

# Hydrogen Storage Materials for Fuel Cell Powered Vehicles

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Project ID # ST048

# Overview

## Timeline

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

## Budget

- Total Project Value:\$3,026K
- Cost Share:\$609K
- DOE Share:\$2,417K
- DOE Funding Spent\*:\$2,405K  
\*as of 3/31/14
- 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.

# Approach

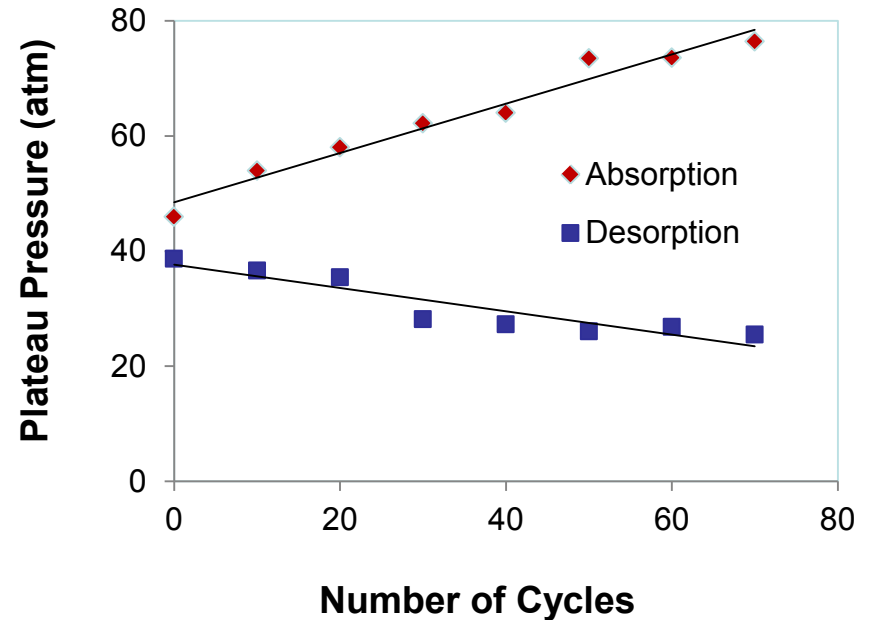
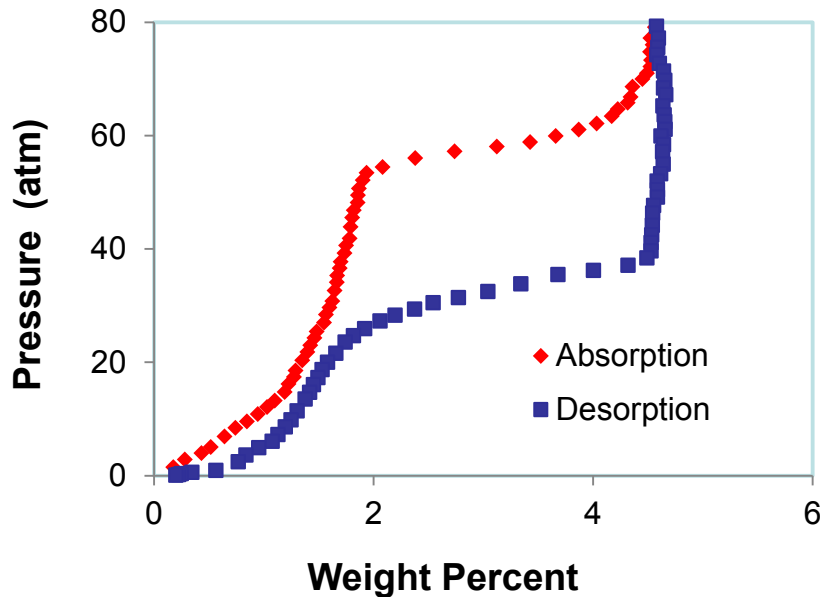
- Task 1 – Design suitable methods for analysis
  - Synthesis of mixtures using mechanical alloying
  - Determine thermal stability using TGA or TPD
  - Use XRD to determine phase purity and crystal structure
  - Use PCI analyses to determine thermodynamic stability
- Task 2 – Synthesize catalysts for making the hydriding faster and reversible
  - Use reactive ball milling to synthesize alkali metal catalysts
- 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, HPVA, XRD and TGA

