IV.B.4i Rapid Throughput Catalyst Synthesis and Testing for Chemical Hydrogen Storage

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Objectives

- Discover cost-effective catalysts for release of hydrogen from chemical hydrogen storage systems.
- Discover cost-effective catalysts for the regeneration of spent chemical hydrogen storage materials.

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) System Cost
(D) Durability/Operability
(E) Charging/Discharging Rates
(R) Regeneration Processes

Technical Targets

This project is conducting the search for effective, low-cost catalysts for hydrogen release from hydrogen storage materials. (Storage materials identified by Chemical Hydrogen Center of Excellence partners.) As the project progresses, the research will also encompass the search for effective, low-cost catalysts for the regeneration of spent hydrogen storage materials. Guidelines for the off-board regeneration of hydrogen storage materials have not been outlined. For hydrogen release, the DOE targets for 2007, 2010 and 2015 which this project can help address are:

- Minimum full flow rate: 0.02 g H_2/s/kW
- Fuel purity: 99.99% H_2
- Storage system cost: $6/kWh (2007)

Accomplishments

- Developed catalyst library screening methodologies, including air-free methods for screening of dehydrogenation vs. hydrolysis mechanisms.
- Screened hundreds of combinatorial compositions for $NaBH_4$ hydrolysis catalysis. Found several low-cost compositions with catalytic activity on par with ruthenium.
- Synthesized and tested several lead $NaBH_4$ hydrolysis catalysts on bulk scale (gram scale). Results validated microscale procedures: several low-cost catalysts found with activity on par with ruthenium and thus potential to help meet DOE targets.
- Screened hundreds of combinatorial compositions for catalytic H_2 release via NH_3BH_3 dehydrogenation. Found a few low-cost compositions with catalytic activity on par with ruthenium/$NaBH_4$ systems.
- Screened a hundred combinatorial compositions for catalytic H_2 release via NH_3BH_3 hydrolysis. Found a few low-cost compositions with catalytic activity on par with ruthenium/$NaBH_4$ systems.
- Screened a hundred combinatorial compositions for catalytic H_2 release via polyhedral borane hydrolysis.

Introduction

One important facet of hydrogen release in chemical hydrogen storage systems is the catalyst employed. Catalysts are known for many different storage systems, but the cost and availability of these metals (such as platinum and rhodium) makes their widespread implementation infeasible. The cost of the active catalyst itself could cost on the order of thousands of dollars per vehicle to be able to deliver the amounts of hydrogen required.

So long as the catalyst is able to catalyze the release of hydrogen, the amount of catalyst used can be increased to meet the required H_2 delivery rate (0.02 g H_2/s/kW). However, the amount of catalyst used will factor into the system weight (1.5 kWh/kg for 2007) and the system volume (1.2 kWh/L for 2007). The amount and cost of the catalyst will factor into the system cost ($6/kWh for 2007).

Approach

Intematix applies its proprietary combinatorial synthesis technologies (Figure 1) to create libraries of potential heterogeneous catalysts. These libraries will be made from both higher cost metals with known catalytic activity and lower cost metals. Libraries will then be qualitatively screened for catalytic activity using proprietary screening techniques. Lead candidates are measured quantitatively in a microreactor; the known catalytic materials are used as a standard. The best candidates are scaled up (from microgram to gram scale) for further testing.

Methodologies are first applied to the sodium borohydride hydrolysis system. Testing on this well-studied system enables validation of the hardware and techniques. Collaboration with other Center members helps establish reaction conditions and clarify reaction mechanisms, which can aid the process to regenerate spent fuel.

Results

Screening was carried out on numerous libraries with the sodium borohydride hydrolysis system, coupled with iterative feedback into the screening apparatus and techniques. Several hundred potential catalysts were screened, first with proprietary qualitative techniques and then in a microreactor to quantify the qualitative results. Some microreactor results are shown in Figure 2.

Roughly 100 catalyst compositions were screened for the ammonia borane hydrolysis system. A few compositions were found with appreciable catalytic activity. Hydrogen release was on par (within an order of magnitude) with that of ruthenium and sodium borohydride hydrolysis.

Several hundred catalyst compositions were screened for the ammonia borane dehydrogenation system. A few compositions were found with appreciable catalytic activity. Hydrogen release was on par with that of ruthenium and sodium borohydride hydrolysis. Some microreactor results are shown in Figure 3.

