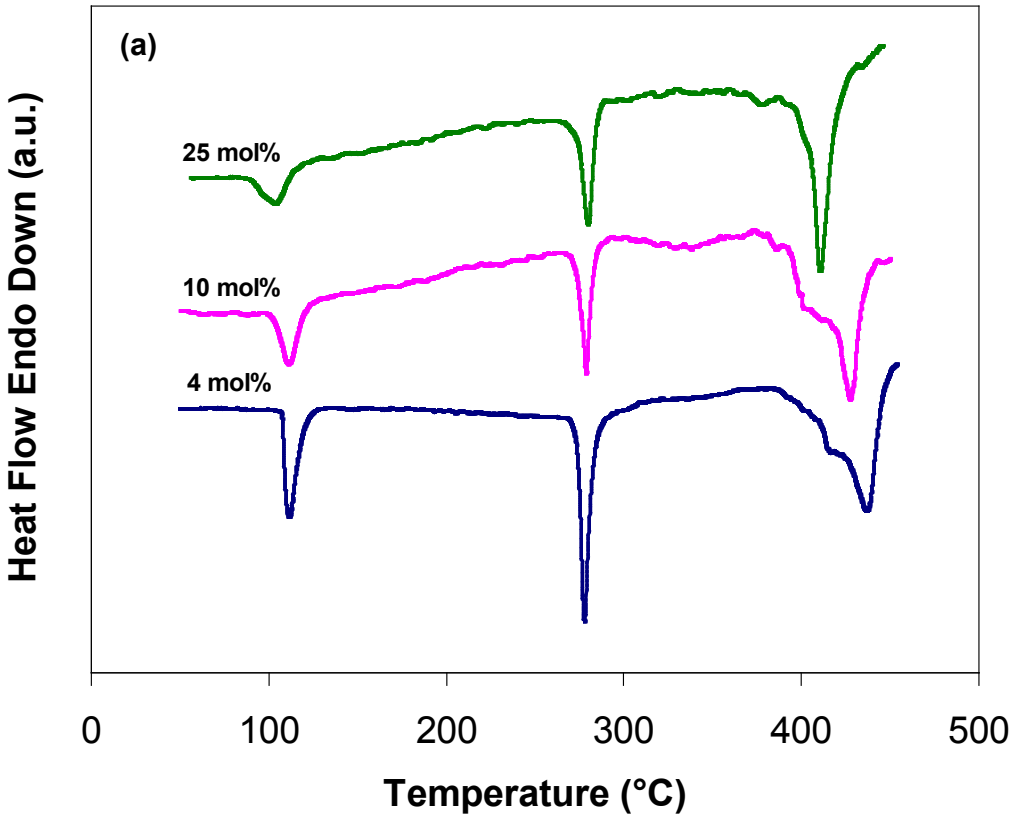
DTA Curves of a $CaH_2/LiBH_4$ Mixture With 4 mol% of Various Additives



- The third peak in each curve corresponds to hydrogen desorption. Desorption temperatures are 454, 442, and 437 °C for TiO_2, TiF_3 and $TiCl_3$, respectively.

Accomplishments

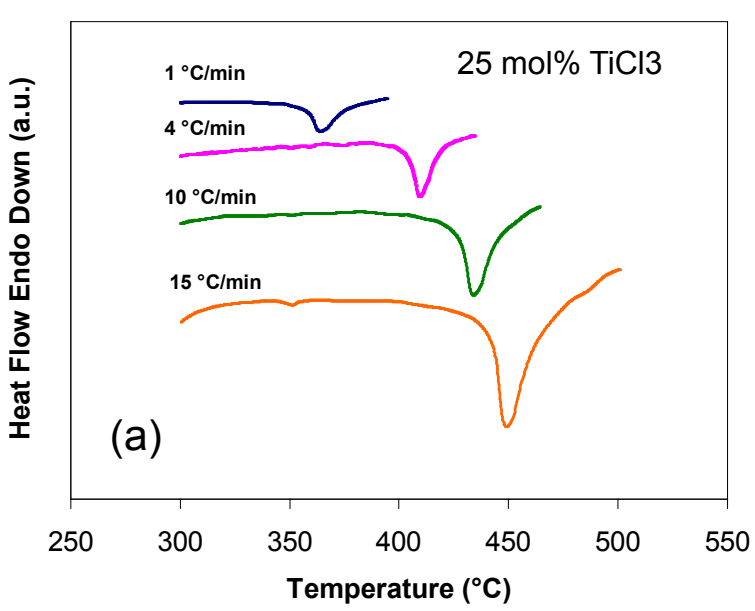
DTA Curves of a CaH_2-$LiBH_4$ Mixture With 4, 10 and 25 mol% $TiCl_3$

