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Hydrogen Storage Materials for Fuel Cell Powered Vehicles

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May 15, 2013

Project ID # ST048

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start – July 1, 2006
  – Renewed– June 1, 2009
- Finish – May 30, 2013
- 90% complete

Budget

- Total project funding
  - DOE $2,417 K
  - DSU $609K
- Congressionally Funded Project, Appropriations Received in FY06 and FY09

Barriers

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

Partners

- Interactions/ collaborations
  - Cal Tech
  - Georgia Tech
  - University of Pittsburgh
  - University of Delaware

Relevance

- The objectives of this project are to:
- Identify complex hydrides that have the potential to meet DOE's goals for onboard 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 metal organic frameworks, MOFs, which also have potential for hydrogen storage.
- Improve the rate at which the hydrogen gas can be charged into a hydride-based hydrogen storage tank, and to improve the hydrogen storage density. This is being done in collaboration with the University of Delaware.

Rubidium Hydride – An Exceptional Dehydrogenation Catalytic Additive for the $LiNH_2/MgH_2$ System

Desorption reaction in the $2LiNH_2/MgH_2$ system:

$$MgH_2 + 2LiNH_2 \rightarrow Mg(NH)_2 + 2LiH \qquad (1)$$

$$Mg(NH)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \qquad (2)$$

RbH is the most effective catalyst to date for enhancing the kinetics of this system. Modeling studies have provided a plausible explanation for the improved kinetics.

Approach

- Task 1 – Design suitable methods for analysis
  - Synthesis of mixtures using mechanical alloying
  - 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
  - Use reactive ball milling to synthesize new catalyst, RbH

- Task 3 - Kinetic modeling study
  - Determine kinetic rate curves using constant pressure driving forces
  - Perform modeling to gain understanding of the mechanism

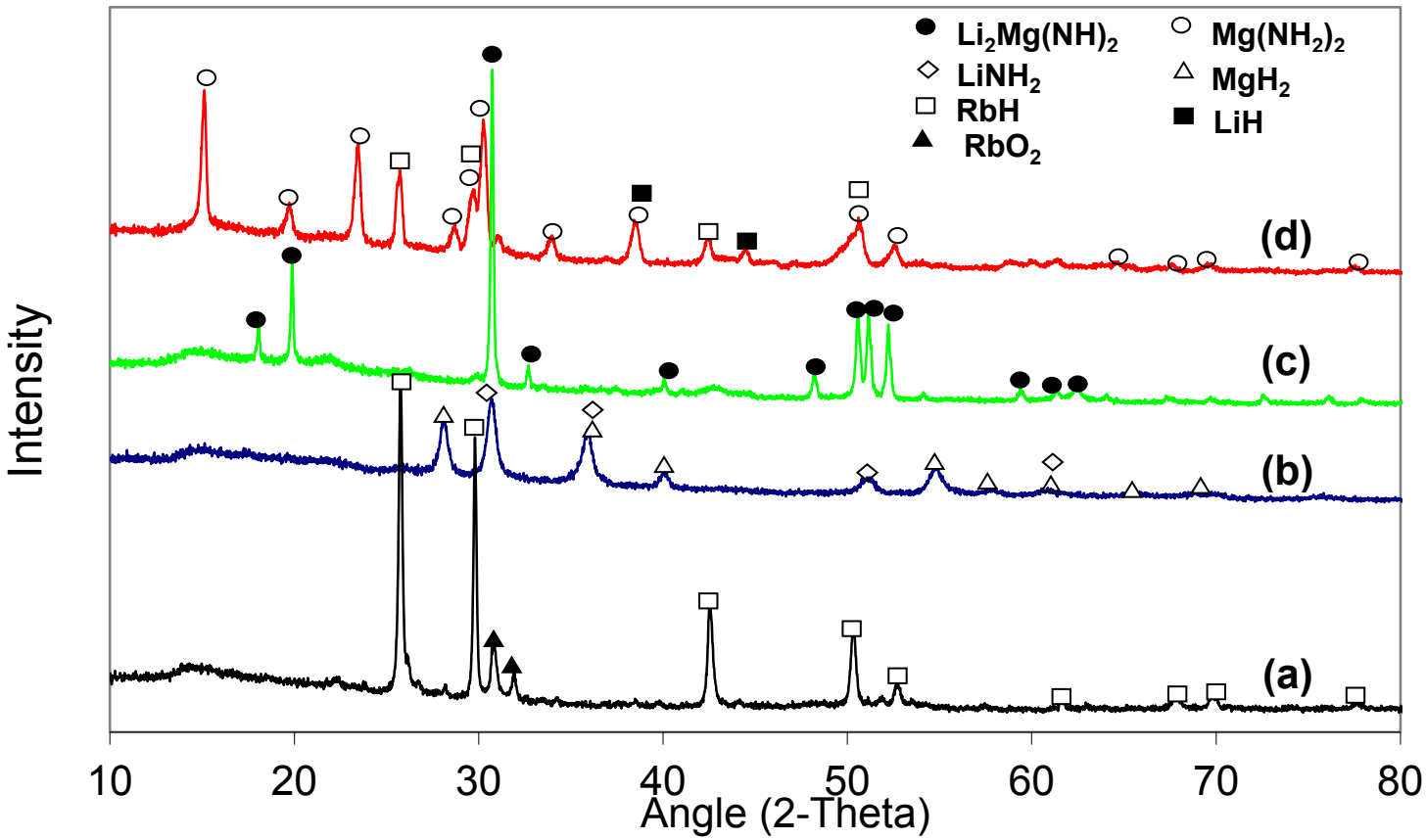
- Task 4 – Study other classes of promising hydrogen storage materials
  - Synthesize MOFs and characterize them using techniques such as BET, XRD and TGA

