IV.A.5i High Throughput Combinatorial Chemistry Development of Complex Hydrides

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Accomplishments

- Validated two combinatorial synthesis techniques.
- Validated three high throughput screening techniques.
- Screened >50 metals and alloys as potential catalysts.
- Found better catalyst for MgH_2 + Si dehydrogenation.
  - High throughput screening did not identify any effective rehydrogenation catalyst up to reactor's pressure and temperature limitations.
  - Down-selected system due to lack of rehydrogenation.
  - High throughput screening enabled a rapid decision on system, enabling focus on newer, possibly regenerable systems.
- Found a few catalyst leads for LiH+MgB_2 system.
- Initiated thin film material syntheses on both known and novel materials.
- Filed two patent applications.
- Validated various tools for combinatorial synthesis and high-throughput catalyst screening roughly nine months ahead of schedule.

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Introduction

In this project, we synthesize and identify new metal hydride systems, as well as catalysts, using combinatorial techniques. Combinatorial synthesis enables preparation of arrays of materials with multiple elements and various ratios in one batch. To screen these materials we have developed high-throughput screening apparatuses which allow these materials to be studied in parallel for targeted properties via their optical and reflective properties. During this year we have combined combinatorial synthesis and high-throughput screening for metal hydride catalyst discovery.

The materials systems we have chosen, in conjunction with Metal Hydride Center of Excellence (MHCoE) partners, for catalyst screening were MgH_2+Si, $LiBH_4$+MgH_2, and $LiBH_4$ in powder, slurry or thin film formats. We screened more than 50 catalysts for the MgH_2+Si system and ~50 catalysts for the $LiBH_4$+MgH_2 system to look for the kinetic improvement required to meet DOE targets for on-board hydrogen storage systems.

Approach

Rational design is adopted for metal hydride and catalyst screening. First, metal hydride systems are screened based on thermodynamic calculation. Then, the identified metal hydrides are synthesized in an approach suitable for catalyst synthesis and screening. In some cases, metal hydride powders are received from MHCoE partners to identify suitable catalysts. These materials were applied on suitable substrates by making a uniform layer for subsequent deposition of catalyst on it. Combinatorial ion beam sputtering and high-throughput screening techniques are used to incorporate the catalyst. Thermodynamic calculation, thin film synthesis, catalyst deposition and subsequent screening are carried out independently. After obtaining initial leads for effective catalysts from screening, we work in close collaboration with MHCoE partners to confirm the results more quantitatively.

Results

MgH_2+Si System

- Ball-milled MgH_2+Si mixture without catalyst was obtained from Hughes Research Laboratory (HRL).
- The mixture was applied to a substrate without changing morphology or particle size. Approximately 50 catalysts were synthesized on

the mixture by combinatorial ion beam sputtering system.

- Under Ar atmosphere in a glove box, the catalysts and hydride material were transferred to a reactor cell fitted with an optical window.
- Each catalyst library was screened for dehydrogenation and hydrogenation. The temperature profile of optical property variations matched previously reported results well for the known catalyst. This supports the validity of the screening methodology.
  - The catalyst libraries were heated at 5°C/min up to 350°C in 1.5 atm H_2. The optical properties of libraries were monitored but no changes were observed, confirming the stability of the system under H_2 pressure. Alternatively, the samples were also heated under Ar at 3°C/min up to 170°C and then at 1°C/min up to 250°C. Temperature was held at 250°C for 20 minutes before cooling. Among the catalysts screened, a few showed obvious changes in optical properties. Out of those, a few examples are shown in Figure 1.
  - The temperatures and pressures were varied widely from high to low to moderate for more experimental results.
- It was found that nano-Mn and nano-Ni were effective dehydrogenation catalysts from our preliminary and thorough optical screening. Cu, Fe and a few others are determined to be non–effective catalysts for improving kinetics.
- Ni had previously been identified as the most effective catalyst by other groups prior to our work. Mn had not previously been reported as an effective catalyst for this system. HRL confirmed our Mn catalyst results, as depicted in Figure 2.
  - Catalyst screening for Mg_2Si hydrogenation was also performed. More than 20 catalysts were screened e.g., Mn, Ni, Ti, V, Cr, Nb, Pt, etc. and combinatorial alloys of the same. Unfortunately, none of the catalysts screened were found to be effective for hydrogenation of the material system.
  - Since the system does not hydrogenate, further work on it was suspended (no-go).
  - In another approach, we synthesized a thin film of Mg to make MgH_2. To confirm the formation of MgH_2, we utilized optical imaging technique as well as reflectivity measurement. The results are shown in Figure 3.

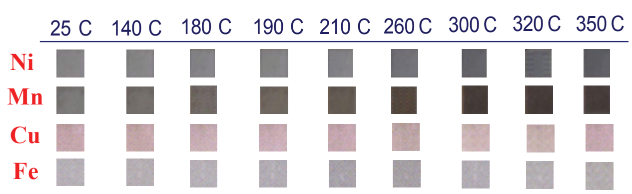

FIGURE 1. Temperature vs. optical images of various catalysts incorporated on the MgH_2+Si system. A color change of catalysts during high temperature/pressure dehydrogenation reaction suggests possible catalytic effect.

LiH+MgB_2 System ($LiBH_4$)

- Intematix is using a similar strategy for the LiH+MgB_2 system as was used for the MgH_2+Si system, and will continue to use this methodology for new metal hydride systems received from MHCoE partners.
- Typical optical screening results are shown in Figure 4, indicating potential catalytic activity of niobium and a chromium/manganese alloy.

