DOE Hydrogen Program

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

Jonathan Melman, Yanfeng Chen and Xiao-Dong Xiang
Intematix Corporation
Fremont, CA

May 16, 2007

Project ID # STP13

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start – Mar. 2005
- Finish – Feb. 2010
- 45% complete

Barriers

- System Cost
- System weight and volume
- H_2 discharge rate
- Regeneration processes

Budget

- Total project funding
  - DOE share: $1,579K
  - Contractor share: $395K
- Funding received in FY06: $300K
- Funding for FY07: $300K

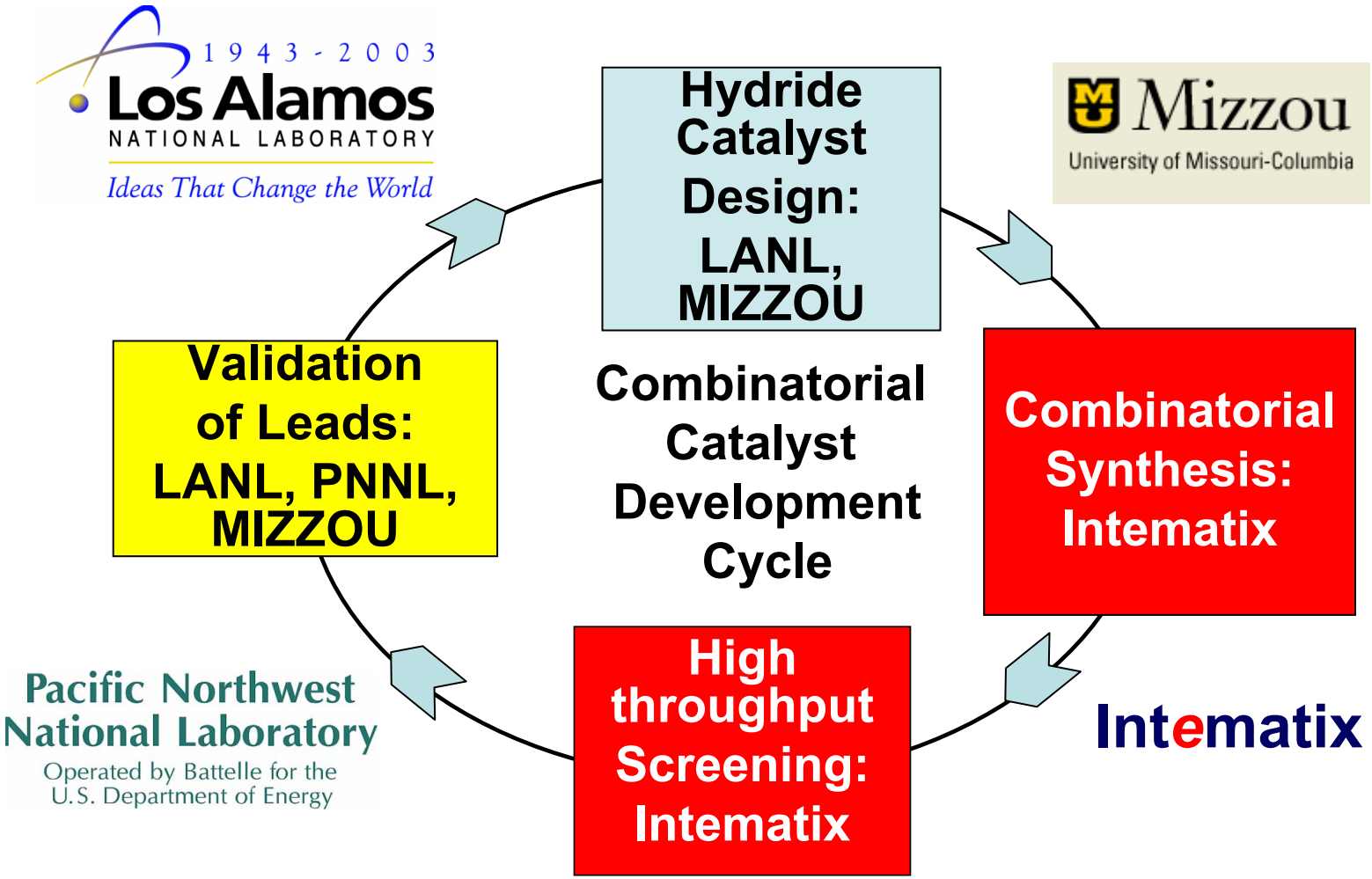
Partners

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

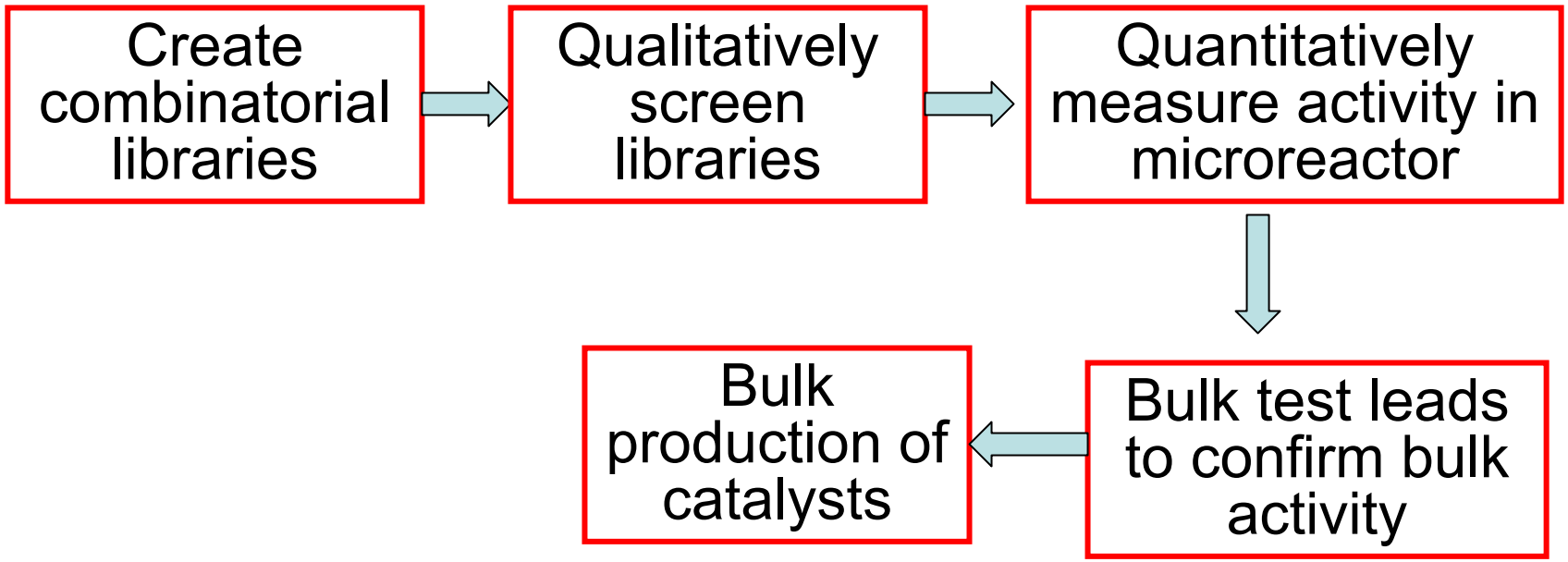
Objectives

Overall	Discover cost-effective catalysts for release of hydrogen from chemical hydrogen storage systems; and discover cost-effective catalysts for the regeneration of spent storage materials • Low cost to meet Storage systems cost targets $4/kWh (2010) • High rate to meet system discharge rates of 0.02 g/s/kW
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
2007	• Synthesis and screening of hydrogen-release catalyst libraries (in nano-particle and thin-film forms) to identify catalyst leads • Bulk tests of catalyst leads on gram scale to confirm scale-up • Bulk production of chosen catalyst leads for further study among Center partners