Technical Accomplishments/ Progress/Results

Hydrogen desorption from a $MgH_2/LiNH_2$ system

- Have developed a reactive ball milling method for synthesizing RbH, a new catalyst for the $MgH_2/LiNH_2$ system. Mixtures with an initial molar composition of ($2LiNH_2 + MgH_2$) were studied with and without the presence of 3.3 mol% RbH and KH dopants.
- XRD analyses showed that the KH catalyst appears in the dehydrogenated pattern along with $Li_2Mg(NH)_2$ but the RbH does not. This is due to the low decomposition temperature of RbH.
- TPD analyses showed that the RbH and KH doped samples had about the same onset temperature. Both of these catalyzed mixtures desorbed hydrogen about 90 degrees lower than the un-catalyzed mixture.
- PCT isotherms were constructed for the catalyzed and un catalyzed mixtures. Desorption enthalpies, determined from van't Hoff plots, showed that the enthalpies for the catalyzed mixtures were both ~42 kJ/mol whereas the enthalpy for the un-catalyzed mixture was 65 kJ/mol.
- The dehydrogenation kinetics of the doped and un-catalyzed mixtures was compared at 210°C. In each case a constant pressure thermodynamic driving force was applied in which the ratio of the plateau pressure to the applied hydrogen pressure was set at 10. This ratio has been designated as the N-Value. Under these conditions, the RbH doped mixture desorbed hydrogen about twice as fast as the KH doped mixture and about 60 times faster than the un-doped mixture.
- Modeling studies were done using two different methods. Both methods showed that diffusion is the rate-controlling process. The faster kinetics of the RbH doped mixture can be explained, in part, based on the fact that the larger atomic size of Rb expands the lattice and allows for faster diffusion than that in the KH doped sample.
- Results of these studies are presented in the following eight slides.

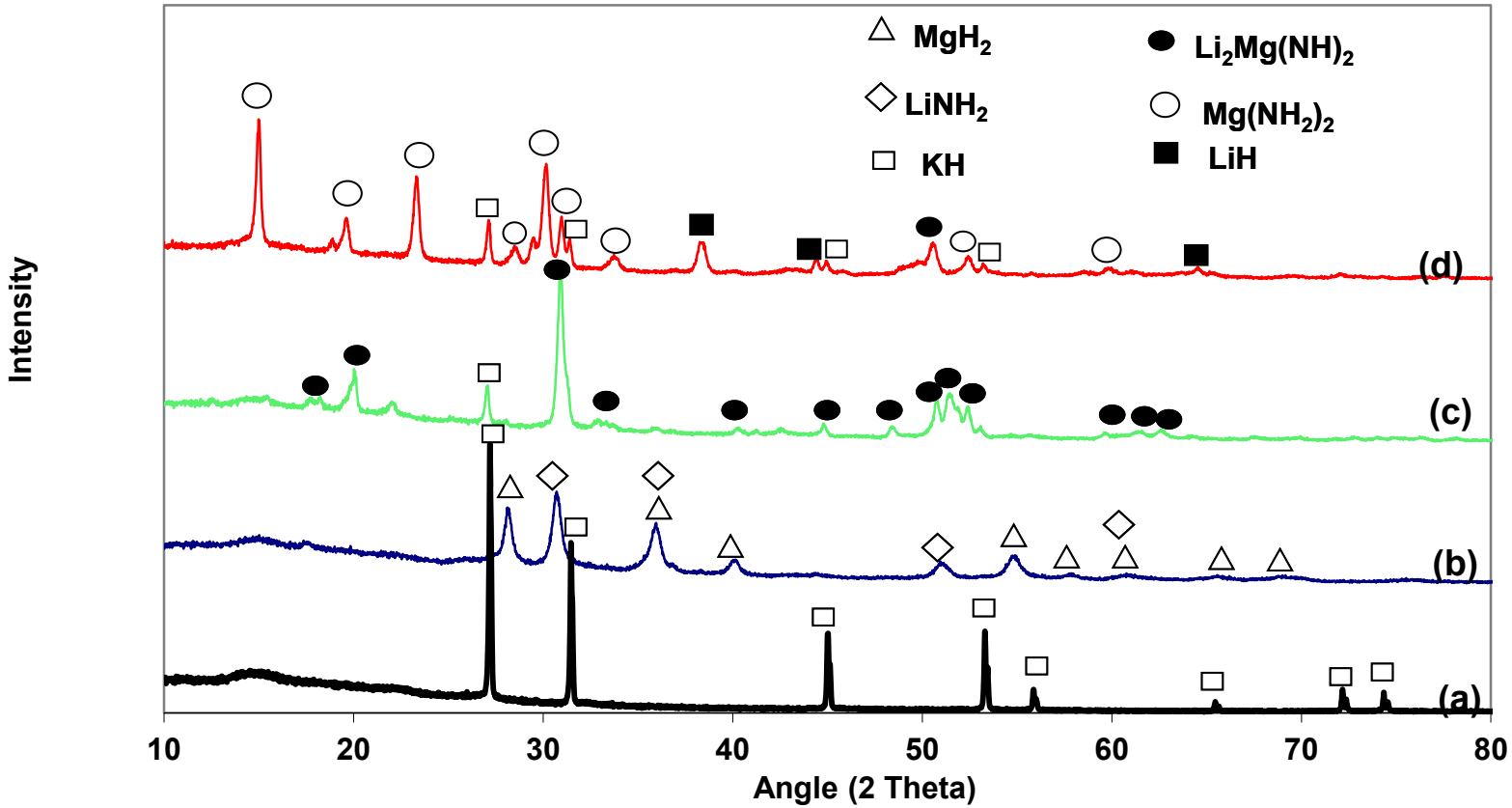
XRD Patterns for the $LiNH_2/MgH_2$ System Catalyzed by RbH



(a) Is the pattern for the RbH catalyst, (b) is the as-milled sample, (c) is the dehydrided mixture and (d) is the re-hydrided mixture.