Conclusion and Future Work

During this year, we validated our tools for combinatorial synthesis and high-throughput screening techniques on simple and complex metal hydride systems. We found a better catalyst for the MgH_2+Si system and down-selected the system because of its inability to be re-hydrogenated after dehydrogenation. We also found few lead catalysts for the LiH+MgB_2 system and will continue to search for better catalysts. The following lists the future work we will pursue:

- Continue combinatorial catalyst screening for the LiH+MgB_2 system after further characterizing the current catalyst library in collaboration with HRL (through December 2007).

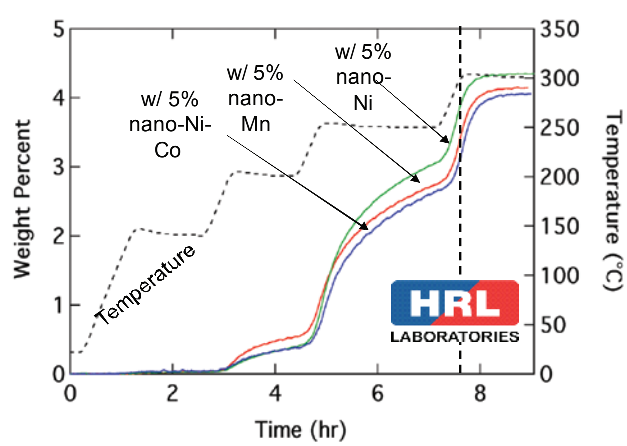

FIGURE 2. Effect of Nano-Mn and Nano-Ni Catalysts on MgH_2+Si Dehydrogenation Confirmed by HRL

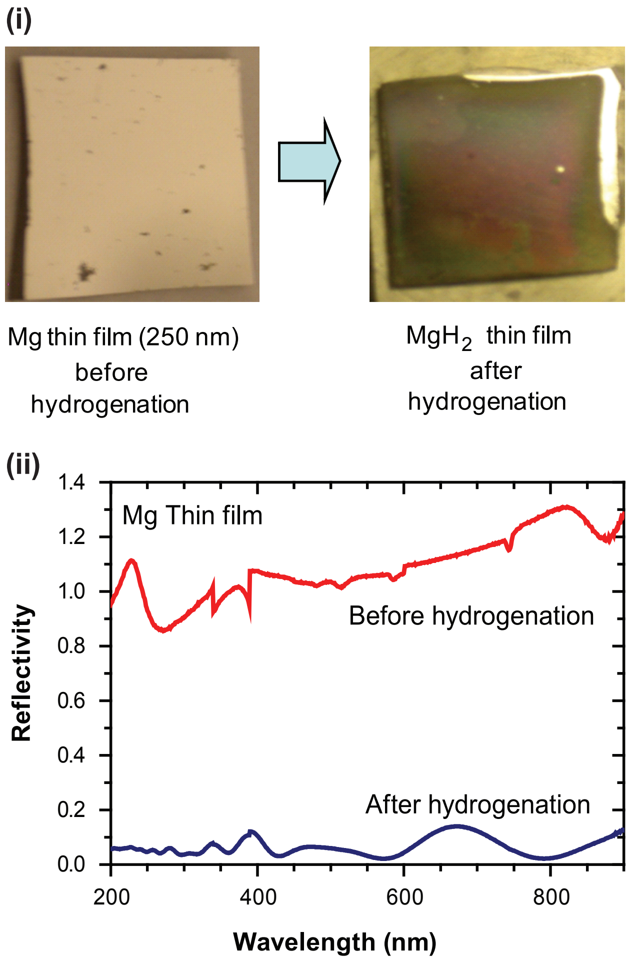

FIGURE 3. (i) Optical variation of Mg thin films before and after hydrogenation. (ii) Reflectivity measurements on Mg thin films before and after hydrogenation. The change in reflectivity corresponds to the incorporation of H_2 in Mg to form MgH_2.

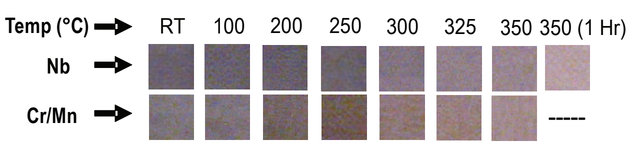

FIGURE 4. Temperature vs. optical images of various catalysts incorporated on the $LiH+MgB_2$ system. Color change during reaction suggests possible catalytic effect.

- Investigate HRL's observation that $LiBH_4+MgH_2$ melts during dehydrogenation by using Int*e*matix's tools. It has been realized that starting with this mixture for desorption does not give good reversibility because $LiBH_4$ melts (August 2007).
- Perform complementary characterization techniques such as *in situ* X-ray diffraction, Raman spectroscopy, and high-temperature/high-pressure testing of complex metal hydride thin films in collaboration with Sandia National Laboratories (SNL) (through March 2008).
- Synthesize $Ca(BH_4)_2$ thin films and screen catalysts using combinatorial sputtering technique, after determining the reaction kinetics for the hydrogen desorption from bulk $Ca(BH_4)_2$ (through March 2008).
- Conduct deposition of complex hydride and catalysts on micro-hotplates provided by SNL using combinatorial ion beam sputtering (September 2008).
- Perform combinatorial synthesis and search of new complex metal hydride systems and catalysts for new complex metal hydride materials (through September 2008).