IV.A.4e High Throughput Combinatorial Chemistry Development of Complex Metal Hydrides

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Introduction

This project is intended to identify and synthesize metal hydride systems, and identify catalysts to improve the kinetics of the hydride systems to meet DOE targets for on-board hydrogen storage systems. Hundreds of reactions were screened for hydrogen storage based on thermodynamic data; about ten reactions were identified having the potential to meet or close to DOE target of storage capacity. These reaction systems will provide directions for following experimental screening.

Meanwhile, combinatorial tools were upgraded for metal hydride and catalyst synthesis; and high throughput screening tools were built for reaction characterization. Nano-Mg_2Si has been synthesized and more than 20 catalysts have been screened for Mg_2Si hydrogenation.

Approach

Rational design was adopted for metal hydride and catalyst screening. First, metal hydride systems were screened based on thermodynamic calculations. Then, the identified metal hydrides were synthesized in an approach suitable for catalyst synthesis and screening. Finally, combinatorial catalyst synthesis and high throughput screening were used to identify effective catalysts for the targeted metal hydride system. First and third steps were carried out independently; second step was achieved by close collaboration with MHCoE partners.

Results

Metal hydride candidates were screened based on thermodynamic data provided by the HSC Chemistry® software. In the first step, the possible compounds with high hydrogen capacity were identified, and the equilibrium hydrogen pressure as a function of temperature was calculated. Most compounds identified in the first step have much higher hydrogen release temperatures than the DOE target. In the second step, compounds were selected to destabilize the candidates identified in the first step to lower the hydrogen release temperature. In such way, about ten reaction systems were selected with hydrogen release temperatures close to DOE targets. In addition, several hydride systems without thermodynamic data were estimated to have the potential to meet DOE targets. Most of the reaction systems currently under investigation in the MHCoE were "found" by this screening, including $LiBH_4$+MgH_2, MgH_2+Si, $Mg(BH_4)_2$, $NaAlH_4$ and Li-Mg-N-H, which proved the viability of this approach.

The experimental tools include a combinatorial thin-film synthesis system, a combinatorial nano-particle synthesis system, multiple high pressure and temperature catalyst screening systems, and a glove-box. Synthesizing the metal hydrides in the same system as the combinatorial catalyst synthesis creates the best contact between the hydrides and the catalysts; though this scenario poses stringent requirements for the synthesis tools, such as high temperature, high pressure and an oxygen-free environment. A comprehensive system upgrade was carried out to achieve such requirements. A new base station was constructed to support the glove-box in the same level as the loading-dock for the combinatorial thin-film synthesis system and a rigid transfer channel was constructed to connect the two. The loading dock for the combinatorial thin-film synthesis system was revised to allow sample transfer between glove-box and loading-dock under oxygen-free environment. A portable carrier was designed and assembled to allow sample transfer under oxygen-free environment between combinatorial nano-particle synthesis system and the glove-box.

Some metal hydride samples were obtained from partners due to the limitation of our synthesis capabilities. The hydrides received from the partners were in a format which did not allow combinatorial catalyst synthesis directly onto them. A new synthesis

process was designed to allow the combination and broaden our screening capabilities.

A high pressure and temperature reactor was built for catalyst screening. The reactor was designed in such way that it could be transferred in and out of globe-box for sample loading and unloading without exposing the sample to air. With an optical window, the reactor allows real-time and parallel metal hydride characterization, thus to achieve fast catalyst screening. The reactor can be operated under both pressurized hydrogen and vacuum, which helps to understand the reaction mechanism under different circumstances. A rigid cage was constructed to cover the reactor to contain broken pieces of glass in the event of a pressure burst from the reactor cell. The cage also keeps the reactor cell from overheating if a fire occurs outside. All electrical distribution has been verified to be in compliance with the National Electric Code and located outside the cage.

Vast efforts in the first year were devoted to metal hydride candidate screening using thermodynamic data and to the system upgrades mentioned above, which allow a smooth start of experimental metal hydride synthesis and catalyst screening.

