IV.D.2 Hydrogen Storage Materials for Fuel Cell-Powered Vehicles

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Overall Objectives

The objectives of this project are to:

- Identify complex hydrides that have great hydrogen storage potential.

- Develop new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures.

- Perform kinetic modeling studies that will identify the rate-controlling processes in the hydrogen desorption reactions.

- Evaluate the parameters that affect the ability of metal-organic frameworks (MOFs) to adsorb gases.

Fiscal Year (FY) 2014 Objectives

- Perform absorption and desorption kinetics on the $LiNH_2/MgH_2$ system using RbH as a catalytic additive.

- Perform kinetic modeling studies on both absorption and desorption reactions to identify the rate-controlling processes in the $LiNH_2/MgH_2$ system.

- Perform absorption/desorption cycling measurements to determine the cyclic stability of the $LiNH_2/MgH_2$ system.

- Evaluate the parameters that affect the ability of selected MOFs to adsorb gases such as H_2, CH_4 and CO_2.

- Determine the effect of nano-confinement on the hydrogen sorption capacity of the $LiNH_2/MgH_2$ system.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(D) Durability/Operability

(E) Charging/Discharging Rates

Technical Targets

This project is conducting fundamental studies of complex amide materials and other promising hydrogen storage materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet DOE's 2015 gravimetric goal of 5.5 wt% hydrogen storage for the system. Table 1 summarizes the targets.

TABLE 1. Project Technical Targets

Storage Parameter	Target	$LiNH_2/MgH_2$
System Gravimetric Capacity:	0.055 kg H_2/kg System	To Be Determined
System Volumetric Capacity:	0.040 kg H_2/L System	To Be Determined

FY 2014 Accomplishments

- Have developed a reactive ball milling method for synthesizing RbH and CsH catalysts for the $MgH_2/LiNH_2$ system.

- Cycling studies have been done in which absorption and desorption pressure-concentration-temperature 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°C and at the same thermodynamic driving forces. Under these conditions, absorption reaction proceeds faster than the desorption reaction.

- Since many MOFs have been found to adsorb more gas than expected based on surface areas, sticking efficiencies (θ) were determined to see how this could

be explained. The MOFs that were studied include: Zn-NDC, Zn-BDC, Zn-Mim, Cu-BTC, Fe-BTC and Mil-53(Al). NDC is naphthalenedicarboxylic acid; BDC is benzenedicarboxylic acid; Mim is methyl imidazole and BTC is benzenetricarboxylic acid. Since three of the MOFs contain the same metal and different linkers, whereas two others contain the same linker but different metals, it was possible to determine the possible effects of type of metal and linker on θ.

- The three gases studied include: H_2, CH_4 and CO_2. Results show that of 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 θ 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 nano-confinement of complex hydrides in MOFs would affect hydrogen desorption temperature. It was found that nano-confinement of a $2LiNH_2/MgH_2$ mixture in isoreticular MOF-8 (IRMOF-8) results in a lowering of the desorption temperature of the mixture.

✧   ✧   ✧   ✧   ✧

INTRODUCTION

The $2LiNH_2/MgH_2$ system has been identified as an important "near-term" system for hydrogen storage. This is because of its good long-term cycling behavior and high hydrogen capacity. Current efforts in our research lab are

focused on performing hydrogen storage studies on this system. We have developed methods for the synthesis, characterization, and modeling of this system. New catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures have also been developed. We have also extended these studies to include MOFs as potential hydrogen storage materials. Once a suitable material has been identified for hydrogen storage it will be necessary to design, fabricate and test a hydride-based hydrogen storage system for fuel cell applications.

APPROACH

To achieve the project objectives, it was first necessary to design suitable methods for synthesizing, characterizing, and testing the materials. These methods included synthesis of new materials by mechanical alloying using ball milling, determining thermal stability using thermal gravimetric analysis or thermally programmed desorption (TPD), using X-ray diffraction to determine phase purity and crystal structure, using pressure-composition isotherm (PCI) analyses to determine thermodynamic stability, finding catalysts for making the hydriding faster and reversible, determining kinetic rate curves using constant pressure driving forces, and performing modeling to gain understanding of the mechanism.

