Combinatorial Synthesis and High Throughput Screening of Effective Catalysts for Chemical Hydrides

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Project ID # ST8

Overview

Timeline

- Start – Mar. 2005
- Finish – Sep. 2009
- 30% complete

Barriers

- Catalyst Cost
- System life-cycle
- Regeneration processes

Budget

- Total project funding
  - DOE share: $1,100K
  - Contractor share: $277K
- Funding received in FY05: $200K
- Funding for FY06: $300K

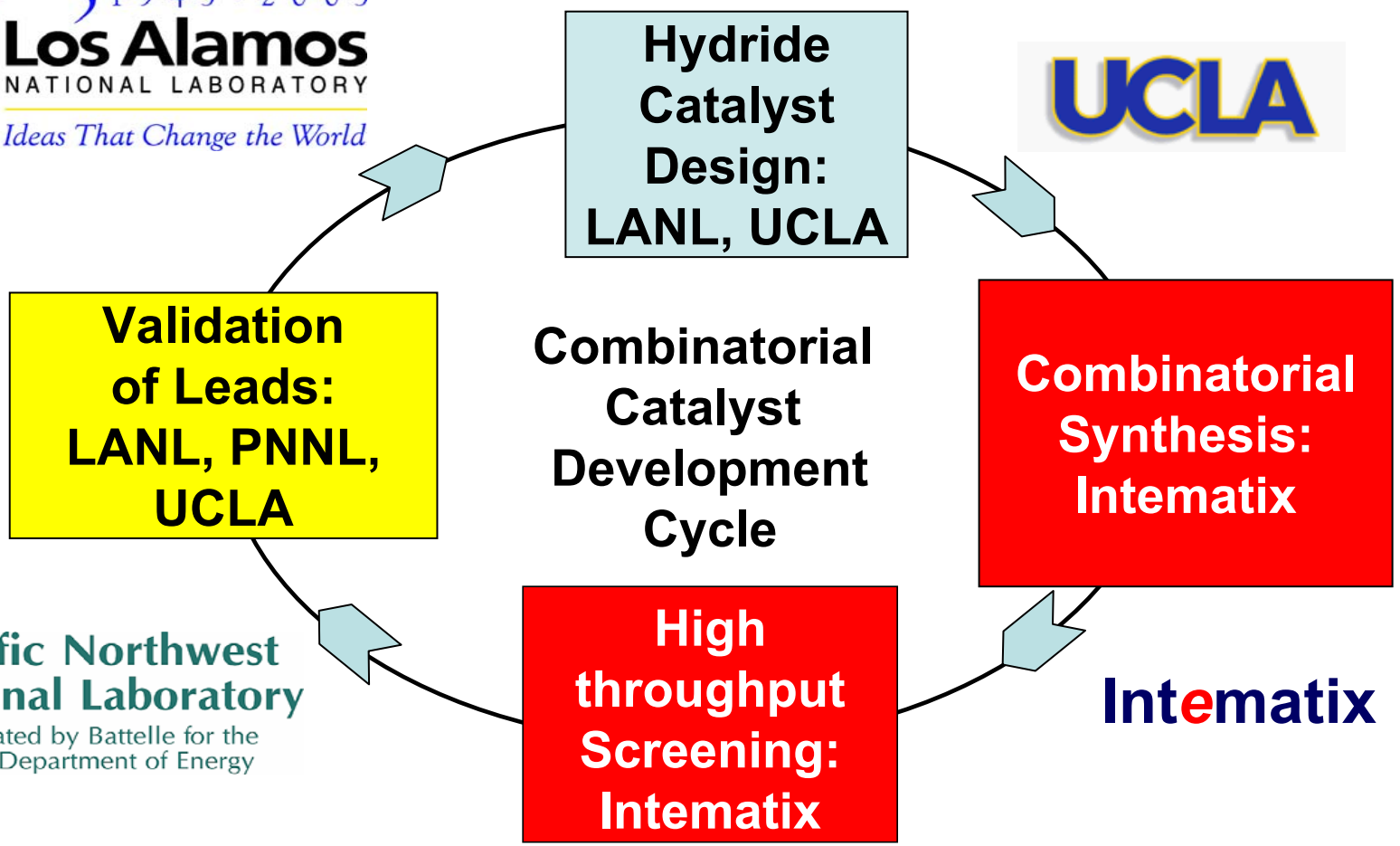
Partners

- Collaboration with PNNL, LANL, Penn, NAU on amine-boranes
- Collaboration with UCLA, PNNL, and LANL on novel polyhedral boranes
- Other collaborations with Center partners based on future discoveries

