IV.B.5i Combinatorial Synthesis and High Throughput Screening of Effective Catalysts for Chemical Hydrides

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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 Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(R) Regeneration Processes

Technical Targets

This project involves the search for effective, low-cost catalysts for hydrogen release from hydrogen storage materials (storage materials identified by Chemical Hydrogen Storage Center of Excellence [CHSCoE] 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

- Screened ~300 combinatorial compositions for catalytic H_2 release via NH_3BH_3 dehydrogenation.
  - Libraries were generated by combining elements from both the precious metals group and lower cost transition metals from the 3rd, 4th and 5th rows of the periodic table, for example, binary compositions such as Co/Fe, Fe/Ni, Co/Ru, Fe/Pt, Ti/Ru, etc.
  - Libraries were screened at multiple temperatures.
  - Leads were generated for further catalyst testing.
- Adapted bulk testing metrology to anaerobic, anhydrous, and elevated temperature conditions dictated by system testing requirements.
  - Found a quick and efficient method to obtain more quantitative catalyst test results.
- Bulk tested several catalyst leads for NH_3BH_3 dehydrogenation.
  - Found approximately five low-cost compositions with appreciable catalytic activity.
  - Sent best candidate, Co-Rh alloy, along with a standard, Rh, to Los Alamos National Laboratory (LANL) for testing.

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Introduction

One important factor in hydrogen release from 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 use infeasible. Use of such precious group metals could push the cost of the active catalyst itself to something on the order of thousands of dollars per vehicle.

As 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, first in-house, and then at project partners' facilities.

FIGURE 1. Tools of the Intematix Discovery Engine

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

Results

Numerous libraries were screened for catalytic activity in the ammonia borane dehydrogenation system. Care was taken to exclude water and oxygen, in order to eliminate the erroneous assignment of hydrolysis results as dehydrogenation results. Concentration of AB in solution was kept low for the screenings in order to decrease the rate of thermal dehydrogenation relative to the rate of catalytic dehydrogenation. (Center results have shown catalytic dehydrogenation is first order, while thermal dehydrogenation is higher order.) In the initial phases of screening, libraries were constructed of binary combinations of precious group metals as well as lower cost metals from all over the periodic table. The intent is to include metals with known catalytic activity, as well as lower cost materials, which will decrease cost while maintaining or enhancing catalytic activity. The combinations may be alloys or simple mixtures depending on the materials used. Examples of binary compositions tested include Co/Fe, Fe/Ni, Co/Ru, Fe/Pt and Ti/Ru. Preliminary screenings were done at several temperatures. Room temperature screenings, as well as screenings at 50°C, showed little activity. Screenings between 70 and 80°C yielded several leads.

Catalyst candidates were examined in a 1 mL microreactor. The reactor was loaded with catalyst and 0.5 mL 5% NH_3BH_3 in diglyme in a glove-box. The reactor was then immersed in a 75°C oil bath, and pressure recorded as a function of time. The results of a non-catalyzed blank cell were subtracted to eliminate the effects of heating a solvent based material in a closed cell. The voltage output was then mathematically transformed into moles of H_2, via the calibration of the sensor and the ideal gas law. As was done in the room temperature validation work with sodium borohydride, selected "negative" leads were moved forward to the microreactor stage in addition to the positive leads. This was done to help validate the methodology on the new system, with the new (higher temperature) parameters. Several overlaid, normalized runs are shown in Figure 2.