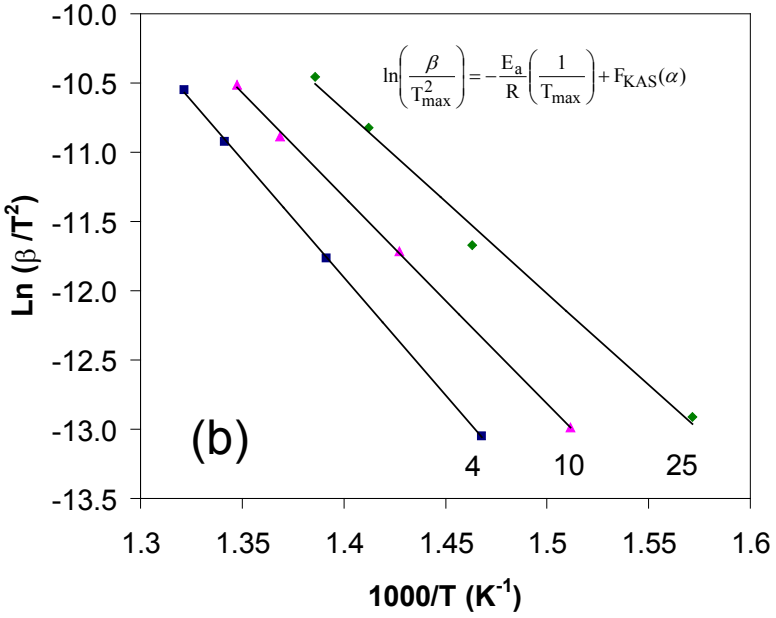


- The third peak in each curve corresponds to hydrogen desorption. The curves show that the desorption temperature decreases with increasing amounts of $TiCl_3$.

Accomplishments

Activation Energy Plots using the Kissinger Equation for the $LiBH_4$/ CaH_2 mixtures with 4, 10 and 25 mol% $TiCl_3$





- DTA scans in figure (a) were run for a mixture containing 25 mol% of $TiCl_3$. The activations energies for mixtures containing 4, 10 and 25 mol% of $TiCl_3$ were calculated to be 141, 126 and 110 kJ/mol, respectively based on the Kissinger plots in figure (b).

Technical Accomplishments/ Progress/Results

- The following six systems based on $Mg(BH_4)_2$ have also been studied to determine their reversibility and thermodynamic behavior:

  $3Mg(BH_4)_2 + CaH_2 + 3NaH \rightarrow 3NaMgH_3 + CaB_6 + 10H_2$

  $3Mg(BH_4)_2 + CaH_2 \rightarrow 3MgH2 + CaB_6 + 10H_2$

  $3Mg(BH_4)_2 + 3Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5\ MgH_2 + 13\ H_2$