Objectives

Overall	Discover cost-effective catalysts for release of hydrogen from chemical hydrogen storage systems to enable deployment of on-board automotive hydrogen systems; and discover cost-effective catalysts for the regeneration of spent chemical hydrogen storage materials
2005	• Setup and validate combinatorial catalyst synthesis equipment • Setup and validate high throughput catalyst screening methodologies • Validate technologies on $NaBH_4$ hydroloysis system
2006	• Validate scale-up of catalyst from microgram to gram scale • Screen catalyst libraries for H_2 release from ammonia borane • Screen catalyst libraries for H_2 release from polyhedral boranes

Approach



1943 - 2003 Los Alamos NATIONAL LABORATORY *Ideas That Change the World*

UCLA

Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Intematix

Approach

- **Combinatorial Synthesis**
  - Intematix's proprietary combinatorial synthesis technology can efficiently generate hundreds of different catalyst compositions

- **High-throughput Screening**
  - Intematix's proprietary combinatorial high-throughput screening technology can efficiently test promising catalysts enabling rapid discovery and optimization of catalysts and catalyst composition

Approach

- Create combinatorial libraries consisting of both higher cost known catalytic metals and lower cost metals
- Qualitatively screen libraries for catalytic activity
- Quantitatively measure activity in microreactor
- Test scaled-up system to confirm bulk activity

Task Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Development of high-throughput screening and testing methods for in-situ monitoring hydrogen release from borohydrides or BNH compounds	03/01/06			95%	Ongoing
2	Development of high quality nanoparticle and thin films using combinatorial synthesis methods	02/01/06			90%	Ongoing
3	Synthesis and screening of hydrogen-release catalyst libraries (in nano-particle or/and thin-film forms)	03/01/08			35%	Ongoing
4	Synthesis and screening of hydrogen-release catalyst libraries	03/01/08			0%	Not started.
5	Characterization of materials properties of candidate catalysts	03/01/08			This task is in parallel with Tasks 1-4	Ongoing.

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

Accomplishments

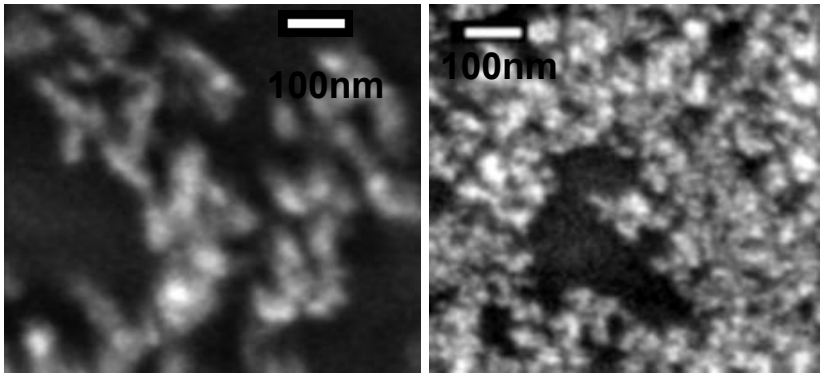
- Screened hundreds of combinatorial compositions for catalytic H_2 release via NH_3BH_3 dehydrogenation
  - Found a few low-cost compositions with catalytic activity on par with Ruthenium/$NaBH_4$ systems
- Screened a hundred combinatorial compositions for catalytic H_2 release via NH_3BH_3 hydrolysis
  - 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
  - Found little activity under neutral aqueous conditions