RESULTS

The thermodynamics and kinetics of the $2LiNH_2/MgH_2$ system have been reported but it is also necessary to know how stable the system is upon continuous pressurizations and depressurizations. Therefore a series of absorption/desorption cycling measurements were done on this system at 200°C. Figure 1 (left) contains a pair of absorption/desorption

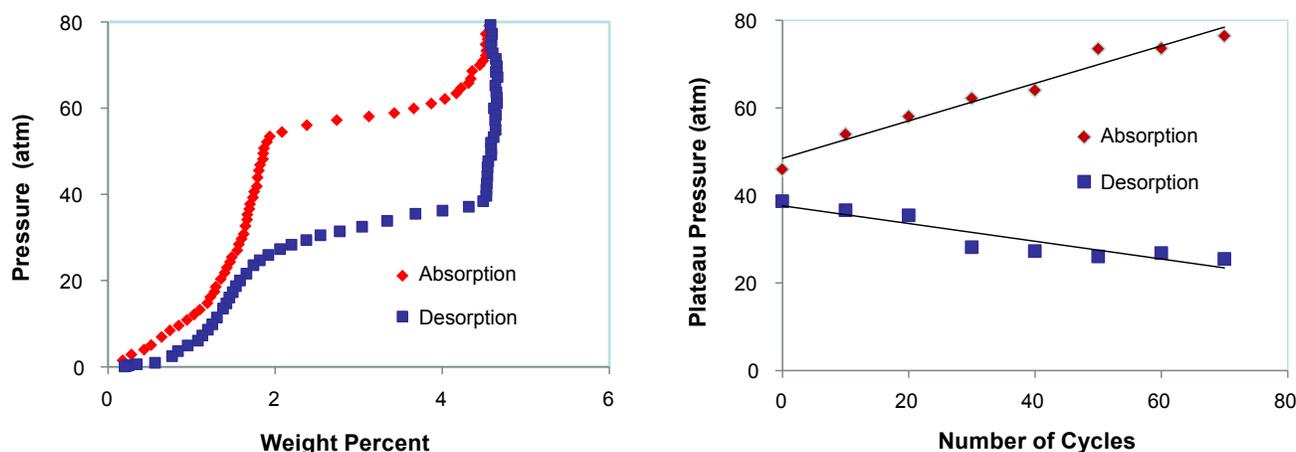**FIGURE 1.** Cycling Study for the $LiNH_2/MgH_2$ System – The absorption and desorption PCIs shown above on the left were done at 160°C after 20 cycles. The plots show that there is a significant amount of hysteresis. The graph on the right gives the absorption and desorption plateau pressures after every 10 cycles up to 70 cycles. It is evident that the hysteresis increases as a result of cycling.

isotherms that were obtained at 200°C after 20 cycles. The plots show that there is a significant amount of hysteresis. Figure 1 (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. Since the amount of hysteresis usually remains fairly constant, regardless of cycling, this was an unexpected result. Additional measurements using other catalysts such as KH will also be done to determine if similar effects exist. It was also found that the hydrogen capacity decreased by about 25% during the course of 70 cycles.

The kinetics of hydrogen uptake and release from the 2LiNH$_2$/MgH$_2$ system was also measured in the two-phase region. The absorption and desorption kinetics of the RbH catalyzed mixtures were compared at 160°C using a constant pressure thermodynamic driving force. This was achieved by using a ratio of the plateau pressure to the applied hydrogen pressure of 3 (desorption) or a ratio of the applied pressure to the plateau pressure of 3 (absorption). Figure 2 contains plots for the rates of hydrogen absorption and desorption from the RbH-catalyzed mixtures. 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.

An attempt was also made to determine the rate-controlling process in these samples by doing kinetic modeling. The theoretical equations that were used are shown below:

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

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

Where τ is a constant that depends on several parameters such as the initial radius of the hydride particles, the gas

phase concentration of reactant, the density of the metal hydride, etc.