# Technical Accomplishments/ Progress/Results

## Hydrogen desorption from a $\text{MgH}_2/\text{LiNH}_2$ system

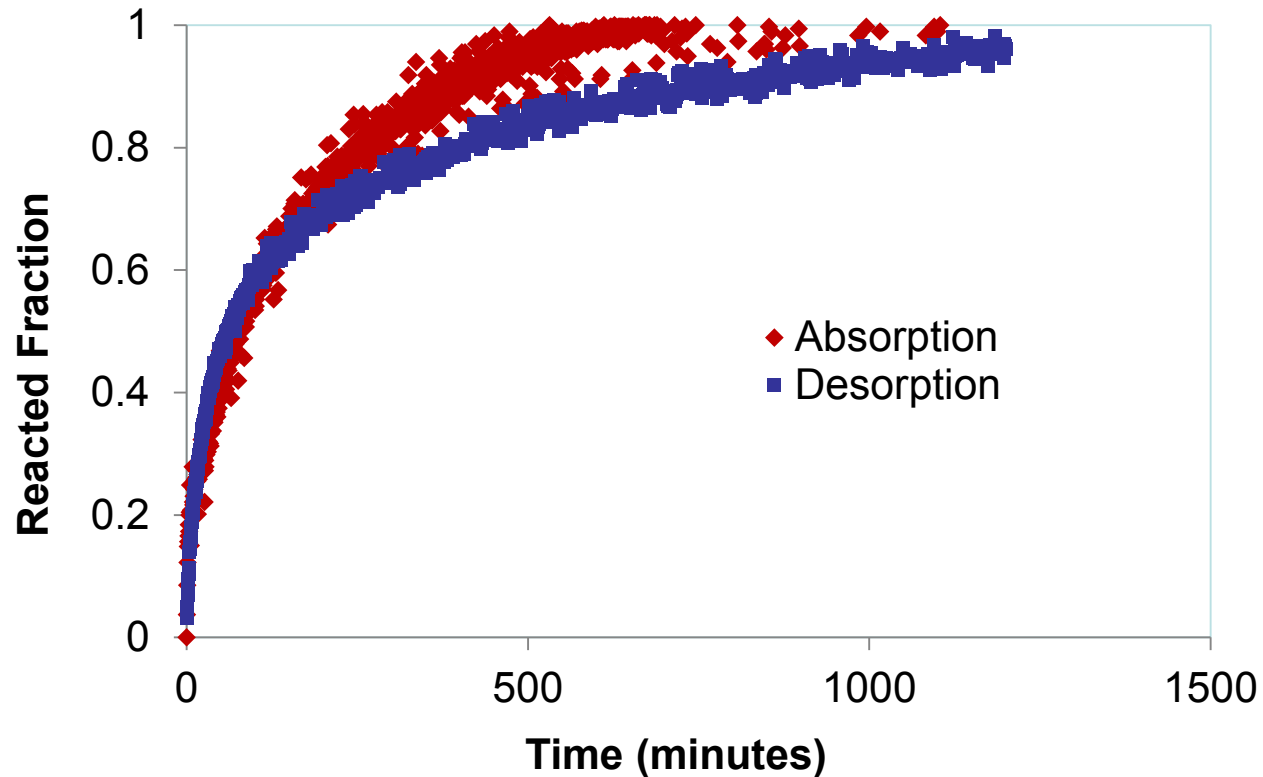
- Have developed a reactive ball milling method for synthesizing RbH and CsH catalysts for the  $\text{MgH}_2/\text{LiNH}_2$  system. Mixtures with an initial molar composition of  $(2\text{LiNH}_2 + \text{MgH}_2)$  were studied with and without the presence of 3.3 mol% RbH dopant.
- Cycling studies have been done in which absorption and desorption PCT isotherms were constructed for the RbH doped mixtures after every 10 cycles. The results showed that the absorption plateau pressure increased during cycling while the desorption plateau pressure decreased. Also the amount of hydrogen absorbed and desorbed gradually decreased during cycling
- The absorption and desorption kinetics of the RbH-catalyzed mixtures were compared at  $160^\circ\text{C}$ . In the case of desorption, a constant pressure thermodynamic driving force was applied in which the ratio of the plateau pressure to the applied hydrogen pressure was set at 3. For absorption, the ratio of the applied pressure to the plateau pressure was set to 3. This ratio has been designated as the N-Value. Under these conditions, absorption reaction proceeds faster than the desorption reaction.
- Modeling studies showed that diffusion is the rate-controlling process for both absorption and desorption.
- Results of these studies are presented in the following three slides.