Catalyst Library Synthesis and Testing

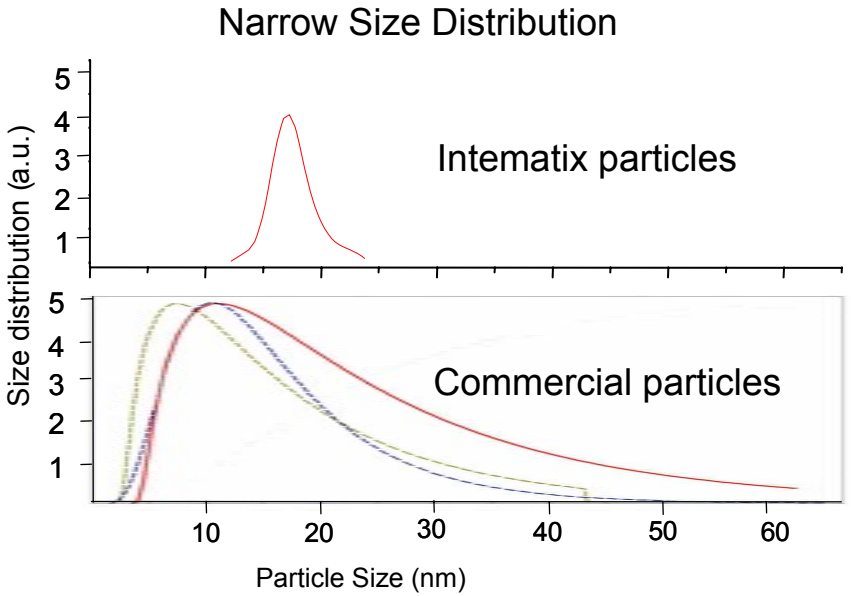
- Intematix Nano-Discovery Engine™
  - Generate nanoscale high surface area catalyst libraries for testing
  - Catalyst library samples can be handled under moisture-free environment
  - Handling under moisture-free environment enables differentiation between dehydrogenation and hydrolysis mechanisms (NH_3BH_3)
  - Proprietary screening of libraries for catalytic activity

- Lead candidates further validated in microreactor
- Rate of H_2 release is monitored by chamber gas pressure change

Example of Nano-Particle Libraries

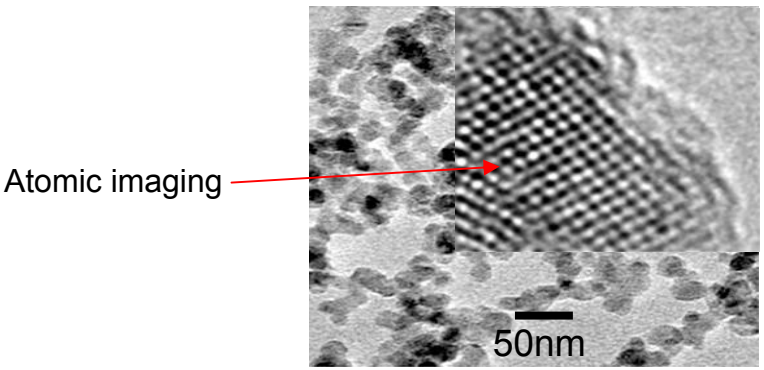


Particle size and morphology screening



- Precise particle size control enables direct correlation between size and property
- Broad size distributions can obscure size dependent properties
- Same size particles, different composition
- Same composition, different sizes

Intematix's High Quality Crystalline Nano-particles



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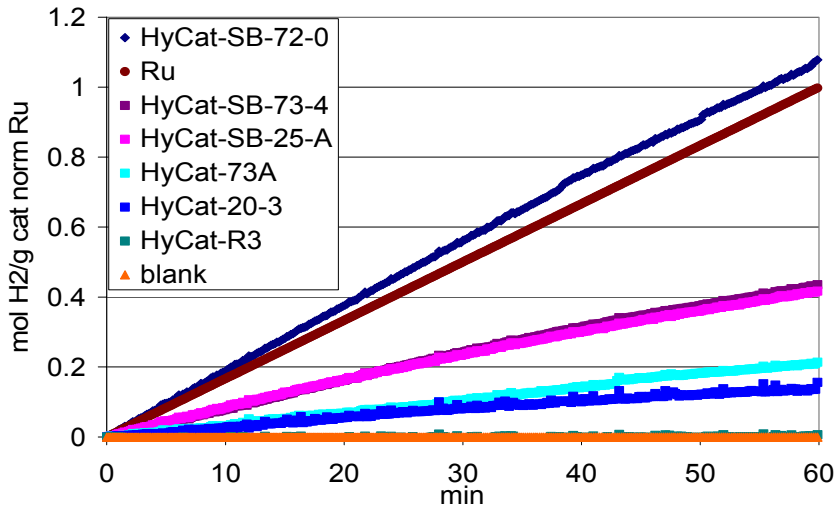
DOE Chemical Hydrogen Storage CENTER OF EXCELLENCE