The model based on Eq. (1) will have chemical reaction at the phase boundary controlling the reaction rate whereas a model based on Eq. (2) is one in which diffusion controls the overall reaction rate. Both equations were fitted to the kinetic data for LiNH$_2$/MgH$_2$ system. Figure 2 (right) contains modeling plots for the 2LiNH$_2$/MgH$_2$ system catalyzed by RbH. In the graph, one curve is an experimental curve, a second curve is based on the overall rate being controlled by diffusion, and a third curve is calculated based on chemical reaction controlling the rate. The results show a good fit between the experimental curve and the diffusion controlled curve. This indicates that diffusion controls the rate of absorption over the entire course of the reaction. The desorption reaction (curves are not shown) is also diffusion controlled but only during the first 50% of reaction.

Since many MOFs have been found to adsorb more gas than expected based on surface areas alone, 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 (θ). The sticking factor (θ) can be calculated based on the following equation:

$$\theta = \frac{\% \text{ Hydrogen Adsorbed X Avogadro's No.}}{\text{Surface Area} \left(\frac{\text{m}^2}{\text{g}} \right) \text{ X Mol. Wt.}} \quad (3)$$

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 two others contain the same linker but different metals, it was possible to determine the possible effect of metal and linker on θ. The three gases studied include: H$_2$, CH$_4$ and CO$_2$. Results show that in the three Zn-containing
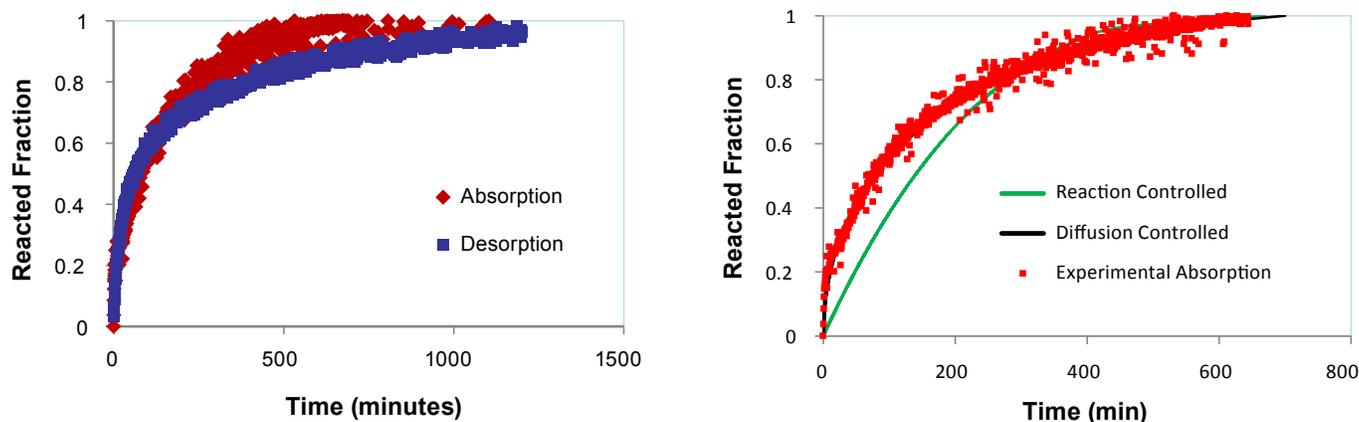

FIGURE 2. Kinetics and Modeling for the RbH-Doped LiNH$_2$/MgH$_2$ System – Kinetics were done in the two-phase region at 160°C and N=3. The graph on the left shows that absorption occurs faster than desorption under the same conditions. It takes ~350 minutes to attain 90% absorption whereas ~740 minutes are required for 90% desorption. The graph on the right contains absorption modeling results for the system. The experimental curve fits the diffusion controlled curve over the entire course of the reaction.