Approach

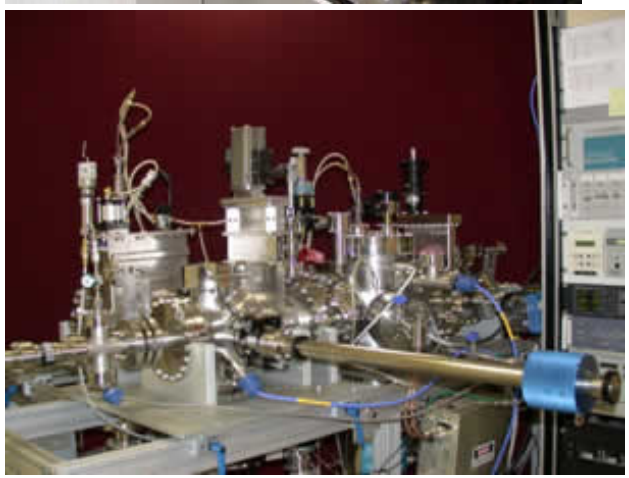

1943 - 2003
Los Alamos
NATIONAL LABORATORY
Ideas That Change the World
Hydride Catalyst Design: LANL, MIZZOU
Mizzou
University of Missouri-Columbia
Combinatorial Catalyst Development Cycle
Validation of Leads: LANL, PNNL, MIZZOU
Combinatorial Synthesis: Intematix
High throughput Screening: Intematix
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
Intematix

Approach


Create combinatorial libraries
Qualitatively screen libraries
Quantitatively measure activity in microreactor
Bulk test leads to confirm bulk activity
Bulk production of catalysts

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



Accomplishments

- Screened ~300 hundred 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
  - Generated leads for further catalyst testing

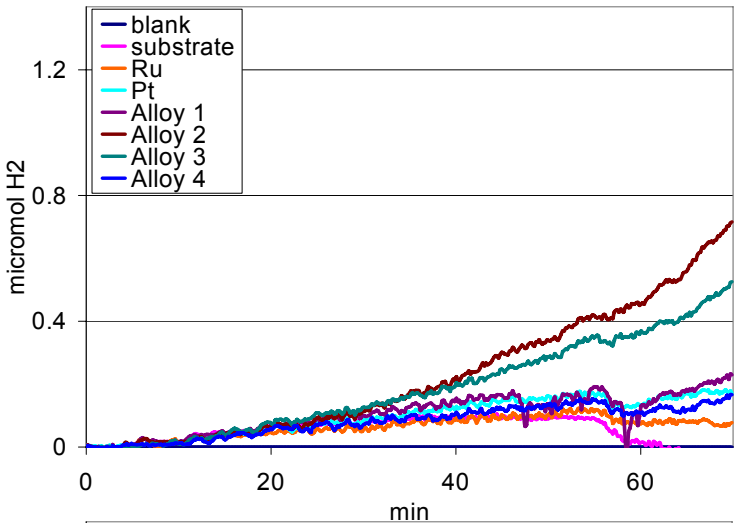
- Adapted bulk test metrology for anaerobic, anhydrous and elevated temperature conditions dictated by system testing requirements
  - Found a quick and efficient method to obtain more quantitative catalyst test results

