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.
- Develop techniques for improving the sorption capabilities of metal-organic frameworks (MOFs).

Fiscal Year (FY) 2013 Objectives

- Develop a new catalyst for the $LiNH_2/MgH_2$ system that will increase reaction rates and lower reaction temperatures.
- Perform kinetic modeling studies that will identify the rate-controlling processes in the $LiNH_2/MgH_2$ system.
- Determine the effects of nitro-functionalization on the gas sorption capability of isoreticular metal-organic framework (IRMOF)-8.

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

(O) Lack of Understanding of Hydrogen Physisorption and Chemisorption

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 weight percent 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 2013 Accomplishments

- The $LiNH_2/MgH_2$ system has been kinetically modeled, and the rate controlling process has been identified.
- Have compared the dehydriding kinetics of the $LiNH_2/MgH_2$ system at constant pressure driving forces and found that the rates of hydrogen release from the catalyzed and un-catalyzed mixtures are in the order RbH > KH > un-catalyzed.
- Have shown that the nitro-functionalization of IRMOF-8 leads to a reduction in the surface area and a decreased pore volume. However, the decrease is not as great as one would expect based solely on the change in surface area and pore volume.
- A novel concept called the sticking factor was determined for comparison of the adsorption of H_2, CH_4, and CO_2 on the surfaces of IRMOF-8 and IRMOF-8-NO_2 at various temperatures. Since the sticking factors for gases adsorbed on the IRMOF-8-NO_2 were greater than those for gases adsorbed on the IRMOF-8, this indicated that nitro-functionalization of IRMOF-8 increases the sticking efficiency of gases.

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INTRODUCTION

The U.S. Department of Energy Metal Hydride Center of Excellence has described $2LiNH_2$+MgH_2 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 as well as developing new catalysts and engineering techniques for increasing reaction rates and lowering reaction temperatures. We have also extended these studies to include carbon materials, MOFs, and possibly other nanostructured and porous materials 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 $2LiNH_2/MgH_2$ system releases hydrogen according to the following equations:

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

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

TPD curves were constructed for the $2LiNH_2/MgH_2$ system to determine the relative desorption temperatures. The curves shown in Figure 1 indicate that the catalyzed mixtures release hydrogen at a lower temperature than un-catalyzed (pristine) mixture. This is believed to be largely due to the fact that both Rb and K have the same electronegativity and thus similar destabilizing effect on the N-H bond. Figure 2 contains PCI curves for the RbH catalyzed mixtures. Also shown in Figure 2 are the van't

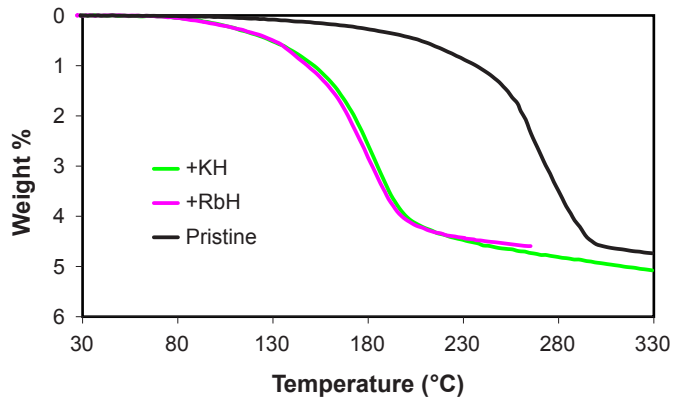

FIGURE 1. TPD curves for the $LiNH_2/MgH_2$ system. The mixtures doped with "catalytic additives" desorb H_2 at ~90°C lower than the un-catalyzed (pristine) mixture. Scans were done at 4°C per minute.