MOFs, Zn-NDC has the highest sticking efficiency. Therefore it was concluded that NDC is a more effective linker than BDC or Mim. Results also showed that Cu is a more effective metal than Fe for gas adsorption. Measurements of adsorption enthalpies showed that θ can be correlated with the isosteric heat of adsorption. The graph on the top left of Figure 3 shows that (θ) for H_2 adsorption on the various MOFs correlates well with adsorption enthalpy. The graph on the top right shows that the same correlation exists for CH_4 adsorption on the MOFs, while the graph on the bottom right shows that a similar correlation exists for CO_2. 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 nano-confinement of complex hydrides in MOFs would affect hydrogen desorption temperature. The TPD in Figure 4 shows that nano-confinement of $LiNH_2/MgH_2$ in IRMOF-8 causes hydrogen to be released at a lower temperature. Doping with RbH produces a further lowering of the desorption temperature.
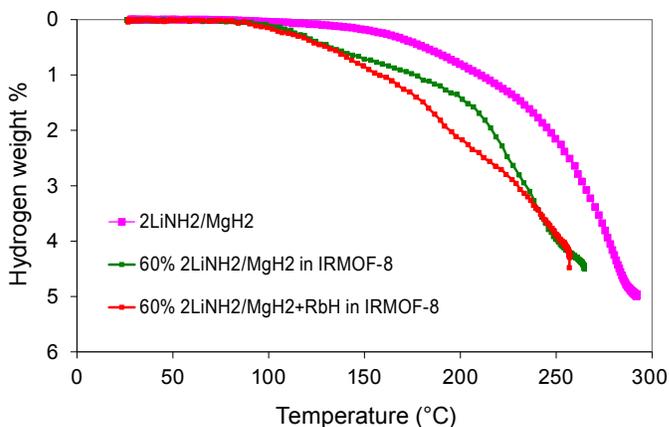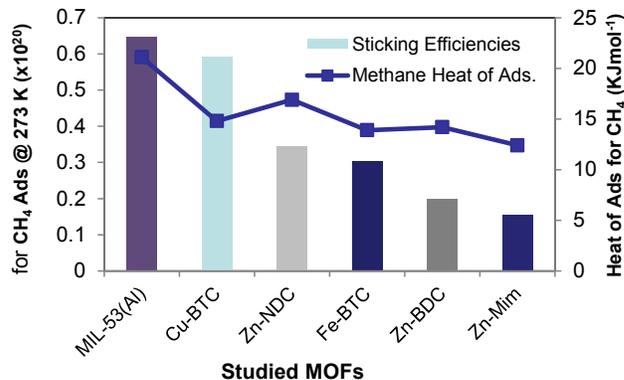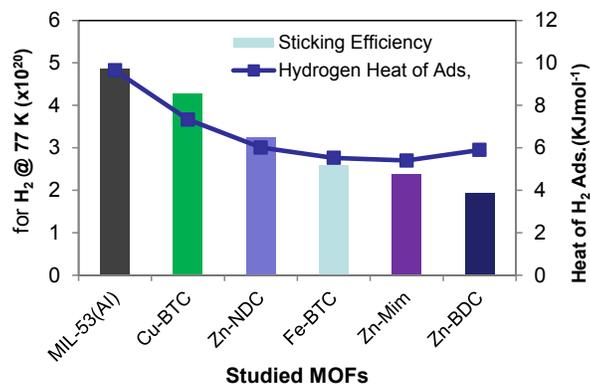

FIGURE 4. Nano-Confinement of $LiNH_2/MgH_2$ in IRMOF-8 – The TPD plots show that nano-confinement of $LiNH_2/MgH_2$ in IRMOF-8 causes hydrogen to be released at a lower temperature. Doping with RbH_2 produces a further lowering of the desorption temperature.

- $$\theta = \frac{\% \text{ Hydrogen Adsorbed X Avogadro's No.}}{\text{Surface Area} \left(\frac{m^2}{g} \right) \text{ X Mol. Wt.}}$$

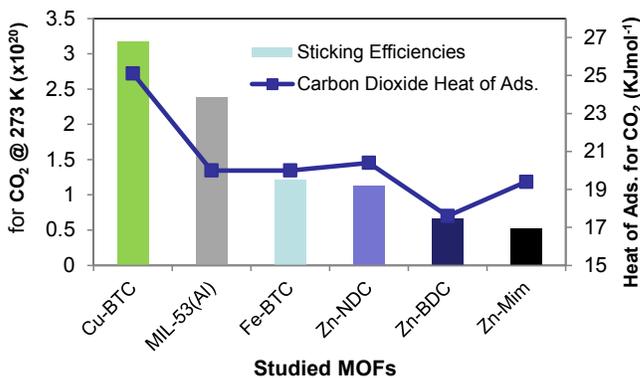- Sticking factors (θ) were calculated from the above equation.