Destabilization of MgH_2 by Si was chosen as the first system to work on. The destabilization has been successfully demonstrated to lower hydrogen release temperature and increase hydrogen pressure [1]; but the reverse reaction, Mg_2Si hydrogenation, has not been achieved yet. Catalyst screening was carried out at Intematix to search effective catalysts for Mg_2Si hydrogenation. As the first step, nano-Mg_2Si was synthesized in the same system as the one for catalyst synthesis. The stoichiometric ratio of Mg to Si was confirmed as 2:1 by Rutherford back scattering (RBS), as shown in Figure 1. X-ray diffraction (XRD) analysis only revealed Mg_2Si crystal formation on alumina substrate as shown in Figure 2. These results suggest that most Mg and Si in the sample are in the form of Mg_2Si.

In the second step, catalysts were synthesized in combinatorial fashion and were applied to the formed Mg_2Si under oxygen-free environment. The approaches used for Mg_2Si and catalyst synthesis provide close contact between each other. More than 20 catalysts have been screened, but to date no effective catalyst has been found for the hydrogenation reaction. More catalysts will be screened later on.

In parallel, catalysts are being screened for MgH_2+Si dehydrogenation. A ball-milled MgH_2+Si mixture without catalyst was obtained from HRL. By using the newly designed process, the mixture was successfully implemented into a structure and loaded into the combinatorial catalyst synthesis system. Catalysts were then synthesized onto the mixture in combinatorial

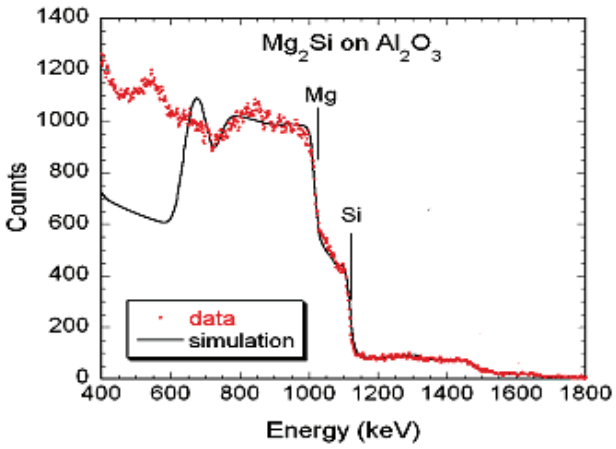

FIGURE 1. Composition Analysis of Prepared Mg_2Si on Al_2O_3 Substrate by Rutherford Back Scattering

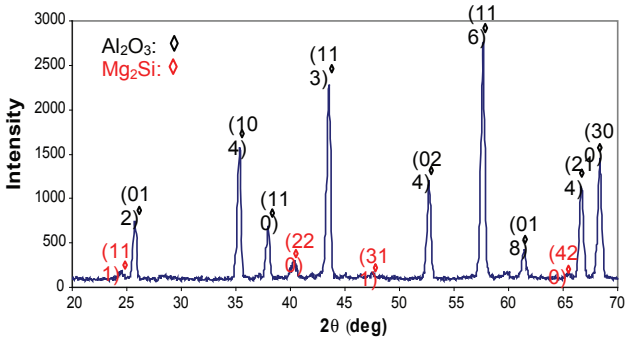

FIGURE 2. X-Ray Diffraction Analysis of Prepared Mg_2Si on Al_2O_3 Substrate

fashion. The catalysts' performance is currently under investigation.

Conclusions and Future Directions

Conclusions

1. Using thermodynamic data for preliminary metal hydride screening is a very efficient approach.
2. Mg_2Si was successfully synthesized in the format suitable for the following combinatorial catalyst synthesis.
3. Catalysts were successfully synthesized in combinatorial fashion onto Mg_2Si, proving the feasibility of the combinatorial method.
4. No effective catalysts were identified during initial screening for Mg_2Si hydrogenation, suggesting a high barrier for the reaction.
5. A new process was designed to apply combinatorial catalyst synthesis to ball-milled metal hydrides.

Future Directions

1. Evaluate the feasibility of the new process to allow combinatorial catalyst synthesis onto metal hydrides obtained from partners.
2. Continue catalyst screening for Mg_2Si hydrogenation.
3. Continue catalyst screening for MgH_2 destabilization by Si.
4. Start catalyst screening for $LiBH_4 + MgH_2$ system.
5. Perform catalyst screening for $Mg(BH_4)_2$ and $Ca(BH_4)_2$ depending on synthesis progress at partner sites.

References

1. Vajo, J.J., et al., *Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH2 destabilized with Si.* Journal Of Physical Chemistry B, 2004. **108**(37): p. 13977-13983.