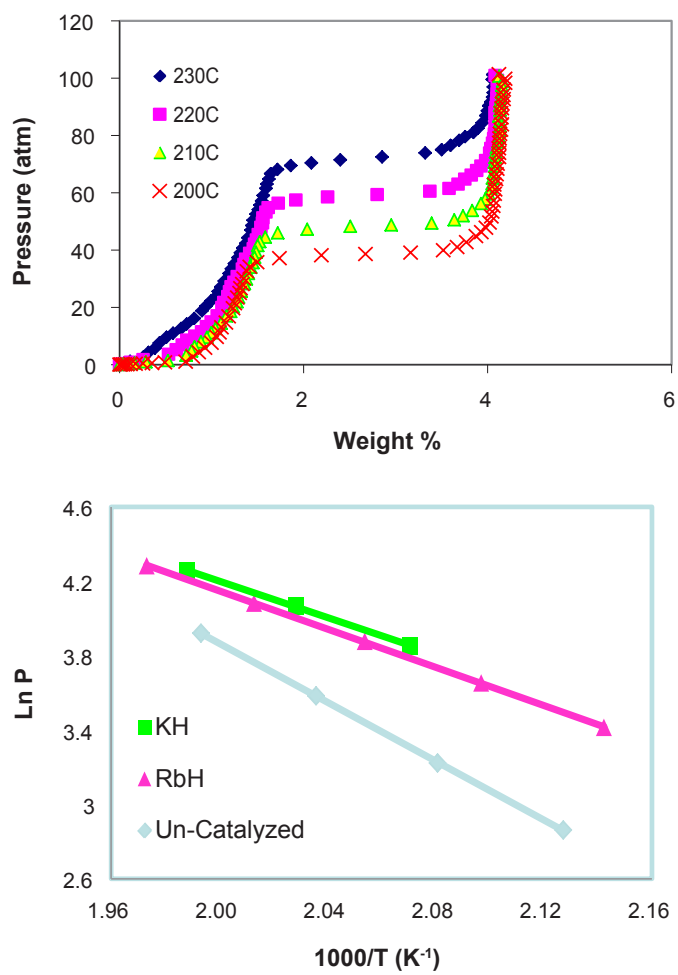

FIGURE 2. Thermodynamics for the $LiNH_2/MgH_2$ system. The graph on the top contains PCI curves for $2LiNH_2/MgH_2$ doped with RbH, which is typical of these systems. The graph on the bottom contains van't Hoff plots for $2LiNH_2/MgH_2$ doped and un-catalyzed mixtures.

Hoff curves that were used to determine the enthalpies of desorption for the catalyzed 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. The fact that the desorption enthalpy for hydrogen release from the un-catalyzed mixture was much higher than that from the catalyzed mixtures is consistent with the TPD findings.

The kinetics of hydrogen release from the $2LiNH_2/MgH_2$ system was also measured. The dehydrogenation kinetics of the catalyzed 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. Figure 3 contains plots for the rate of hydrogen release from the catalyzed and un-catalyzed mixtures. Kinetics was 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.

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:

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

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \quad (4)$$

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. (3) will have chemical reaction at the phase boundary controlling the reaction rate, whereas the model based on Eq. (4) is one in which diffusion controls the overall reaction rate. Both equations were fitted to the kinetic data for the $LiNH_2/MgH_2$ system. Figure 3 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 plots show a good fit for a diffusion controlled model up to 70% of the reaction but not beyond. This means that the process controlling hydrogen desorption at the later stage of the reaction is different from that at the beginning. The kinetic modeling plots for the KH catalyzed and the un-catalyzed systems showed that diffusion was the rate-controlling process.

We have also developed a rapid solvothermal method for synthesizing IRMOF-8 and have functionalized it by adding $–NO_2$ groups to the linker. It was found that functionalization decreased the surface area and decreased the amount of gas adsorption. However, functionalization increased the

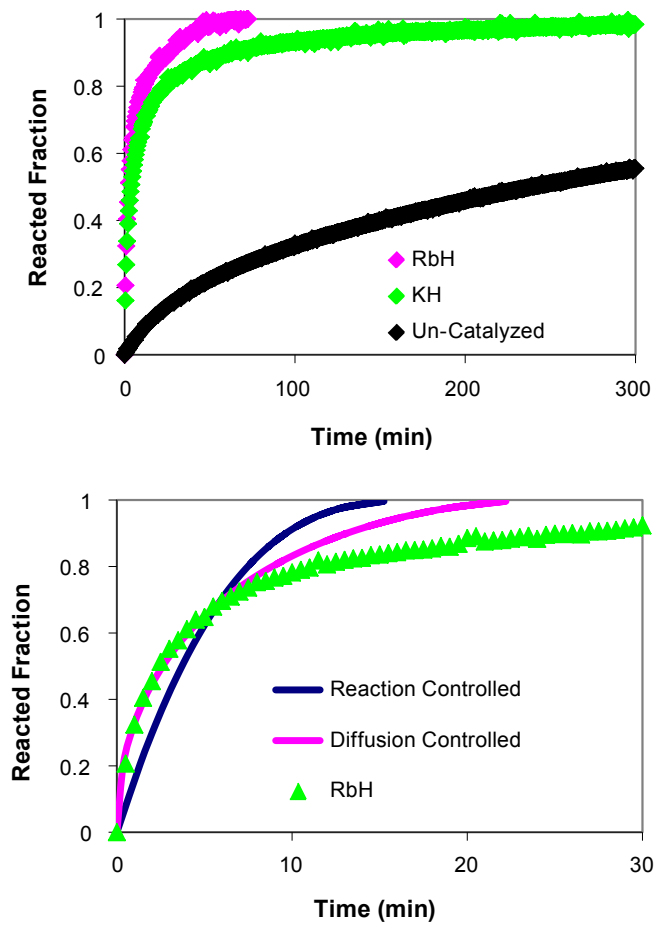

FIGURE 3. Kinetics and modeling plots for the $LiNH_2/MgH_2$ system. Measurements were done at 210°C and N = 10 (where N = plateau pressure/applied pressure).