  $2Mg(BH_4)_2 + NaH \rightarrow NaMgH_3 + MgB_4 + 7H_2$

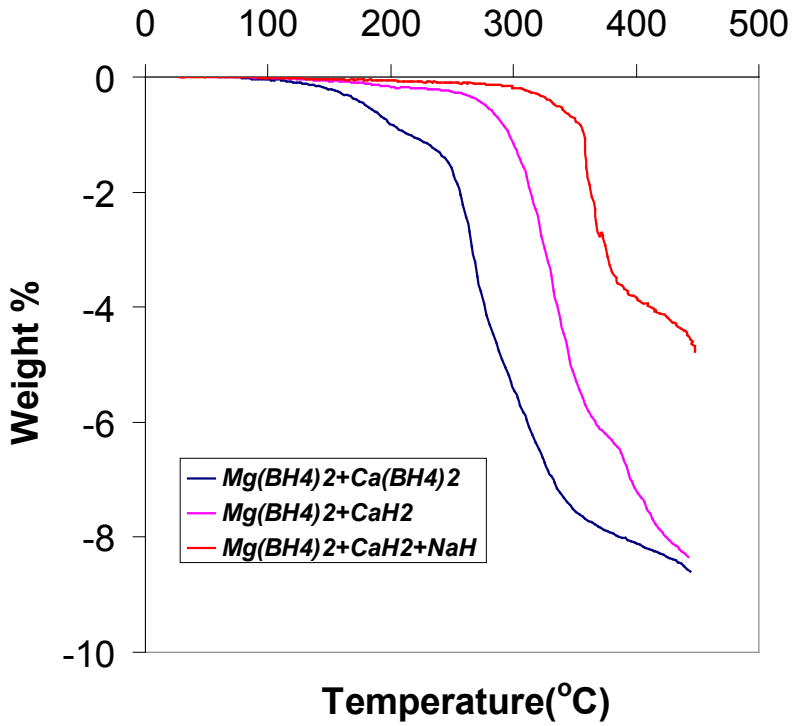
  $3Mg(BH_4)_2 + CaH_2 + 1.5Si \rightarrow CaB_6 + 1.5Mg_2Si + 13H_2$

  $Mg(BH_4)_2 + 2C \rightarrow MgB_2C_2 + 4H_2$

- The systems described in the first three equations are reversible with some releasing as much as 8 wt% hydrogen at temperatures beginning at less than 200 ^oC. The last three reactions did not show any well defined plateau region. Therefore, thermodynamic measurements were done only on the systems described by the first three equations.
- Cycling studies showed that these systems are only partially reversible. The hydrogen-holding capacities diminished to about 2 wt% upon continued cycling.
- Thermodynamic measurements, based on van't Hoff plots showed that the reaction enthalpies were in the 82-88 kJ/mol range.
- Results are given in the following two figures:

Accomplishments

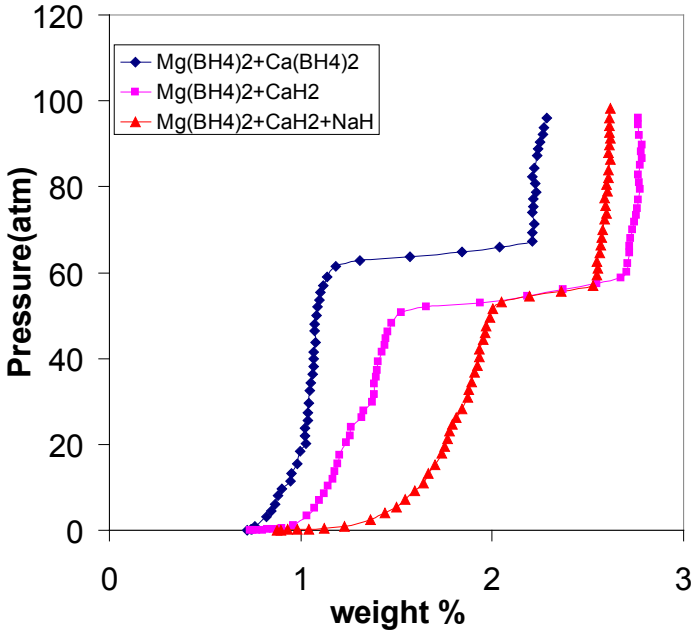
TPD Profiles of the $Mg(BH_4)_2$ Destabilized Systems

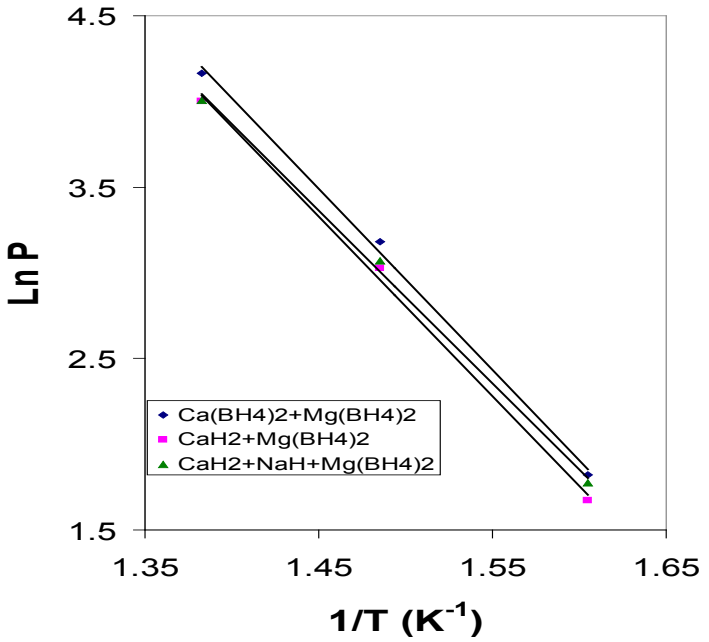


- TPD Profiles were performed in an automated system controlled by Lab View-based software.