Several positive and negative catalyst leads were prepared in bulk form and tested in a flask with the output directed through a mass flow controller. The reaction conditions were the same as for the microreactor work (75°C and 5% NH_3BH_3 in diglyme in a glove-box preparation). Results for instantaneous flow rates and integrated equivalents of hydrogen are shown in Figures 3 and 4 respectively. Rhodium on
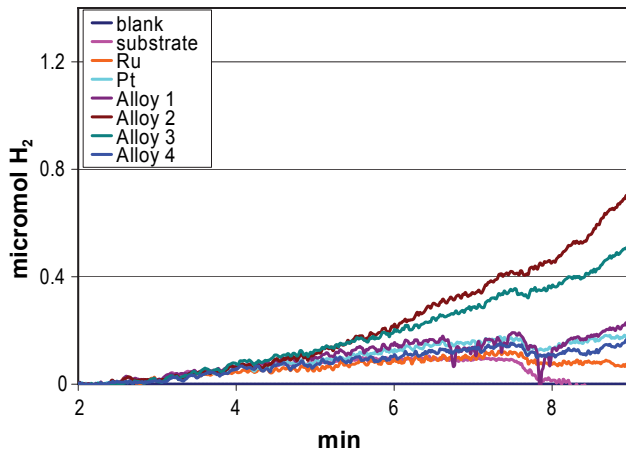
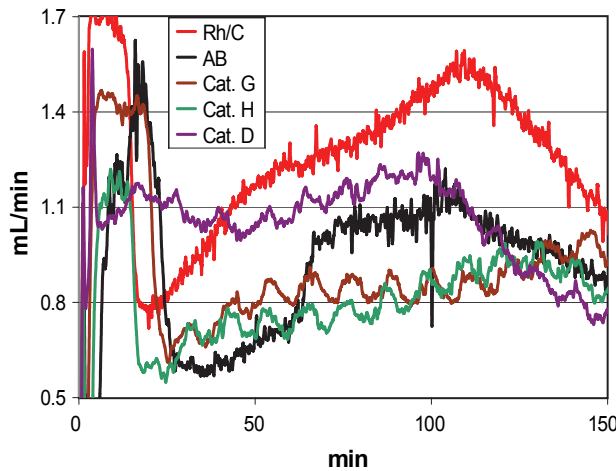**FIGURE 2.** H_2 Release from Microreactor Trials
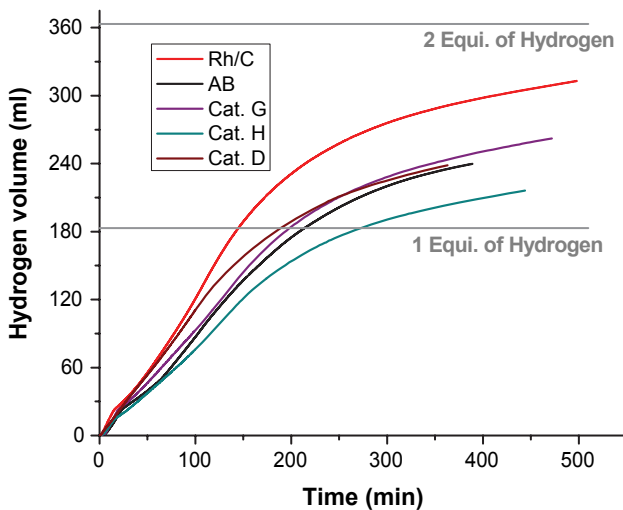

FIGURE 3. H_2 Release from Bulk Tests

FIGURE 4. Integrated H_2 Release from Bulk Tests

carbon was synthesized as a standard and shows the best performance both in terms of kinetics and overall amount of hydrogen released. Catalyst D (Co/Rh) shows the best activity of the other bulk catalysts tested, with hydrogen release rates far above pure AB. Catalyst G (Co on C) and catalyst H (Co/Fe) show activity which is only slightly better then AB thermal decomposition. Pure Ni on carbon (not pictured) appeared to slightly inhibit H_2 release from AB. All of these results are in line with the microreactor test results. Table 1 shows how NH_3BH_3 compares with CHSCoE goals.

Samples of Rh/C and Co/Rh/C were sent to CHSCoE partners at LANL for further testing.

TABLE 1. Current Metrics for NH_3BH_3 Compared to 2010 CHSCoE Goals

2010 DOE Target	Current Metric for NH_3BH_3	2010 CHSCoE Goal
System Gravimetric Capacity (6 wt%)	0.033g H_2/21 g solution (5 wt%), catalyst, flask *0.16% H_2 storage*	>6.0 wt% Phase I: Material Phase II: System-2010 Phase II: 9% Material-2015
System Volumetric Capacity 0.045 kg/L	3.3E-5 kgH_2/5E-3L *0.0066 kg/L*	>0.045 kg/L Phase I: Material Phase II: System-2010 Phase II: 0.060 Material-2015
Amount of active catalyst to achieve H_2 flow rate of 0.02 (g/s)/kW for a 80 kW stack assuming no other limit (note: amount of catalyst will decrease as solution concentration increases)	3.3E-4 mol H_2/g cat/s *2.4 kg active catalyst*	
Reactor volume under same conditions	5,000 L	

Note: dilute solution, 5 wt% solution, 1% active catalyst to AB (0.05% to solution) and relatively low temperature give misleadingly low performance metrics.

Conclusions and Future Directions

- Leads for NH_3BH_3 dehydrogenation catalysis were generated from library screening.
- Positive and negative leads were further characterized via microreactor screening.
- Positive and negative leads from microreactor screening were confirmed in bulk tests.
- Base metal catalysis observed.
- Base metal/rhodium alloy catalysis observed.
- Leads sent to partners for confirmation and further testing.

Future work

- AB dehydrogenation catalysis screening will continue.
- Positive catalyst leads will be sent to partners for:
    - Confirmation of catalytic activity.
    - Characterization of gas released.
    - Characterization of spent fuel.
- Catalyst screening for next generation AB storage:
    - Solutions containing initiators to increase rate
    - Mixed AB/MeAB systems.
- When regeneration effort produces a step which can benefit from catalysis, catalyst screening for that step will commence.