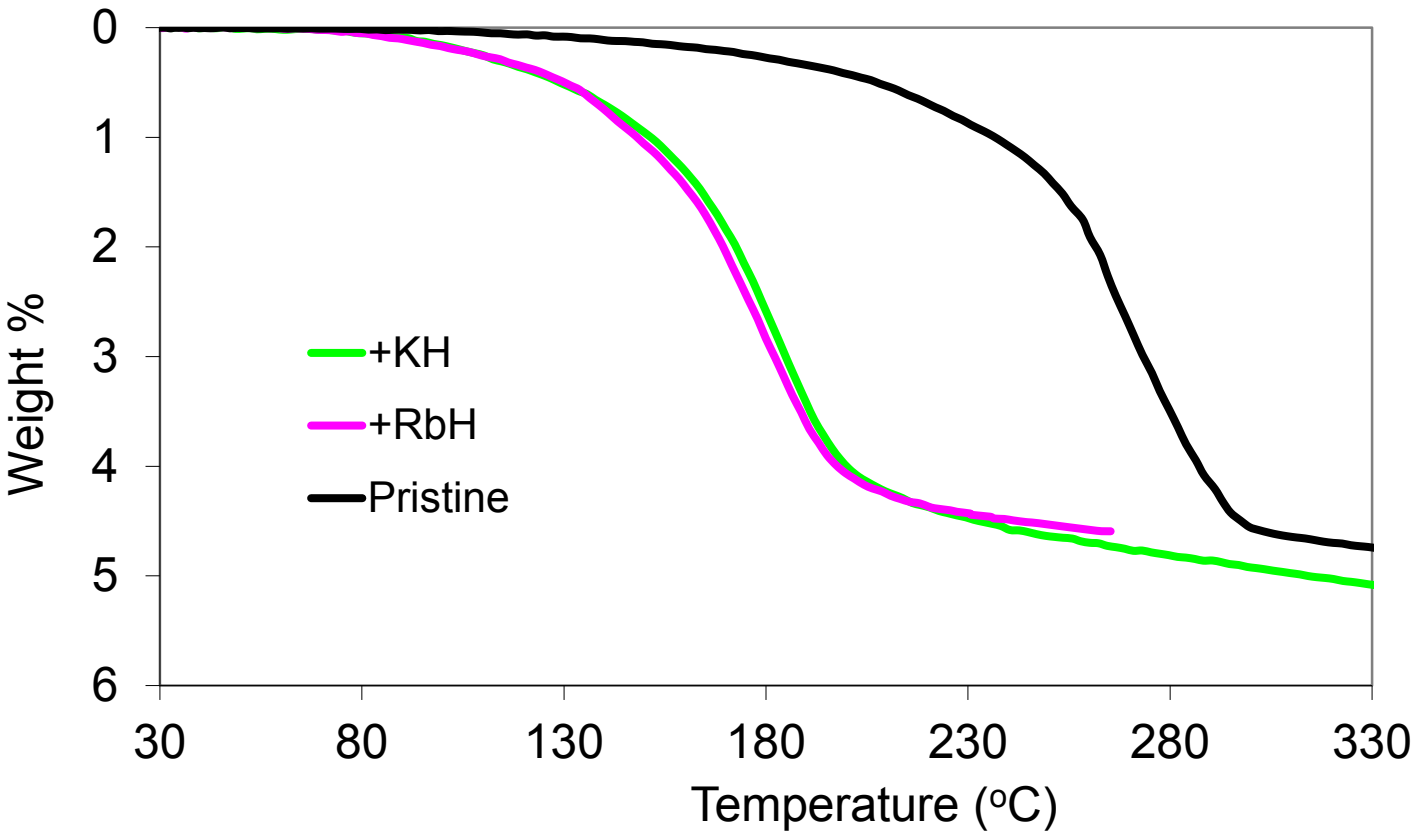
- Since the rehydrided pattern contains peaks for ($Mg(NH_2)_2$ + LiH), as indicated in Equation 2 (slide 4) along with peaks for the RbH catalyst, this confirms that the reaction in Equation 2 occurs reversibly.
- Since RbH was reformed this indicates that it was not consumed during the reaction and that it is truly behaving as a catalyst.

XRD Patterns for the $LiNH_2/MgH_2$ System Catalyzed by KH



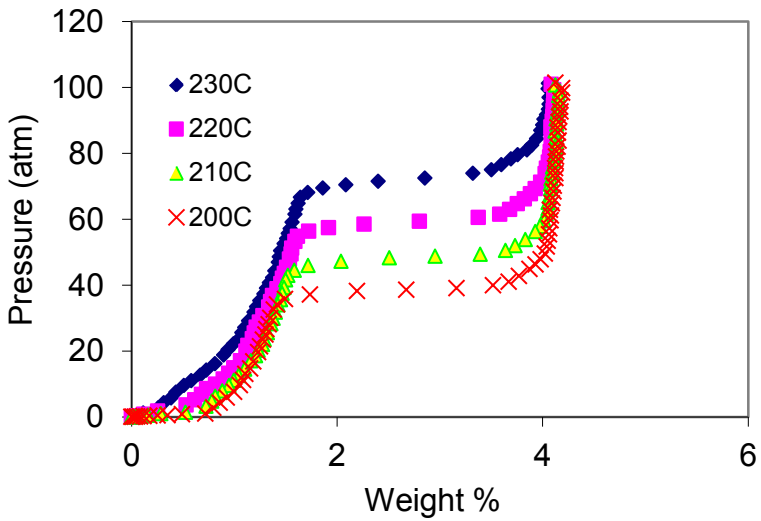
(a) Is the pattern for the KH catalyst, (b) is the as-milled sample, (c) is the dehydrided mixture and (d) is the re-hydrided mixture. The behavior is similar to that which was observed in slide 7 for the RbH catalyzed system.

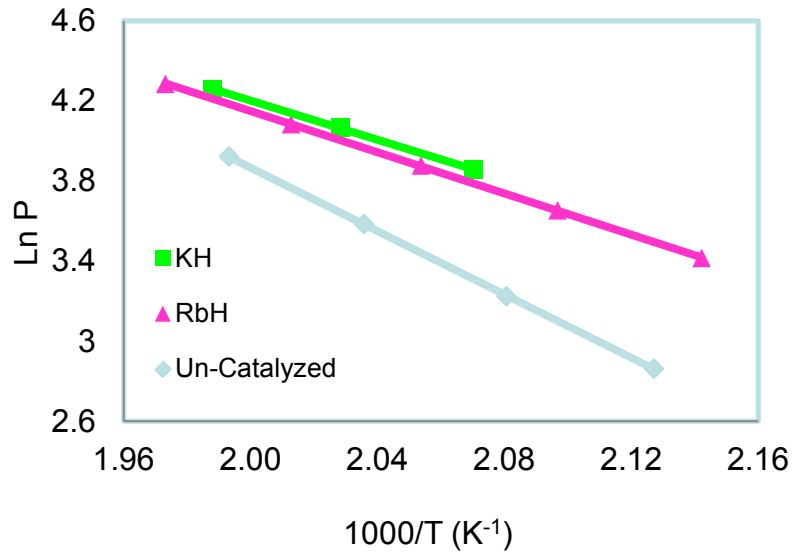
TPD Curves for the $LiNH_2/MgH_2$ System



The mixtures doped with "catalytic additives" desorb H_2 at ~90 °C lower than the un-catalyzed (pristine) mixture. Catalytic additives can affect both the thermodynamics and kinetics. Scans were done at 4 °C per minute.