FIGURE 1. Intematix Corporation's Nano-Discovery Engine™

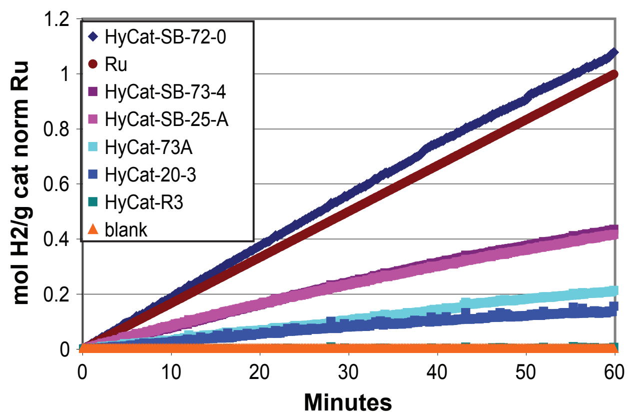

FIGURE 2. Selected $NaBH_4$ Hydrolysis Microreactor Screening Results

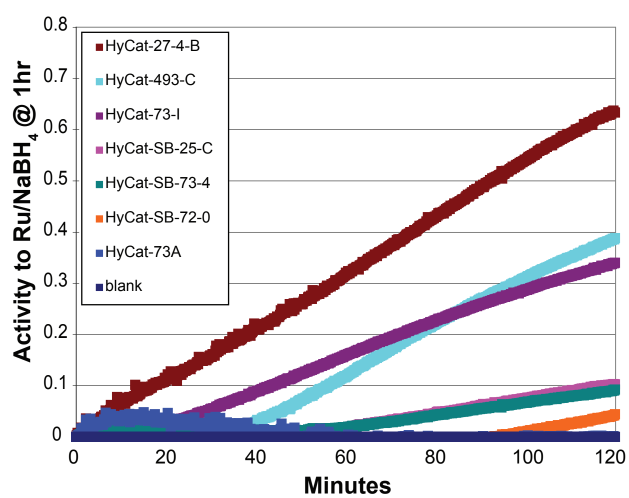

FIGURE 3. Selected NH_3BH_3 Dehydrogenation Screening Results

Scaled up testing of discovered sodium borohydride hydrolysis catalysts confirmed activity seen on the microscale. Ruthenium catalyzed the release of 2,400 mL/min/g catalyst, while three compositions were found to catalyze the release of at least 1,000 mL/min/g catalyst.

Calculations indicate that for a 75 kW power plant, H_2 supply must be 1.1 x 10^6 mL/min. Normalizing all values based on a ruthenium rate of 8,000 mL/min/g, gives three compositions with a normalized rate of at least 3,000 mL/min/g. An estimate of the amount of catalyst needed to meet the minimum H_2 rate and the cost of said catalyst, as outlined in Table 1, shows the potential to reduce the cost of the catalyst portion by more than $1,500.

TABLE 1. Catalysts for $NaBH_4$ Hydrolysis, with Cost Calculated from Current Alfa Catalogue

Catalyst	H_2 Release (mL/min/g catalyst)	g Active Catalyst Required for 75 kW	Cost of Active Catalyst
Ru	8.0 x 10^3	140	$1800
HyCat-SB-25-A	9.2 x 10^3	120	$50
HyCat-SB-72-1	8.0 x 10^3	140	$35
HyCat-SB-73-4	2.8 x 10^3	390	$125

Conclusions

Infrastructure has been created and validated for the discovery of catalysts for hydrogen release from chemical hydrogen storage materials. The catalyst discovery process has been validated on the well-known sodium borohydride hydrolysis system. Collaboration with Chemical Hydrogen Center of Excellence partners helped elucidate that ammonia borane hydrolysis was being measured, rather than dehydrogenation in some screenings.

Several lower cost catalysts have been found for hydrogen release from a variety of hydrogen storage systems. Catalysts for the sodium borohydride system have been confirmed on the bulk scale.

Future Directions

Screenings for ammonia borane dehydrogenation catalysts will continue, with emphasis on characterization of spent fuel. Now that the Hawthorne group has identified conditions under which hydrolysis catalysis of polyhedral boranes occurs, screening of catalyst libraries for these hydrolysis reactions will proceed. Additionally, as spent fuel regeneration schemes begin to be addressed, screening of catalyst libraries will commence.

FY 2006 Publications/Presentations

1. X. Xiang, "Combinatorial Development of Cost-Effective Catalysts for Solid State Hydride Materials," 2006 MRS Spring Meeting, San Francisco, CA, April 2006, EE6.5.