# Cycling Study for the $\text{LiNH}_2/\text{MgH}_2$ System



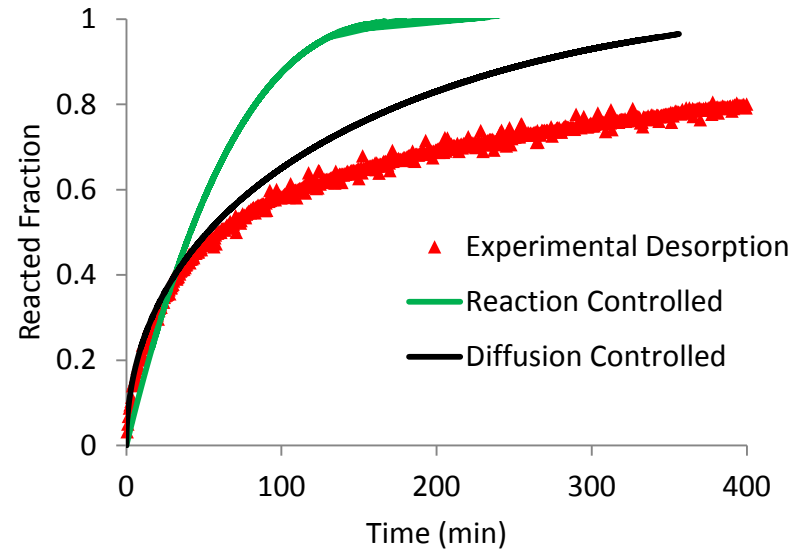
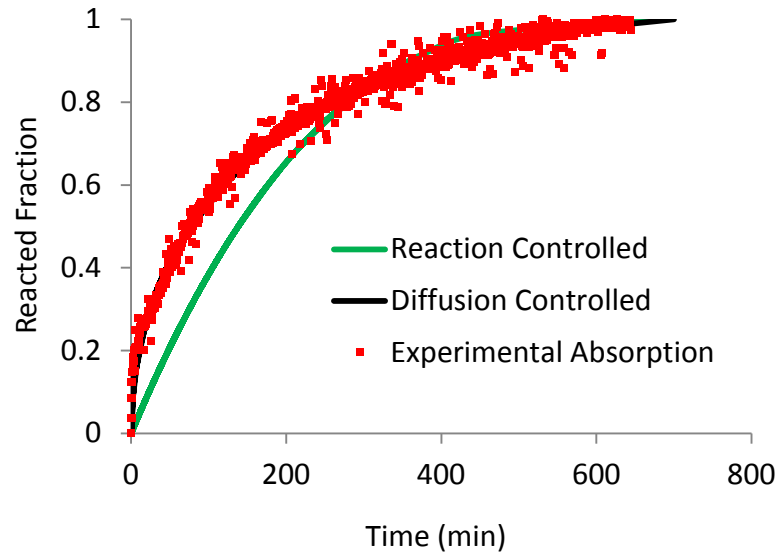
- The absorption and desorption PCIs shown above on the left were done at 160 °C after 20 cycles. The plots show that there is a significant amount of hysteresis. The graph on the right gives the absorption and desorption plateau pressures after every 10 cycles up to 70 cycles. It is evident that the hysteresis increases as a result of cycling.