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). The sticking factor is defined by:

$$\theta = \frac{\%\ \text{Hydrogen Adsorbed}}{\text{Surface Area}\ (\frac{m^2}{g})} \quad (5)$$

Results showed that θ increases with ΔH and molecular weight. Also, θ decreases with increasing temperature. Results are given in Figure 4.

CONCLUSIONS AND FUTURE DIRECTIONS

- The results of this study show that the new catalytic additive, RbH, is significantly better than KH for enhancing hydrogen desorption from the $2LiNH_2/MgH_2$ system, but the RbH and KH additives have nearly the same capability for lowering the hydrogen desorption temperature of the $2LiNH_2/MgH_2$ mixture.

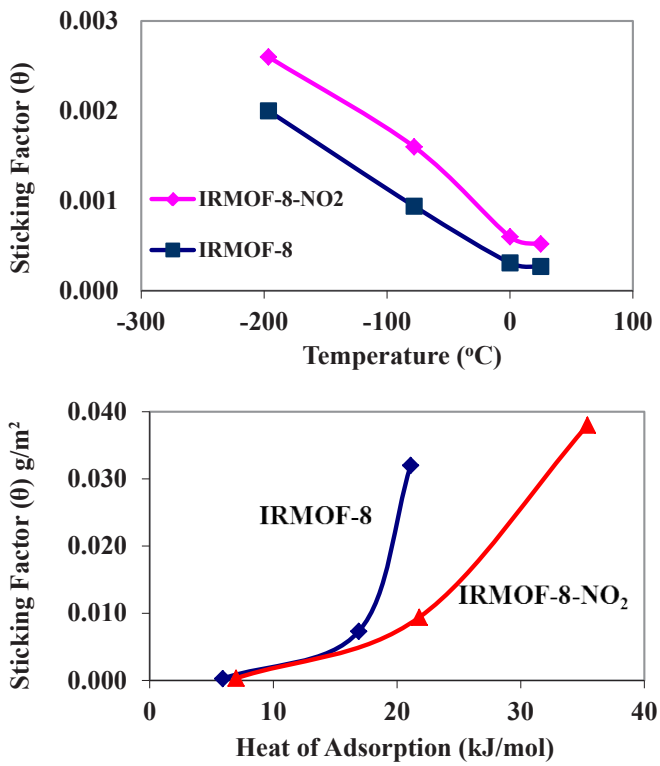

FIGURE 4. Sticking efficiencies and adsorption enthalpies for MOFs. The graph at the top shows sticking factor (θ) vs. temperature for H_2 on the MOFs. The graph at the bottom is θ vs. ΔH of H_2, CH_4, or CO_2 for the MOFs.

- The modeling studies using the shrinking core model and a method developed by Hancock and Sharp both indicated that the reaction rates are controlled by diffusion in the two-phase plateau region. The faster kinetics in the RbH doped mixture is attributed to the fact that Rb has a larger radius and is thereby able to expand the lattice, thus facilitating the diffusion process.
- Results have shown that the nitro-functionalization of IRMOF-8 leads to a reduction in the surface area and a decreased pore volume. However, the decrease is not as great as one would expect based solely on the change in surface area and pore volume.
- A novel concept called the sticking factor was determined for comparison purposes. Since the sticking factors for gases adsorbed on the IRMOF-8-NO_2 were greater than those for gases adsorbed on the IRMOF-8, this indicated that nitro-functionalization of IRMOF-8 increases the sticking efficiency of gases.
- In FY 2013-2014, the following work is planned:
  - Continue to perform kinetics and modeling studies on the $LiNH_2/MgH_2$ 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 residual gas analysis to determine if dehydrogenation is accompanied by the release of other gaseous byproducts such as ammonia.
  - Continue to study the effect of functionalization on MOFs. The goal is to increase ΔH for gas adsorption and thus increase the desorption temperatures.

PATENTS ISSUED

1. A Rubidium Hydride Catalyzed Lithium Amide/Magnesium Hydride System for Hydrogen Storage Applications, (Patent pending).

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