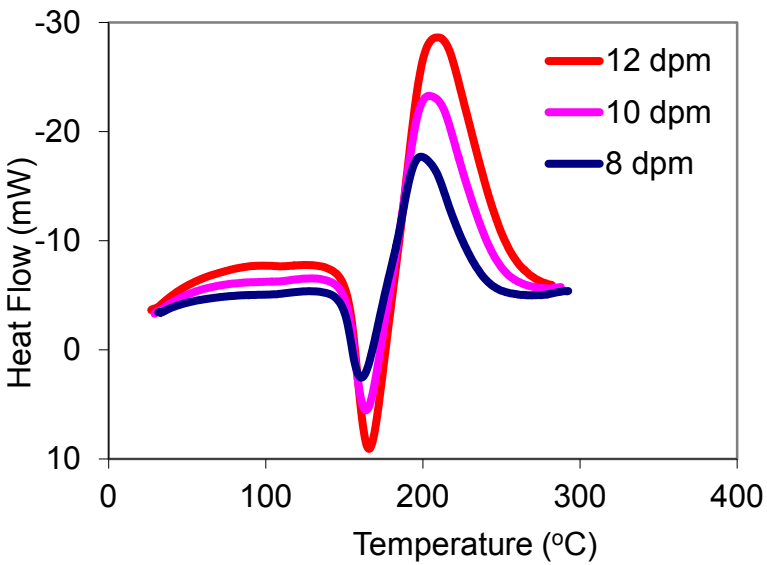
Thermodynamics for the $LiNH_2/MgH_2$ System

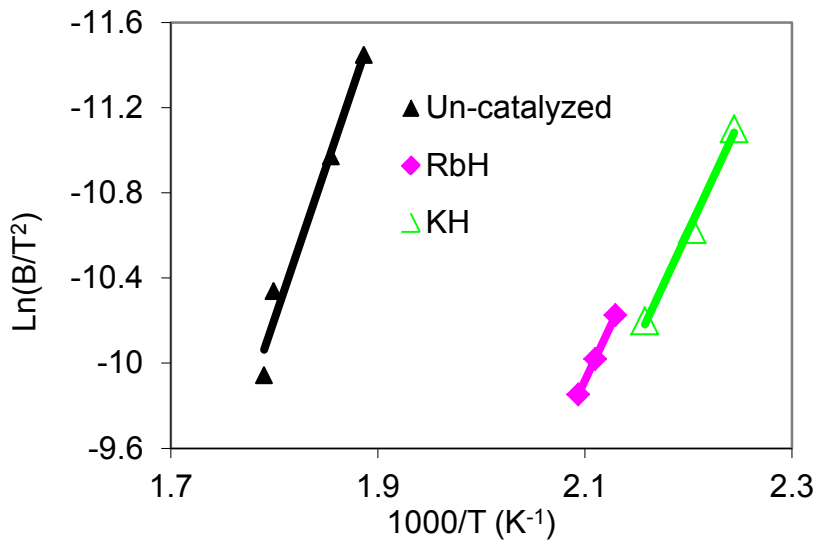




- The graph on the left contains PCT isotherms for $2LiNH_2/MgH_2$ doped with RbH. The graph on the right contains van't Hoff plots for $2LiNH_2/MgH_2$ doped and un-catalyzed mixtures. The desorption enthalpies for the catalyzed mixtures are ~42 kJ/mol whereas the enthalpy for the un-catalyzed mixture is 65 kJ/mol. These findings are consistent with the results of the TPD profiles.

Kissinger Plots for the $LiNH_2/MgH_2$ System

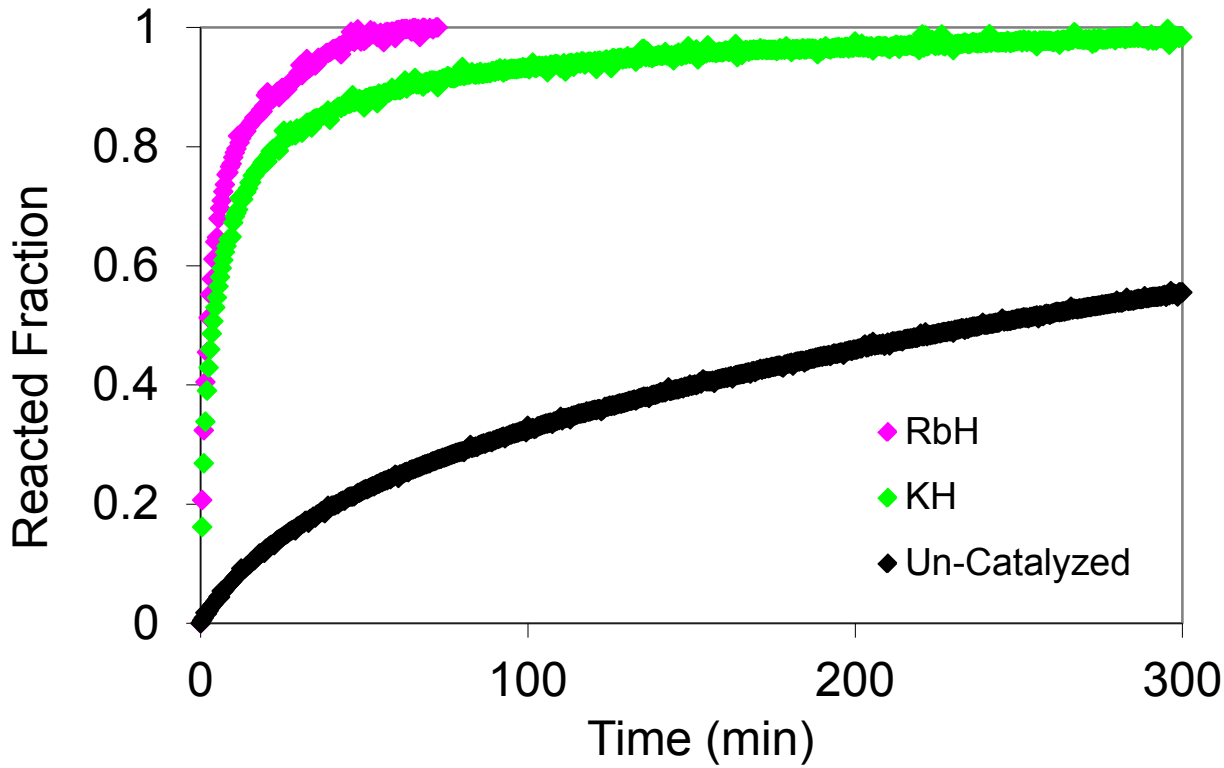




- The Differential Thermal Analysis (DTA) plots, shown on the left, for the RbH doped $LiNH_2/MgH_2$ mixture show that as the scan rate increases the desorption peak moves to higher temperatures. The Kissinger plots on the right were used to determine the activation energies for the various mixtures. Activation energies for the catalyzed samples were both ~87 kJ/mol whereas the activation energy for the un-catalyzed mixture was 119 kJ/mol.