# Kinetic for the RbH Doped $\text{LiNH}_2/\text{MgH}_2$ System



Kinetics were done in the two-phase region at 160 °C and N=3. The results show that absorption occurs faster than desorption under the same conditions. It takes ~350 minutes to attain 90% absorption whereas ~740 minutes are required for 90% desorption.

# Kinetic Modeling for the LiNH<sub>2</sub>/MgH<sub>2</sub> System



- The modeling plots were done based on a shrinking core model in which reaction at the phase boundary or diffusion could control reaction rates.
- The phase boundary controlled reaction is based on the equation:  $\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$
- The diffusion controlled reaction is based on the equation:  $\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$
- Results show that diffusion controls the rate of absorption over the entire course of the reaction whereas the desorption rates is diffusion controlled during the first 50% of reaction.

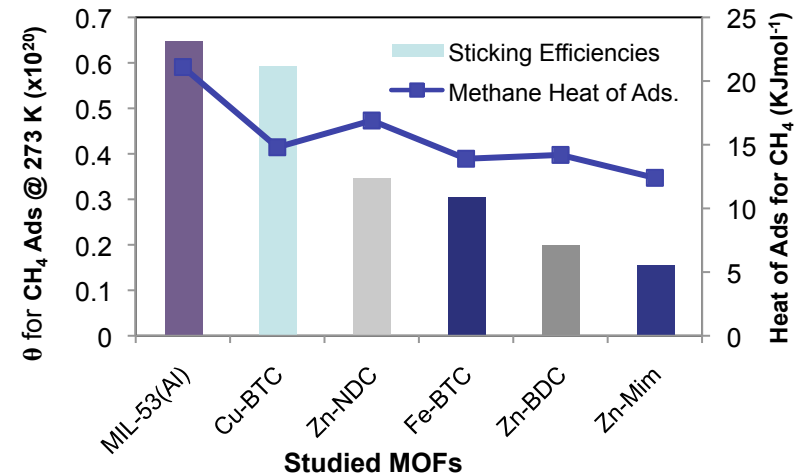
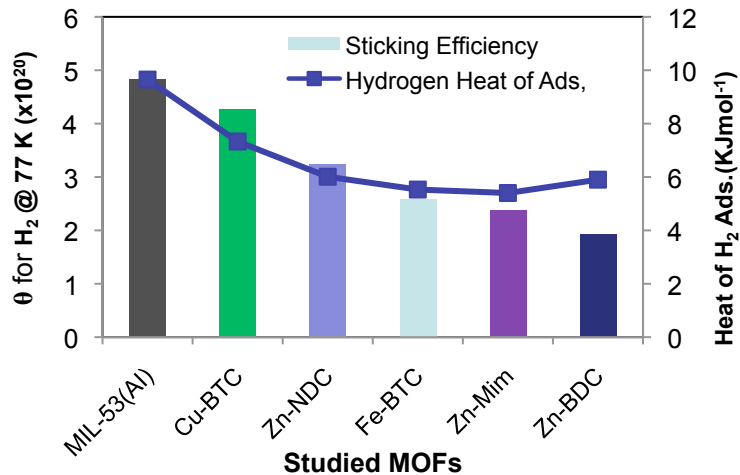