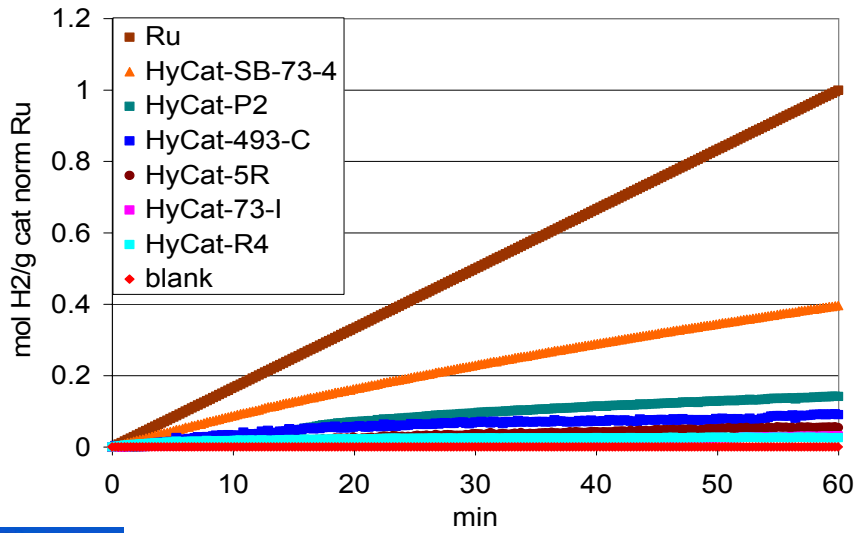
$NaBH_4$ Catalyst Screening

$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2$

Testing: 15% $NaBH_4$, 3% NaOH, aqueous

- Nano-catalyst libraries screened
- Positive and negative “hits” analyzed in microscale reactor
- Rates normalized to mol H_2/g Ru/Al_2O_3/hr.
- Several low cost catalysts identified





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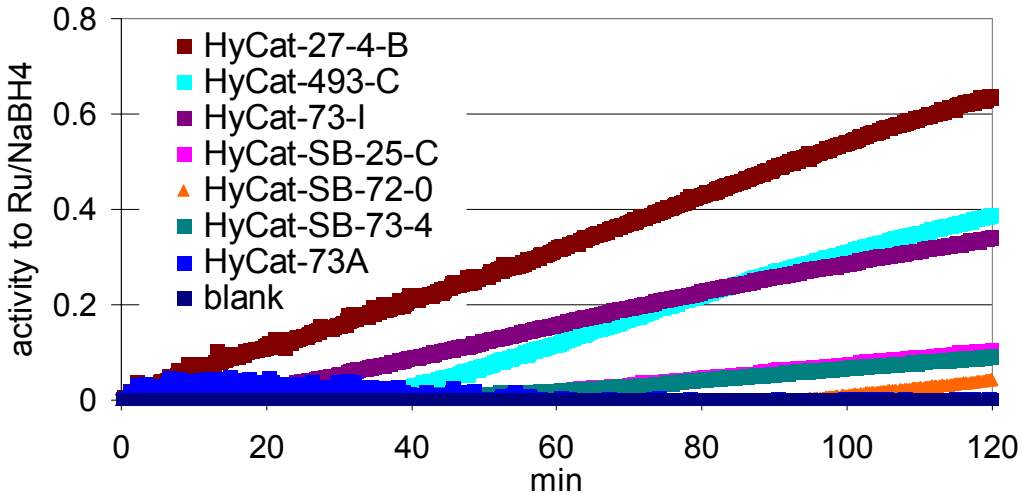
DOE Chemical Hydrogen Storage CENTER OF EXCELLENCE

NH_3BH_3 Dehydrogenation Catalyst Screening

$$NH_3BH_3 \rightarrow \text{“NH}\equiv\text{BH”} + 2H_2$$

Stoich: wt% TBD, <13.1%

- At least three lower cost catalysts identified
- Appreciable activity (15-30% $Ru/NaBH_4$) for dehydrogenation
- Potential to meet DOE release rate targets