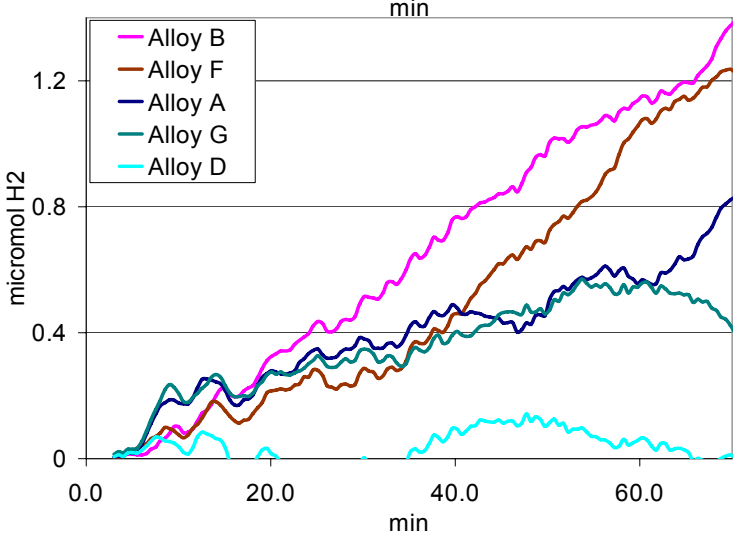
- Bulk tested several catalyst leads for NH_3BH_3 dehydrogenation
  - Found ~5 low-cost compositions with appreciable catalytic activity
  - Sent best candidate, Co-Rh alloy, along with a standard, Rh, to LANL for testing

NH_3BH_3 Dehydrogenation Catalyst Screening

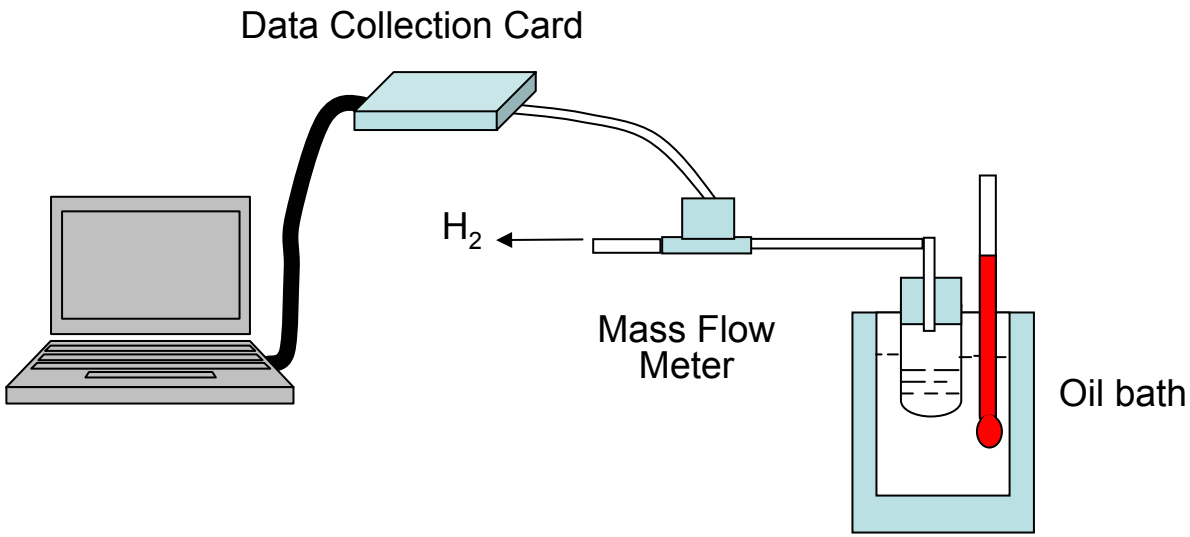
- Performed library and microreactor screening at elevated temperature NH_3BH/diglyme to generate leads
- Sealed cell pressure increase measured @ 70-75ºC, 5% NH_3BH_3/diglyme
- Dilute solution used to enable measurement of catalysis (roughly 1st order) vs. thermal dehydrogenation (roughly 2nd order)
- A few examples shown