# Technical Accomplishments/ Progress/Results

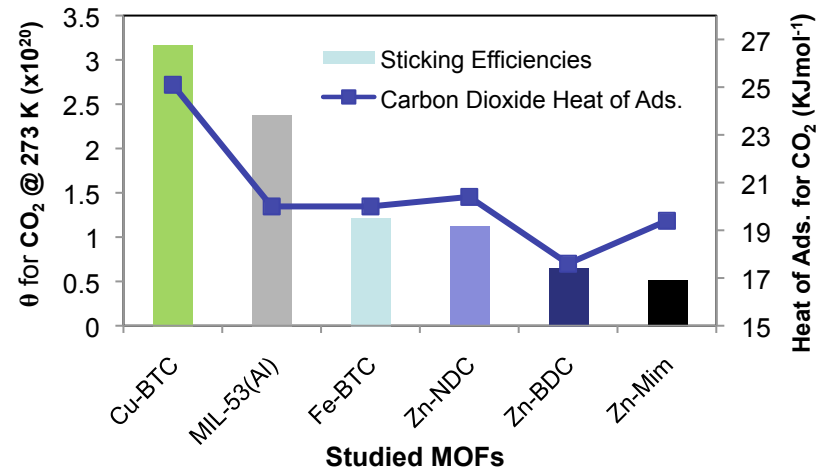
## Hydrogen adsorption on Metal Organic Frameworks

- Since many MOFs have been found to adsorb more gas than expected based on surface areas, sticking efficiencies were determined to see how this could be explained.
- Sticking efficiencies were determined based on a newly developed parameter called the sticking factor ( $\theta$ ). It can be calculated based on the following equation:
- $$\theta = \frac{\% \text{Hydrogen Adsorbed} \times \text{Avogadro's No.}}{\text{Surface Area} \left( \frac{\text{m}^2}{\text{g}} \right) \times \text{Mol. Wt.}}$$
- The MOFs that were studied include: Zn-NDC, Zn-BDC, Zn-Mim, Cu-BTC, Fe-BTC and Mil-53(Al). Since three of the MOFs contain the same metal and different linkers whereas to others contain the same linker but different metals, it was possible to determine the possible effect of metal and linker on  $\theta$ .
- The three gases studied include: H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>.
- Results show that in the three Zn-containing MOFs, Zn-NDC has the highest sticking efficiency. Therefore it was concluded that NDC is a more effective linker than BDC and Mim when it comes to gas adsorption. Results also show that Cu is a more effective metal than Fe for gas adsorption.
- Results also show that  $\theta$  can be correlated with the isosteric heat of adsorption. Thus it seems as though the binding strength can be just as important as surface area in gas adsorptions.
- Experiments were also done to determine how nanoconfinement of complex hydrides in MOFs would affect hydrogen desorption temperature. It was found that nanoconfinement of a LiNH<sub>2</sub>/MgH<sub>2</sub> mixture in IRMOF-8 results in a lowering of the desorption temperature of the mixture.
- Results are given in the following three slides.