FIGURE 3. Relationship between Sticking Efficiency and Heat of Adsorption – The graph on the top left shows that (θ) for H_2 adsorption on the various MOFs correlates well with adsorption enthalpy. The graph on the top right shows that the same correlation exists for CH_4 adsorption on the MOFs. The graph on the bottom right shows that the same correlation exists for CO_2 adsorption on the MOFs.

CONCLUSIONS

- The results of this study show that hydrogen absorption in the RbH catalyzed $2LiNH_2/MgH_2$ system occurs about twice as fast as desorption under the same conditions.

- Absorption/desorption cycling results in an increase in the amount of hysteresis in the RbH-catalyzed $2LiNH_2/MgH_2$ system with a decrease in hydrogen absorption capacity of 25% during the first 70 cycles.

- Modeling studies using the shrinking core model indicated that the absorption and desorption reaction rates are controlled by diffusion in the two-phase plateau region.

- It was found that in the three MOFs containing a common metal but different linkers, the Zn-NDC had the highest sticking efficiency. Therefore it appears that NDC (naphthalene dicarboxylic) acid is the most effective linker for hydrogen adsorption.

- In the two MOFs with the same linker but different metals the Cu-BTC had a greater sticking efficiency than Fe-BTC. Therefore it seems that Cu was a more effective metal than Fe in increasing adsorption capacity.

- Since there is a direct correlation between sticking efficiency and adsorption enthalpy this indicates that the strength of hydrogen adsorption on the surface is an important parameter in determining the quantity of gas adsorption.

- Nano-confinement studies showed that confinement of $2LiNH_2/MgH_2$ in the pores of IRMOF-8 results in a decrease in the dehydriding temperature of the complex hydride. The addition of RbH further decreases the temperature.

FUTURE DIRECTIONS

Although financial support for this work is ending in September 2014, the following future 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 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 $MgH_2/LiNH_2$ system.

- Continue to study nano-confinement 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.

PATENT ISSUED

1. A Rubidium Hydride Catalyzed Lithium Amide/Magnesium Hydride System for Hydrogen Storage Applications, EFS ID 19061394.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. J. Hayes, T. Durojaiye and A.J. Goudy, "Hydriding and Dehydriding Kinetics of the rubidium hydride doped lithium amide/magnesium hydride system", J. Alloys Compds (Submitted).

2. Esosa Iriowen, Samuel Orefuwa, Yang Hongwei, Andrew Goudy, "Comparative Studies of Sticking Efficiencies in Gas Adsorptions Analysis on Selected Metal Organic Frameworks", J. Alloys Compds, (Submitted).

3. Samuel Orefuwa, Esosa Iriowen, Hongwei Yang, Bryan Wakefield and Andrew Goudy, "Effects of Nitro-Functionalization on the Gas Sorption Properties of Isoreticular Metal-Organic Framework-Eight (IRMOF-8)", Micropor. Mesopor. Mater., 177 (2013) 82-90.

4. Durojaiye T, Hayes, J, and Goudy A, "Rubidium Hydride – A Highly Effective Dehydrogenation Catalyst for the lithium amide/magnesium hydride system" J. Phys Chem C, 117 (2013) 6554 – 6560.

5. J. Hayes, T. Durojaiye and A.J. Goudy, "Effects of Alkali Metal Hydrides on $2LiNH_2/MgH_2$ System", Gordon Conference, Lucca, Italy, 2013.

6. E. Iriowen, S.A. Abidemi, H. Yang and A.J. Goudy, "Sticking Efficiencies of Different Gases on Metal Organic Frameworks", Gordon Conference, Lucca, Italy, 2013.