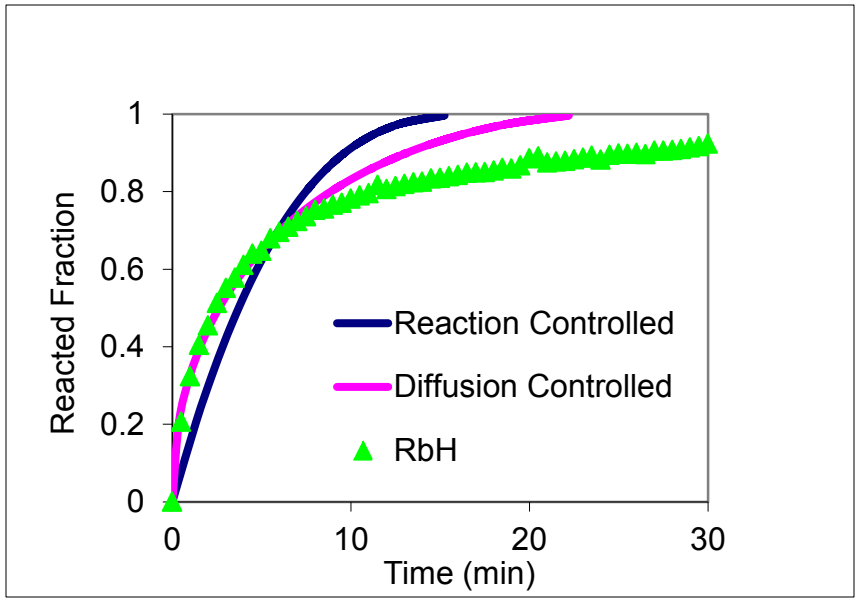
$$\ln\left(\frac{\beta}{T_{max}^2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_{max}}\right) + F_{KAS}(\alpha)$$

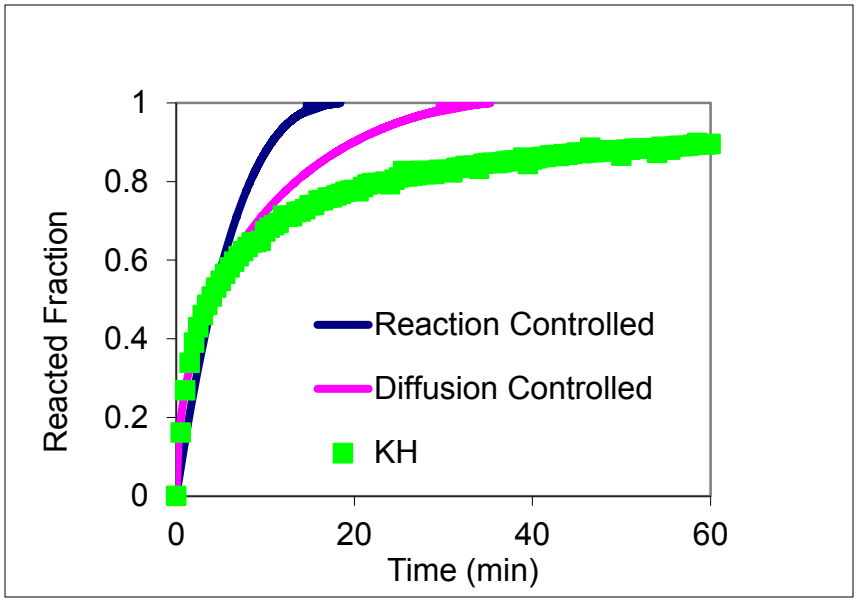
Kinetics Plots for the $LiNH_2/MgH_2$ System



Kinetics were done in the two-phase region. Results show that the RbH catalyzed mixture desorbs H_2 approximately twice as fast as the KH catalyzed mixture and 60 times faster than the un-catalyzed mixture. Measurements were done at 210 ^{o}C and N = 10 (where N = plateau press/applied press).

Kinetic Modeling for the $LiNH_2/MgH_2$ System



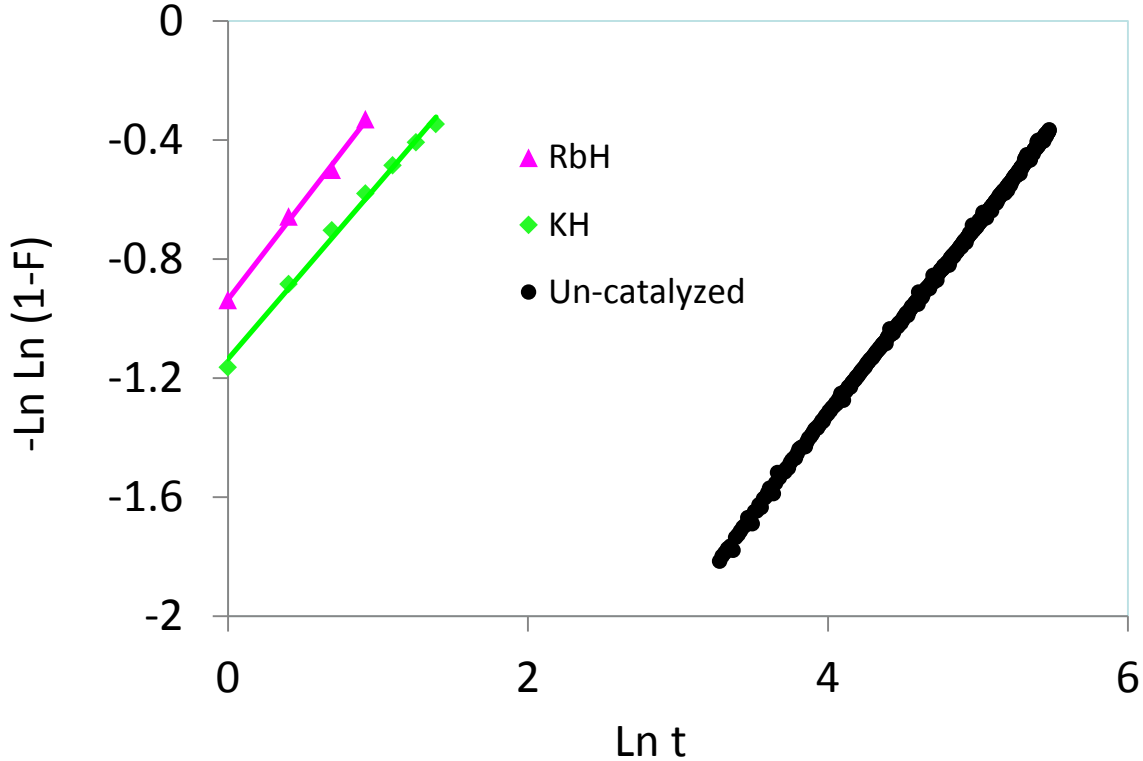


- The modeling plots were based on a shrinking core model in which reaction at the phase boundary or diffusion could control reaction rates. Results show that diffusion controls the rates up to ~70% reaction. This corresponds to the two-phase region.