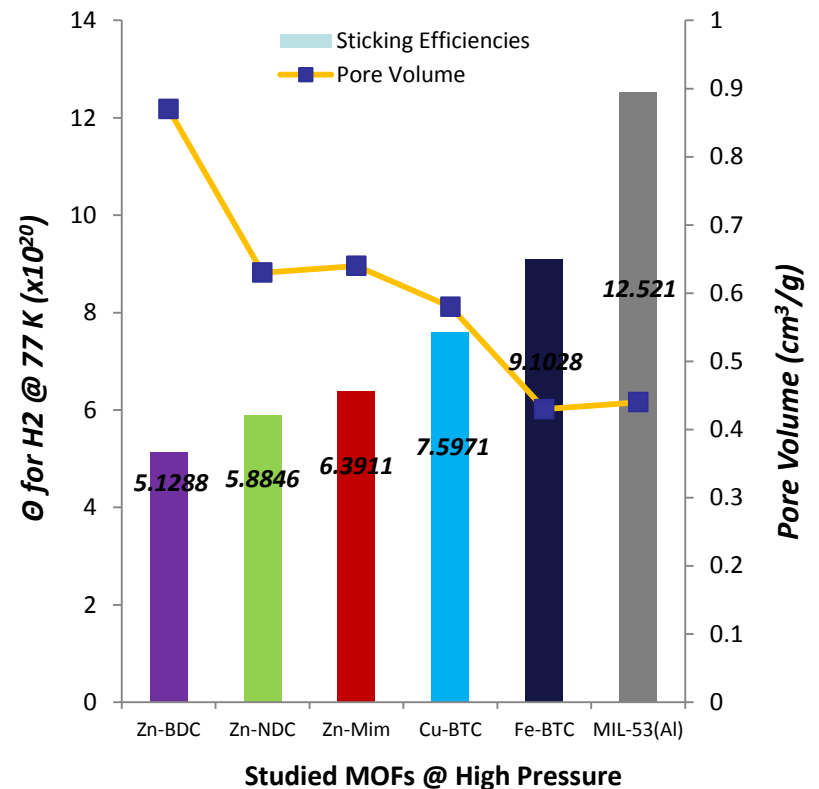
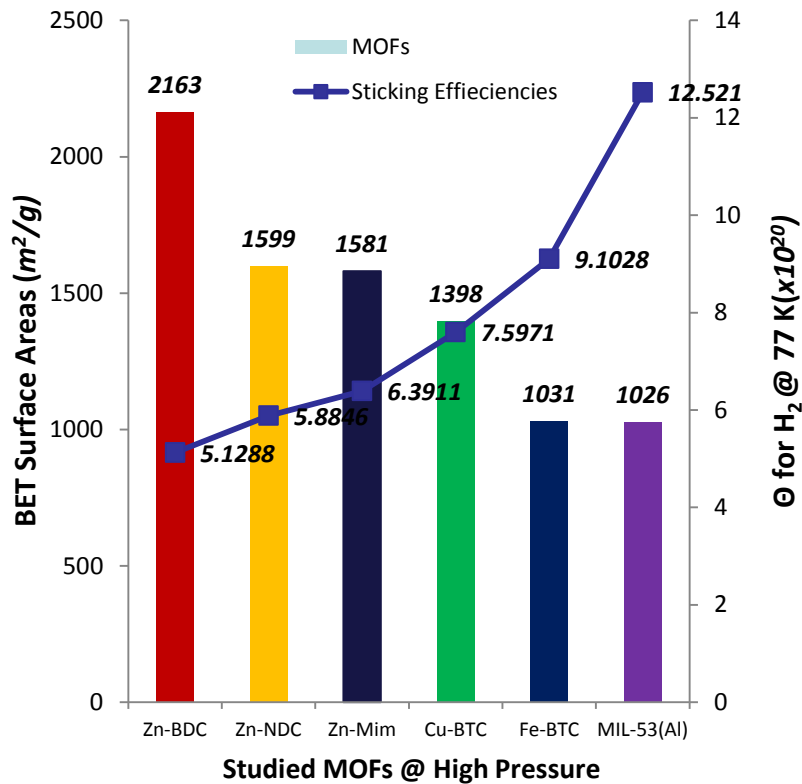
# Relationship between Sticking Efficiency and Heat of Adsorption



- $$\theta = \frac{\% \text{ Hydrogen Adsorbed } \times \text{ Avogadro's No.}}{\text{Surface Area} \left(\frac{m^2}{g}\right) \times \text{Mol. Wt.}}$$
- Sticking factors ( $\theta$ ) were calculated from the above equation.
- The graph on the top left shows that ( $\theta$ ) for H<sub>2</sub> adsorption on the various MOFs correlates well with  $\Delta H_{ads}$ .
- The graph on the top right shows that the same correlation exists for CH<sub>4</sub> adsorption on the MOFs.
- The graph on the bottom right shows that the same correlation exists for CO<sub>2</sub> adsorption on the MOFs.