- **Catalyst leads generated**





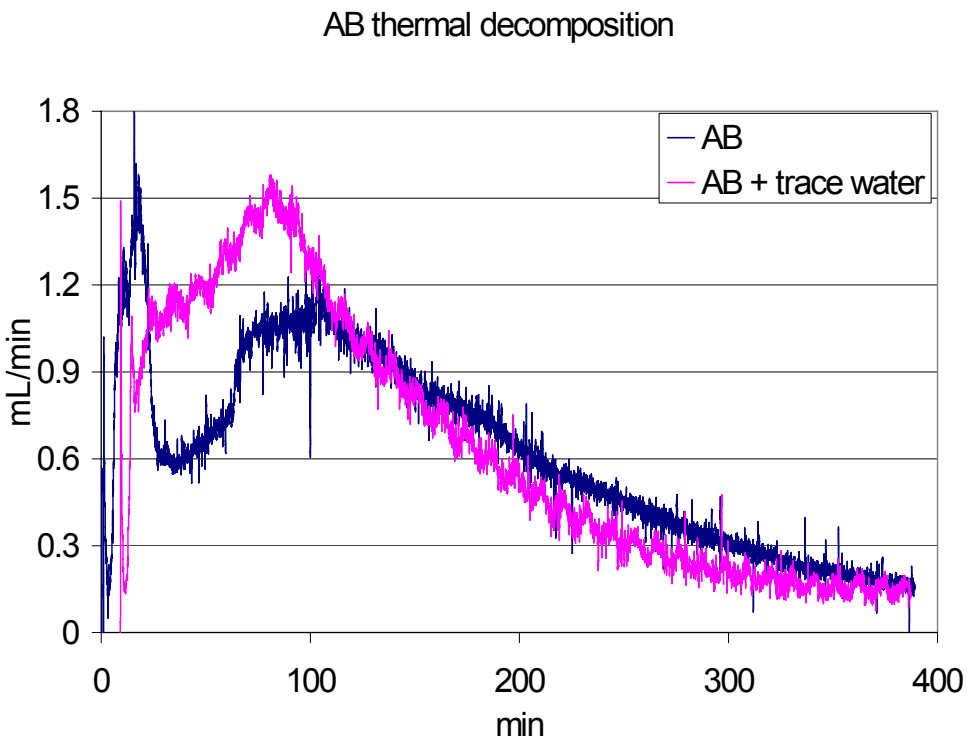
Bulk Test of Catalysts for NH_3BH_3 Dehydrogenation



- A large oil bath was held at temperature to quickly heat reaction
- Gas flow measured and recorded
- Bulk catalysts were prepared based on microreactor leads and tested

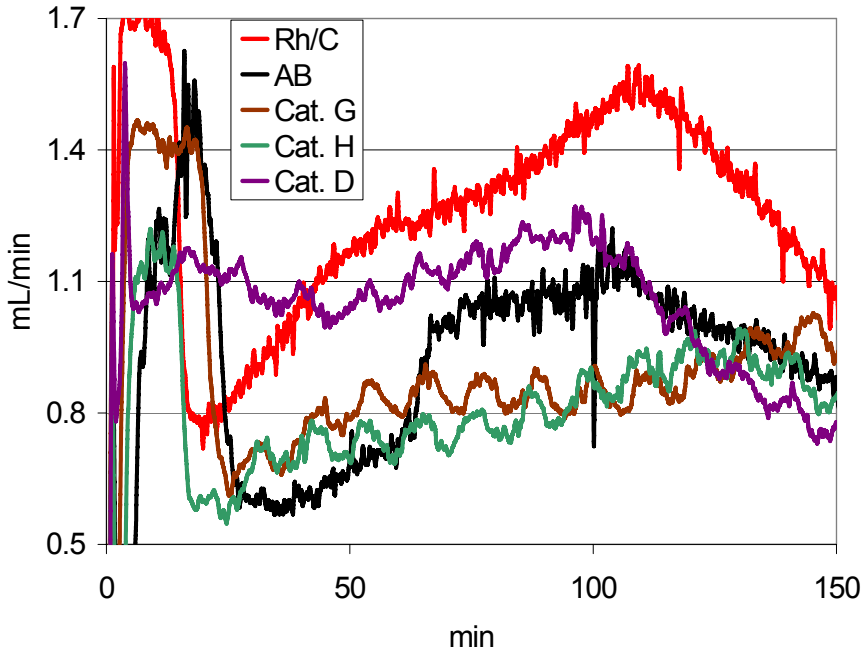
Bulk Test of NH_3BH_3 Dehydrogenation

- Samples were run of 5% wt ammonia borane in diglyme
- Same conditions used as microreactor screening (70°C)
- Trace water impurity, leading to hydrolysis, increases rate, and decreases incubation time of hydrogen release
- $NH_3BH_3 \rightarrow$ "NHΞBH" + $2H_2$
- $NH_3BH_3 + 4H_2O \rightarrow$
  $NH_4^+ + B(OH)_4^- + 3H_2$
- Formation of B-O bond bad for regeneration prospects