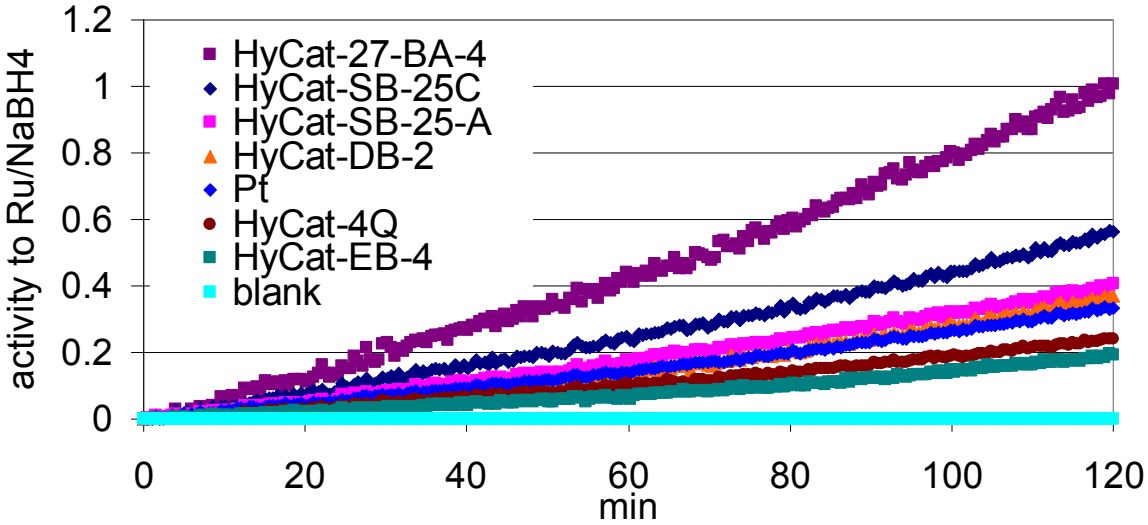
- Test conditions, 5% NH_3BH_3 in dry, organic solvent, under Ar
- Rates normalized to $Ru/NaBH_4$

NH_3BH_3 Hydrolysis Catalyst Screening

$$NH_3BH_3 + 4H_2O \rightarrow NH_4^+ + B(OH)_4^- + 3H_2$$

Stoich: 5.9 wt.% H_2 @ 30 wt.% NH_3BH_3

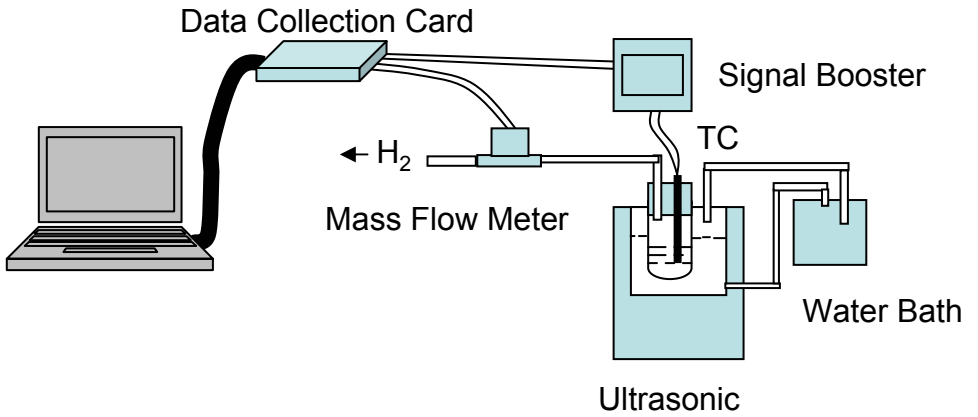
- Several inexpensive catalysts identified
- Appreciable catalytic activity for hydrolysis
- Potential to meet DOE release rate targets



- Test conditions, 9% NH_3BH_3 in wet organic solvent
- Rates normalized to $Ru/NaBH_4$

Bulk Testing – $NaBH_4$ Catalysis

- Bulk testing confirms catalytic activity on par with Ru
- Several low-cost catalysts confirmed with appreciable catalytic activity (35 – 115% Ru)