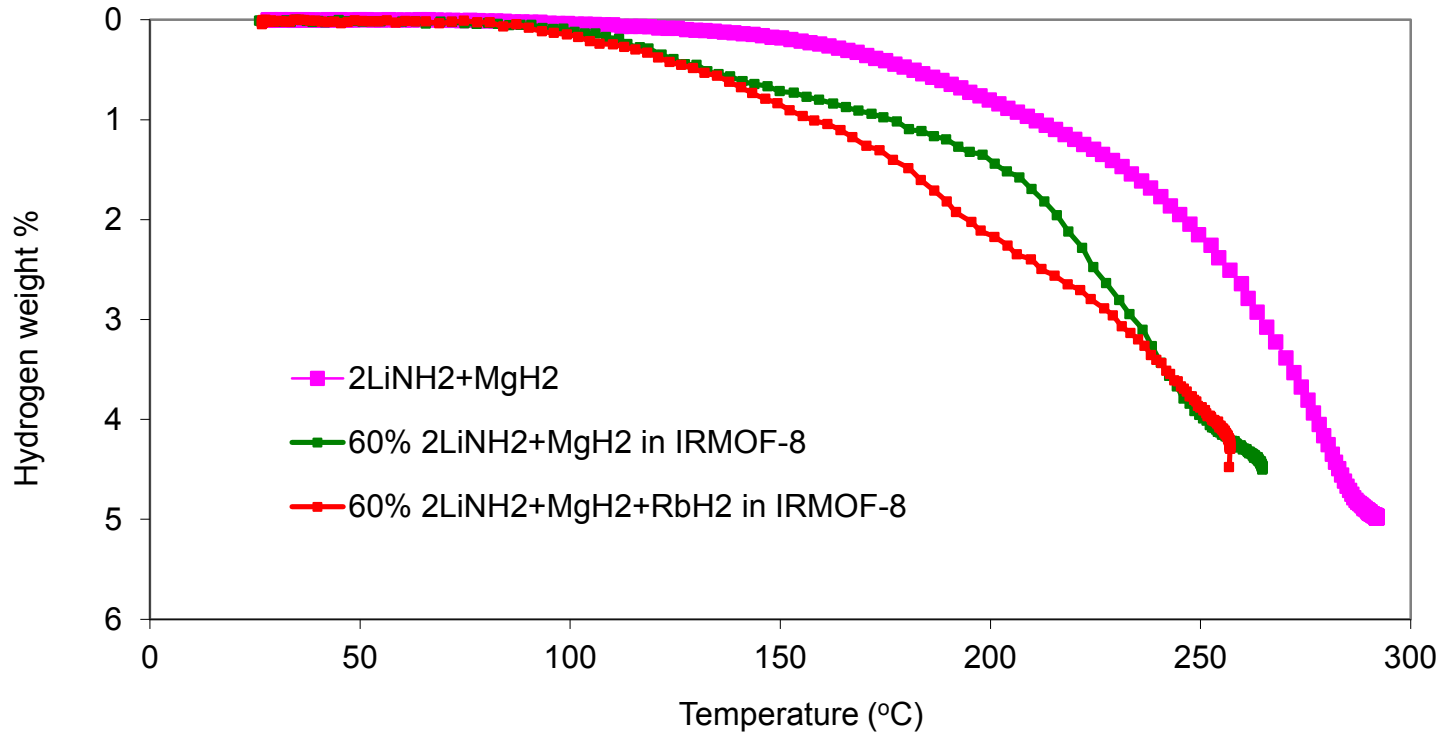


# Relationship between Surface Area/Pore Volume and Sticking Efficiency



The graphs show that there is an inverse correlation between Surface Area/Pore Volume and Sticking Efficiency ( $\theta$ ) of H<sub>2</sub> on the various MOFs. A similar correlation exists for the adsorptions of CH<sub>4</sub> and CO<sub>2</sub>.

# Nanoconfinement of $\text{LiNH}_2/\text{MgH}_2$ in IRMOF-8



The TPD plots show that nanoconfinement of  $\text{LiNH}_2/\text{MgH}_2$  in IRMOF-8 causes hydrogen to be released at a lower temperature. Doping with  $\text{RbH}_2$  produces a further lowering of the desorption temperature.