$$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$$ Phase boundary controlled

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$$ Diffusion controlled

Kinetic Modeling for the $LiNH_2/MgH_2$ System



Modeling was done using the method of Hancock and Sharp. In this model, the slope of the lines, designated as 'm', in the plots shown above were used to determine the rate-controlling process. The slopes were all in the 0.5-0.65 range, which denotes diffusion controlled, based on this model. Values of 'm' are tabulated in Table 1.

Table 1 Summary of desorption parameters for thermodynamics and kinetics results

	KH	RbH	Un-catalyzed
Onset Temp. (^oC)	75	76	109
Desop. Temp., T_d, (^oC)	146	143	237
Desop. ΔH (kJ/mol)	42.0	42.7	65.8
T_{90} (min)	62	27	1600
E_a (kJ/mol)	87.0	86.8	119.0
P_m at 210 ^oC (atm)	46.1	48.3	34.2
'm' values	0.587	0.652	0.647

- The results indicate that both KH and RbH decrease E_a and ΔH.
- Thus they are behaving as more than just catalysts, they are "catalytic additives" capable of affecting the kinetics and thermodynamics.
- RbH is more effective than KH at increasing reaction rates possibly due to the fact that its larger size expands the lattice allowing for faster diffusion rates.

Technical Accomplishments/ Progress/Results

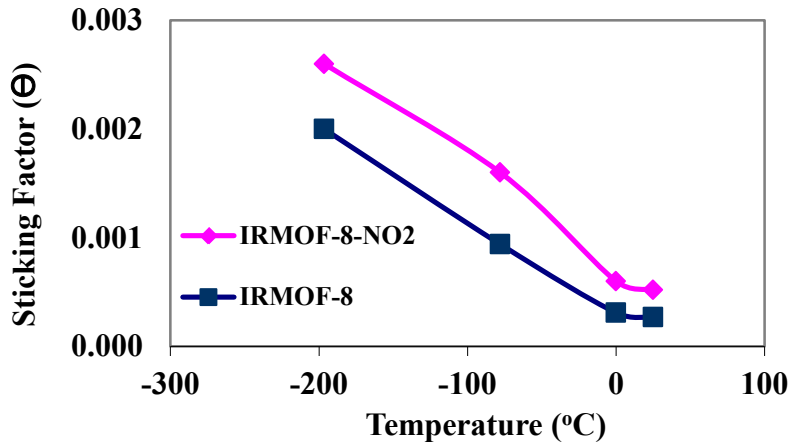
Hydrogen storage in Metal Organic Frameworks

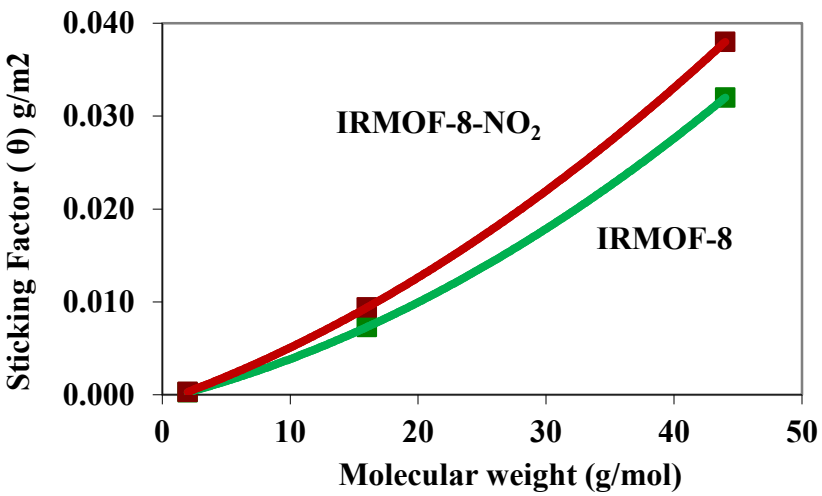
- Have developed a rapid solvothermal method for synthesizing IRMOF-8.
- Have functionalized IRMOF-8 by adding $–NO_2$ groups to the linker.
- Functionalization decreased the surface area and decreases the amount of gas adsorption. However functionalization increased the enthalpy for adsorption of H_2, CH_4 and CO_2 on IRMOF-8.
- Sticking efficiencies of the various gases were increased as a result of NO_2 functionalization. Sticking efficiencies were determined based on a newly developed parameter called the sticking factor (θ).
- Results showed that θ increases with ΔH and molecular weight. Also θ decreases with increasing temperature.
- Results are given in the following two slides.

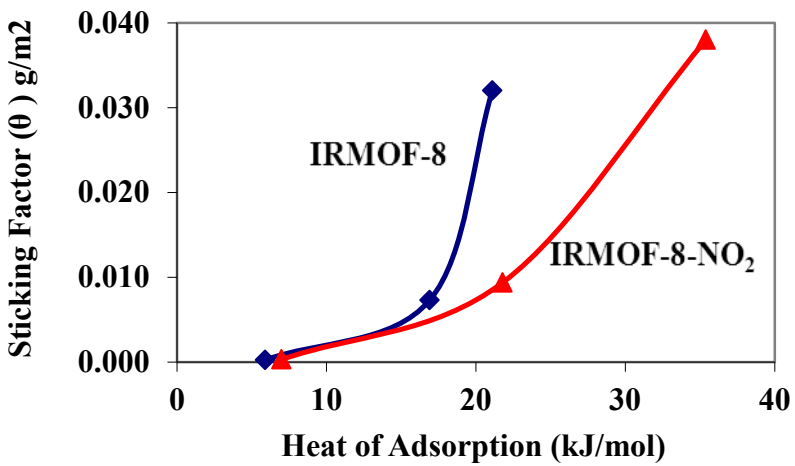
Sticking Efficiencies and Adsorption Enthalpies for MOFs

$$\theta = \frac{\%\ \textbf{Hydrogen}\ \textit{Adsorbed}}{\textbf{Surface Area}\ (\frac{m^2}{g})}$$

- Sticking factors (θ) were calculated from the above equation.
- The graph on the top right shows sticking factor vs. temperature for H_2 on the MOFs.
- The graph on the bottom left is θ vs. molecular weight of H_2, CH_4, or CO_2 for the MOFs.
- The graph on the bottom right is θ vs. ΔH of H_2, CH_4, or CO_2 for the MOFs.