Accomplishments

Desorption Isotherms and Van't Hoff Isochores for the $Mg(BH_4)_2$ system with various additives





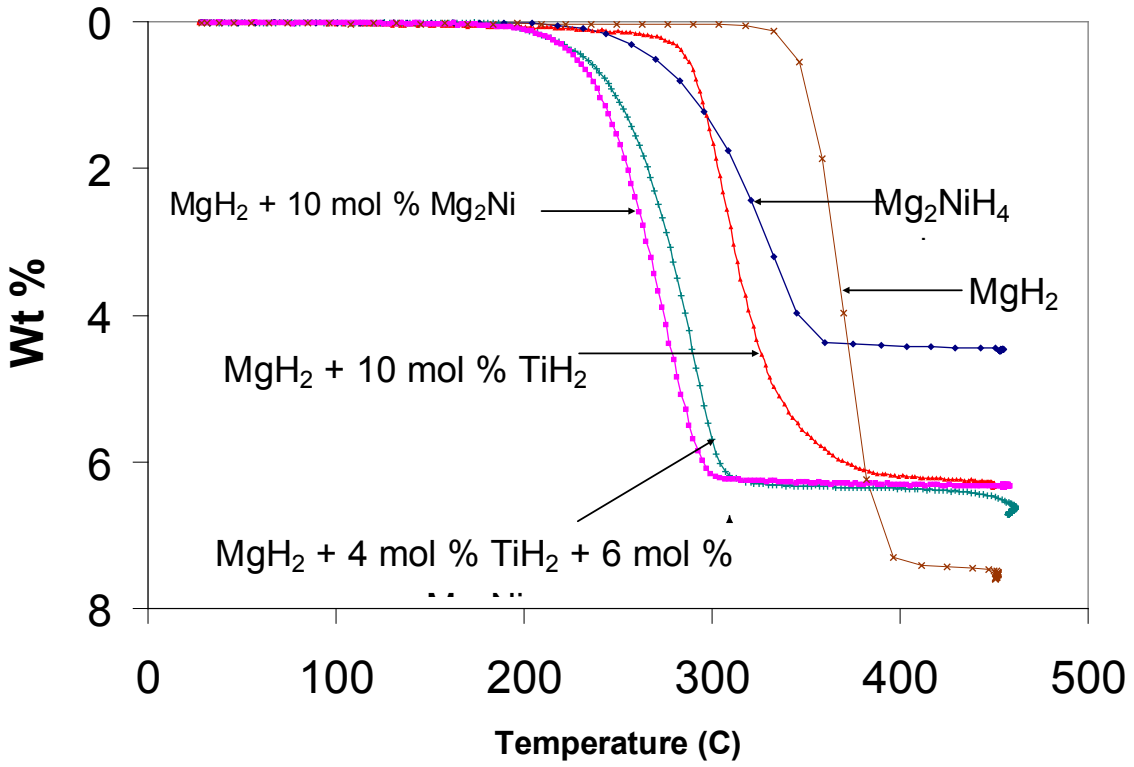
- The isotherms were done at 450 °C. The van't Hoff isochores were obtained from isotherms done at 350, 400, and 450 °C

Technical Accomplishments/ Progress/Results

- Thermodynamics and kinetics measurements were done using MgH_2 as a model system. The goal was to determine what catalysts work best in lowering reaction temperatures and increasing reaction rates. It was found that a mixture of two catalysts was more effective than either catalyst alone. Larger amounts of catalysts were more effective in lowering reaction temperatures but the hydrogen-holding capacity was significantly diminished as the amount of catalyst increased. Results are shown in the following three figures:

Accomplishments

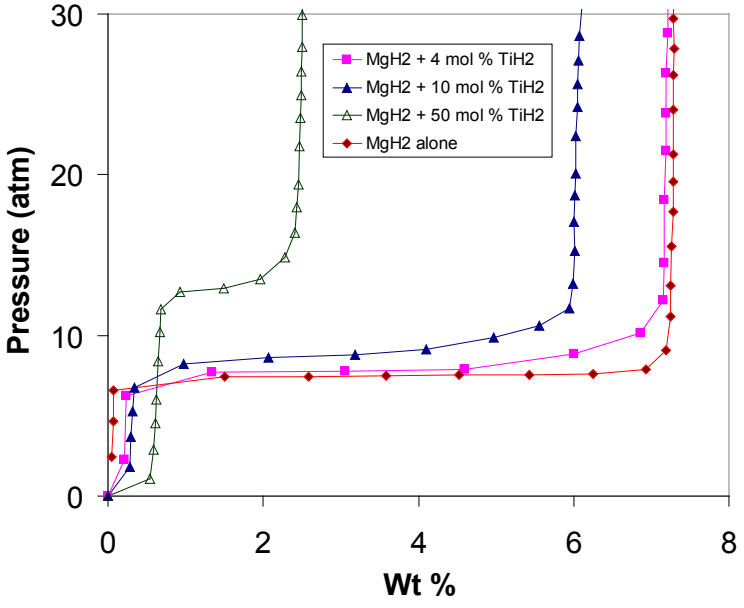
TPD Profiles for MgH_2, Mg_2NiH_4 and several mixtures containing various amounts of TiH_2 and/or Mg_2Ni

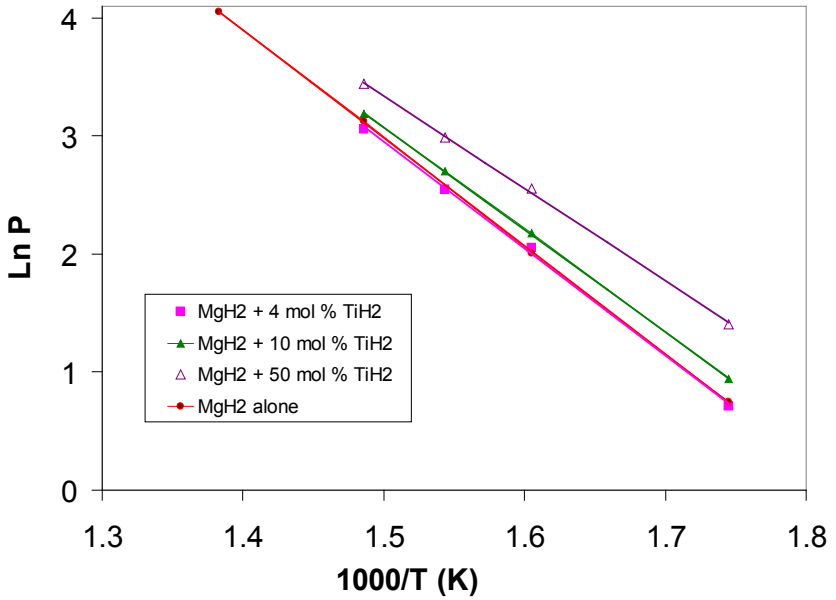


- The curves show that pure MgH_2 has the highest desorption temperature whereas the MgH_2 + 10 mol% Mg_2Ni has the lowest.

Accomplishments

Absorption Isotherms and Van't Hoff Plots for MgH_2 and several TiH_2-MgH_2 Mixtures