# Physisorption Properties of Gases on MOFs

MOFs	Zn-BDC	Zn-NDC	Zn-Mim	Cu-BTC	Fe-BTC	Mil-53(Al)
Surface area (m <sup>2</sup> /g) (BET)	2163	1599	1581	1398	1031	1026
H <sub>2</sub> Wt. % (at 77 K)	3.72	3.15	3.39	3.56	3.14	2.86
H <sub>2</sub> ΔH (kJ/mol)	5.9	6.01	5.40	7.33	5.53	9.65
CH <sub>4</sub> Wt. % (at 273 K)	12.8	15.9	9.26	16.6	11.3	9.75
CH <sub>4</sub> ΔH (kJ/mol)	17.9	16.9	19.6	20.3	9.6	6.04
CO <sub>2</sub> Wt. % (at 273 K)	48.3	61.1	40.0	64.0	55.5	44.1
CO <sub>2</sub> ΔH (kJ/mol)	18.2	24.3	19.6	20.9	20.1	28.9

Gas adsorption measurements were done on six different MOFs using three different gases at high pressure. The temperatures used are indicated in the table.

# 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 $\text{NaAlH}_4$ 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 $\text{CaH}_2/\text{LiBH}_4$ system could reversibly absorb and release approximately 9 weight percent hydrogen, with a desorption enthalpy of 63 kJ/mol $\text{H}_2$ . 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 $\text{H}_2$ .

# Approach/Milestones

Year	Milestone or Go/No-Go Decision
2010	Milestone: It was discovered that some destabilized $\text{Mg}(\text{BH}_4)_2$ -based systems could absorb and release hydrogen reversibly starting at less than 200 °C. Studies on pure $\text{MgH}_2$ 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 $\text{MgH}_2$ - $\text{LiNH}_2$ system.
2012	Milestone: It was demonstrated that a $\text{NbF}_5$ catalyst could dramatically improve the kinetics of a $\text{MgH}_2$ - $\text{LiBH}_4$ 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 $\text{MgH}_2$ - $\text{LiNH}_2$ system than KH.
2014	Milestone: It was found that the hydrogen desorption temperature of the $2\text{MgH}_2$ - $\text{LiNH}_2$ system could be lowered by nanoconfinement in IRMOF-8.

# 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.



# Future Work

- The following efforts will be pursued in the FY 14-15, even though funding for the project is ending:
  - Continue to perform kinetics and modeling studies on the  $\text{MgH}_2/\text{LiNH}_2$  system based destabilized systems using our newly developed RbH catalytic additive as well as KH and CsH additives. 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 KH and CsH catalyzed  $\text{MgH}_2/\text{LiNH}_2$  system .
  - Continue to study nanoconfinement of complex hydrides in other lightweight MOFs such as Mil-53(Al)
  - Continue to study sticking factors as a way to explain different adsorption behaviors in MOFs.
  - Continue collaborating with the University of Delaware on the design, fabrication and demonstration of a Hydride-Based Hydrogen Storage System.

# 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:** Perform kinetics, modeling and cycling measurements on a RbH doped  $2\text{MgH}_2/\text{LiNH}_2$  system. Kinetics are determined using constant pressure driving forces. Synthesize and characterize MOFs using techniques such as BET, HPVA, XRD and TGA. Nanoconfine the  $2\text{MgH}_2/\text{LiNH}_2$  in IRMOF-8 as a way of lowering hydrogen desorption temperature.
- Technical Accomplishments:** We have demonstrated that absorption of hydrogen by the  $2\text{LiNH}_2/\text{MgH}_2$  system occurs faster than desorption. We have also demonstrated that nanoconfinement of a  $2\text{MgH}_2/\text{LiNH}_2$  mixture in IRMOF-8 lowers the hydrogen desorption temperature of the mixture.
- Proposed Future Research:** Perform absorption/desorption kinetics and modeling studies on RbH, CsH and KH doped  $2\text{MgH}_2/\text{LiNH}_2$  mixtures. Continue to study nanoconfinement of complex hydrides in lightweight MOFs such as Mil-53(Al).