Physisorption Properties of IRMOF-8-NO_2 and IRMOF-8

PROPERTIES	IRMOF-8-NO_2 @120 °C	IRMOF-8 @155°C
Surface area (m^2/g)	832	1600
H_2 Wt. % (at 298 K)	0.43	0.43
H_2 ΔH (kJ/mol)	6.6	6.0
H_2 Sticking Factor	0.00052	0.00027
CH_4 Wt. % (at 298K)	7.8	11.7
CH_4 ΔH (kJ/mol)	21.8	16.9
CH_4 Sticking Factor	0.0094	0.0073
CO_2 Wt. % (at 298K)	31.3	51.2
CO_2 ΔH (kJ/mol)	35.4	21.1
CO_2 Sticking Factor	0.038	0.032

- The results show that nitro-functionalization of IRMOF-8 decreases its surface area which generally results in a reduction of the gas sorption (i.e. wt. %) capability.
- However, the adsorption enthalpies and sticking factors are increased, which indicates that nitro-functionalization increases the forces of attraction between the adsorbent and adsorbate.

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.
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.

Approach/Milestones

Year	Milestone or Go/No-Go Decision
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.
2011	Milestone: It was demonstrated that a KH catalyst could dramatically improve the kinetics of a MgH_2-$LiNH_2$ system.
2012	Milestone: It was demonstrated that a NbF_5 catalyst could dramatically improve the kinetics of a MgH_2-$LiBH_4$ system.
2013	Go/No-Go Decision: We decided not to continue studies based on systems with borohydrides as the primary component. Milestone: It was demonstrated that a RbH catalyst was more effective in improving the kinetics of a MgH_2-$LiNH_2$ system than KH.

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. These theoreticians have indicated that funding for these studies has ended.
  - Son-Jong Hwang, at Cal Tech, has performing solid state NMR measurements on several borohydride materials to determine the composition of the products and the nature of any reaction intermediates.
  - The University of Delaware: Suresh Advani's and Ajay Prasad are working with us in an effort to determine the feasibility of testing some hydrogen storage materials in an actual hydrogen storage containment system.
  - Terry Udovic at NIST and I have made plans to perform neutron scattering studies on some catalyzed $2LiNH_2/MgH_2$ mixtures.

Future Work

- In the FY 13-14, the following work is planned:
  - Continue to perform kinetics and modeling studies on the $MgH_2/LiNH_2$ system based destabilized systems using our newly developed RbH catalytic additive. We will focus on absorption studies, including modeling work, since most of the work to date has been on desorption kinetics.
  - Continue the cycling studies on the RbH catalyzed $MgH_2/LiNH_2$ system .
  - Use techniques such as RGA to determine if dehydrogenation is accompanied by the release of other gaseous byproducts such as ammonia.
  - Continue to collaborate with Sonjong Hwang at Cal Tech in solid state NMR analyses of reaction intermediates in hydriding/de-hydriding reactions.
  - Continue to study the effect of functionalization on MOFs. The goal is to increase ΔH for gas adsorption and thus increase the desorption temperatures.
  - Continue with the design, fabrication and demonstration of a Hydride-Based Hydrogen Storage System that is on-going with our collaborators at the University of Delaware.