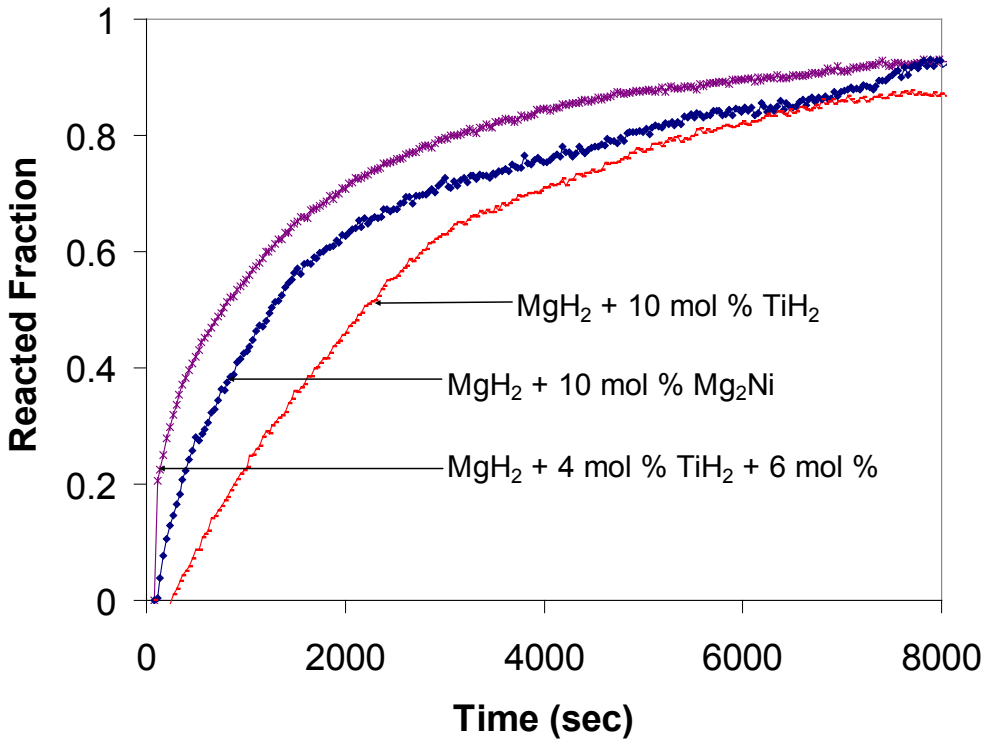




- The PCI curves show that increasing the amount of catalyst increases the plateau pressure and decreases the hydrogen-holding capacity. The slopes of the van't Hoff plots decrease with increasing amounts of catalyst.

Accomplishments

Reaction rate plots for mixtures containing 90 Mol% MgH_2 and 10 mol% TiH_2, Mg_2Ni or both



- The curves show that the mixture containing 10 mol% TiH_2 reacts the slowest whereas the one with the mixed catalyst reacts the fastest.

Collaborations

- Collaborators
  - Theoreticians Karl Johnson and David Scholl, from the University of Pittsburgh and Georgia Tech, respectively have been very useful in helping us choose what destabilized systems to focus on.
  - The University of Delaware and Air Liquide: Suresh Advani's group is working with us in an effort to determine the feasibility of testing some hydrogen storage materials in an actual hydrogen powered vehicle.
  - At West Chester University, Melissa Cichowicz is helping to synthesize and characterize some of the hydrogen storage materials of interest.

Future Work

- In the FY 10-11, the following are planned
  - Prepare and characterize several $Mg(BH_4)_2$ based destabilized systems using ball milling, XRD, TPD and TGA.
  - Perform thermodynamic measurements, such as PCI analyses, on destabilized systems found to be reversible.
  - Perform kinetics and modeling studies on the destabilized systems at constant pressure driving forces in order to establish the rate-controlling process.
  - Use techniques such as RGA to determine if dehydrogenation is accompanied by the release of other gaseous byproducts.
  - Use various catalysts and combinations of catalysts to lower reaction temperatures and increase reaction rates. MgH_2 will be used as a model system in these efforts.

Project Summary

Relevance:	The materials under consideration in this study have the potential to meet the on board hydrogen storage goals established by the DOE. Issues such as reaction temperatures, reaction rates and reversibility are being addressed since they are important in practical uses.
Approach:	Destabilized borohydrides based on $Mg(BH_4)_2$ were prepared by mechanical alloying and characterized by TGA, TPD and PCI analyses in order to compare their hydrogen sorption characteristics and determine their suitability for hydrogen storage.
Technical Accomplishments:	We have determined that several destabilized borohydride systems based on $Mg(BH_4)_2$ can absorb hydrogen reversibly starting at temperatures less than 200 ^oC. We have also determined that mixed catalysts are most effective in catalyzing the MgH_2 system and they may be effective for destabilized systems as well.
Proposed Future Research:	Kinetics at constant pressure driving forces will be done on several destabilized hydride systems that are predicted to absorb greater than 6 weight percent H_2 and have reaction enthalpies less than 50 kJ/mol H_2.