Catalyst	Rate H_2 (ml/min/g)
Ru/Al_2O_3	2400
HyCat-SB-25-A	2750
HyCat-SB-72-0	1750
HyCat-SB-72-1	2400
HyCat-SB-73-4	830

H_2 Release Catalysts On-Board

DOE/FreedomCar Target: 0.02 g H_2/s/kW

- For 75 kW power plant: 1.1 x 10^6 mL H_2/min

Catalyst	H_2 release* (mL/min/g catalyst)	g active catalyst required	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

*Scaled to known value for Ru, **Based on constituent element pricing @ Alfa Aesar

Results Summary

- Several lower cost catalysts have been found for each of a variety of chemical hydrogen storage systems
  - $NaBH_4$: Bulk testing has confirmed catalytic activity on par with Ru. Reduction of on-board system cost by >$1000 possible with new catalysts
  - NH_3BH_3: Several leads generated for each of dehydrogenation and hydrolysis. Collaboration with PNNL and LANL clarified the two different mechanisms. Bulk testing is in progress
- As per Center pathways, now that general conditions for Polyhedral Borane catalysis have been established, high throughput screening for discovery of lower cost catalysts can commence

Future Work

- $NaBH_4$ systems
  - Will continue to use this known system to validate next generation discovery methodologies
- NH_3BH_3 systems
  - Testing under scaled-up conditions to validate library and microreactor results for hydrogen release
  - Further catalyst optimization will be pursued in conjunction with PNNL and LANL collaboration on decomposition pathways related to catalyst composition (i.e. suppression of volatile B or N containing products)
  - Screening of catalysts for regeneration of spent NH_3BH_3, in conjunction with pathways developed by LANL and PNNL
- Polyhedral Borane systems
  - Will make use of recently discovered catalysis conditions (Hawthorne Group - UCLA) to screen for lower cost and/or more efficient catalysts
- Other systems and Regeneration
  - Intematix will assist in the screening of catalysts for hydrogen release from novel systems and regeneration reactions once those reactions are identified

Project Summary

Objective: Identify catalysts for (1) hydrogen release from chemical hydrogen storage systems and (2) regeneration of spent fuel, enabling an on-board hydrogen storage system which meets DOE 2010 targets

Approaches: Combinatorial catalyst synthesis and high throughput screening to reduce the time for catalyst discovery and identify more cost-effective catalysts

Technical Accomplishments and Progress:

- Combinatorial nano-catalyst synthesis apparatus assembled
- High throughput screening techniques developed and validated
- Bulk testing protocols using mass-flow controller established
- Low cost catalysts for $NaBH_4$ hydrolysis found, which help meet DOE 2010 targets for full flow rate (0.02 $gH_2/s/kW$) and system cost ($2/kWh)
- Generated several leads for catalysis of H_2 release from NH_3BH_3

Collaborations: PNNL and LANL on NH_3BH_3 H_2 release catalysis mechanisms. UCLA (Hawthorne group) on polyhedral borane H_2 release catalysis mechanisms.

Proposed Future Research:

- Bulk scale testing of catalysts for H_2 release from NH_3BH_3 systems
- Refinement of catalysts for H_2 release from NH_3BH_3 based on iterative feedback from partners' identification of decomposition products best suited for regeneration
- Catalyst discovery for H_2 release from polyhedral boranes using UCLA conditions
- Other systems – catalyst discovery for H_2 release and storage material regeneration

Publications and Presentations

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

Critical Assumptions and Issues

- Catalysis
  - Systems under study have been screened for thermodynamic feasibility of hydrogen release
  - Hydrogen release should be entropically favorable, therefore elevated temperatures should promote the H_2 release reaction
  - Screening method does not discriminate between H_2 release and other volatiles, such as borazine or ammonia. Partnership with PNNL and ^{11}BNMR can elucidate mechanism, once reaction is scaled up
- Technology scale-up
  - By screening for catalysts with heterogeneous systems, the scale-up from a micro-batch system to a bulk, flow based system can be proceed in a more straight forward manner
- Regeneration/cost of storage material
  - The ability to lower the cost of the storage material through effective regeneration may make these solutions more feasible than a disposable storage material would be