Project Summary

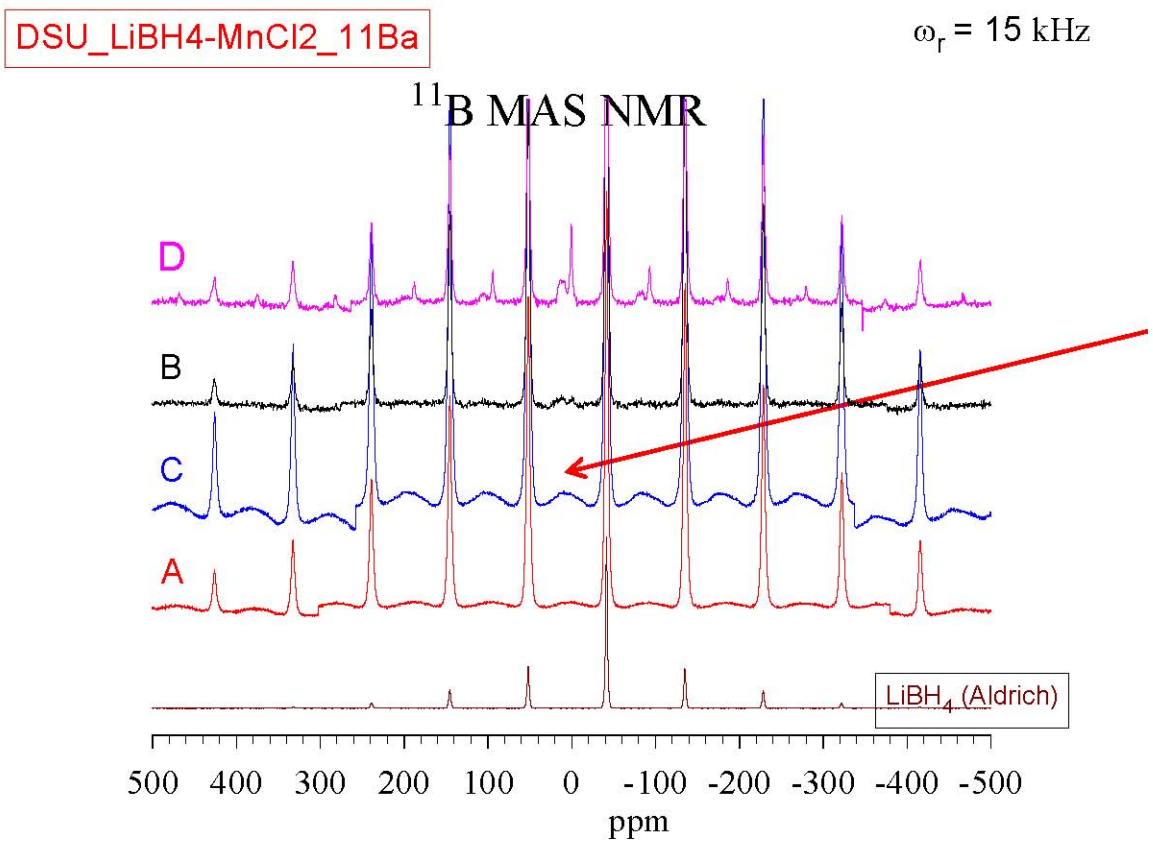
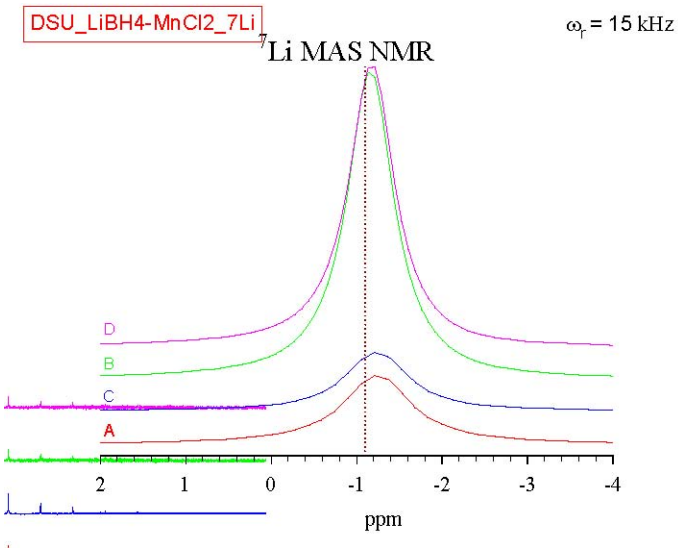
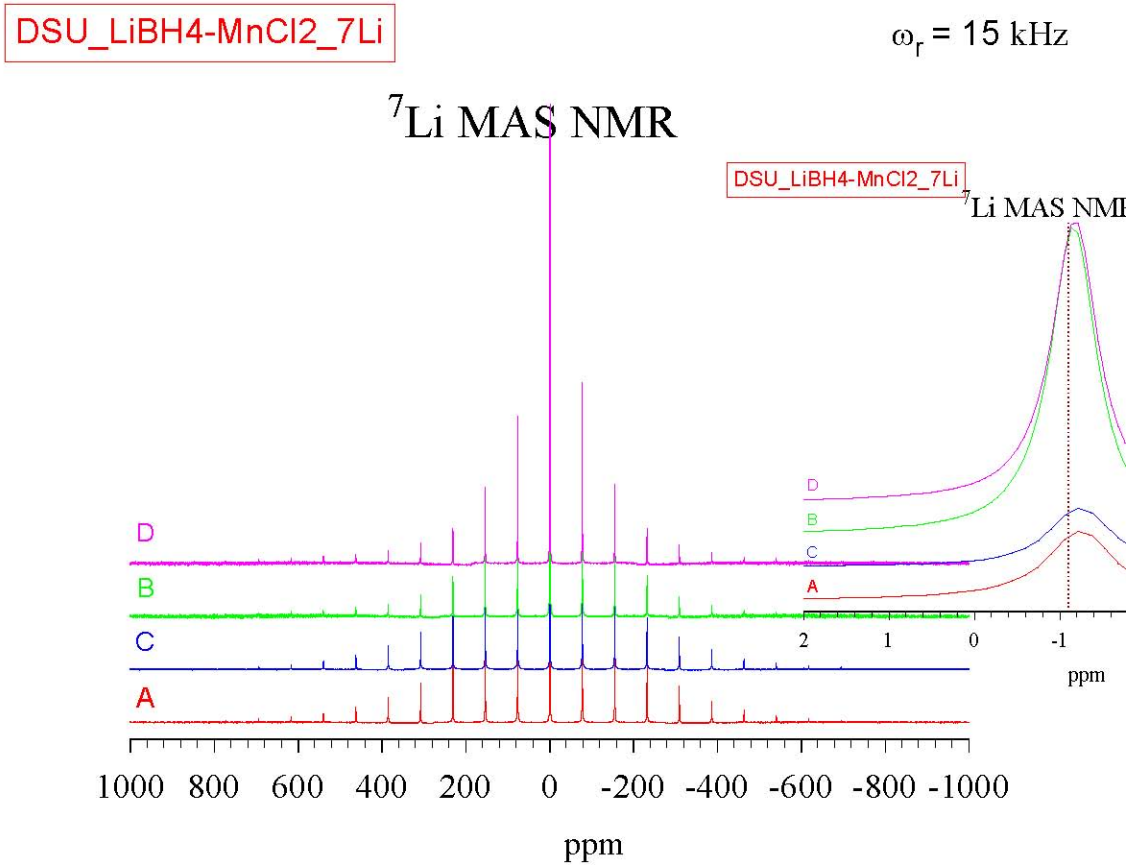
Relevance:	The materials under consideration in this study have the potential to meet the on board hydrogen storage goals established by the DOE. Issues such as reaction temperatures, reaction rates and reversibility are being addressed since they are important in practical uses.
Approach:	A RbH catalytic additive was prepared by reactive ball milling under a hydrogen atmosphere. The effect of this additive on the dehydriding kinetics and mechanism of a $MgH_2/LiNH_2$ system determined at constant pressure driving forces.
Technical Accomplishments:	We have fabricated a RbH catalytic additive that is twice as good as the KH additive in improving the dehydriding kinetics of the $LiNH_2/MgH_2$ system. We have also demonstrated that nitro-functionalization of IRMOF-8 improves gas sticking efficiencies and increases adsorption enthalpy.
Proposed Future Research:	Perform absorption/desorption kinetics and modeling studies on several $MgH_2/LiNH_2$ based destabilized systems. Continue with MOF studies to increase sticking efficiencies and binding strength of gases on surfaces.

Additional Slides

Example of Solid State NMR done by CalTech

It is certain that a broad resonance centered at ~1200 ppm is present. It is not clear at the moment if the peak could be assigned to be $Mn(BH_4)_2$ or related species. Nonetheless, its fraction overall is not sizable.
Analyses were done by Sonjong Hwang

Since $Mn(BH_4)_2$ is amorphous XRD was not useful for identification. We were hoping that NMR would help but the results were inconclusive.



Example of Solid State NMR done by CalTech