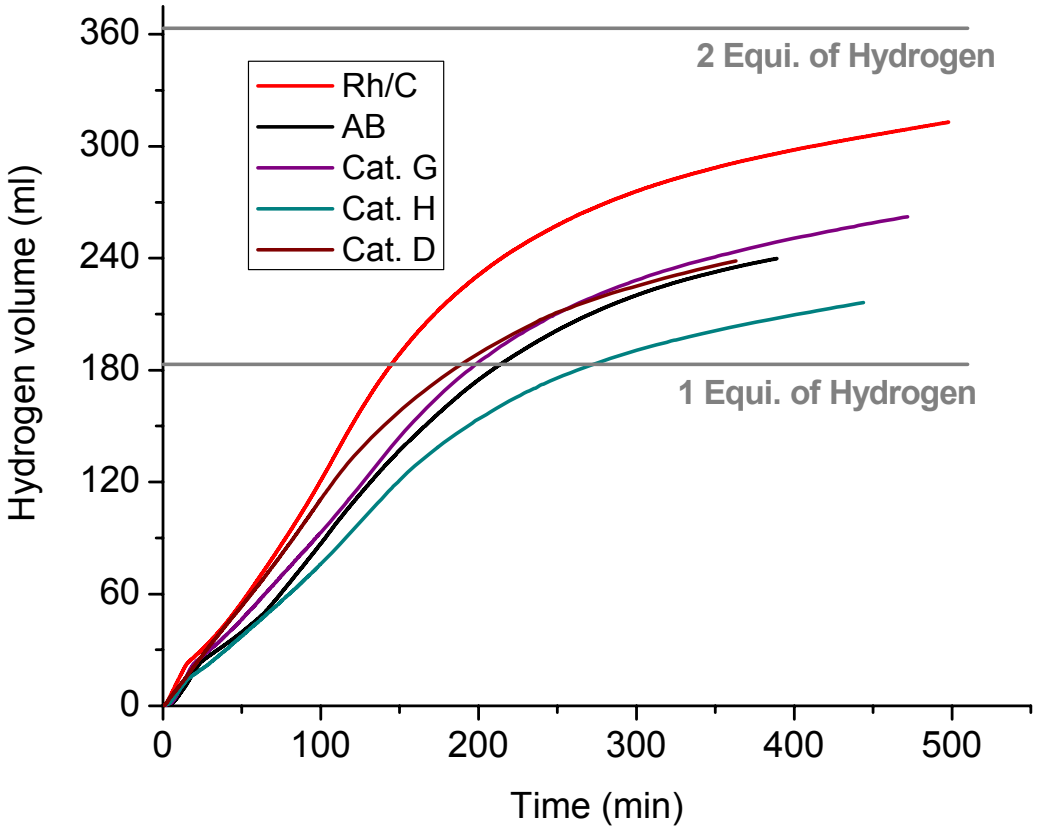
Bulk Test of Catalysts for NH_3BH_3 Dehydrogenation

- Bulk catalysts were prepared based on microreactor leads and tested in a flask (70°C) against Rh and thermal dehydrogenation of AB
- 0-20min data shows a surge which is less than 1 equivalent. Possible causes:
  - Degassing of solution
  - Expansion of gas in head-space upon heating
  - Mass flow controller calibrated to H_2, not N_2, which is the early gas pushed through the system
- **Cat. D (Co-Rh alloy) sent to LANL for validation and further testing**



NH_3BH_3 Dehydrogenation

Integrated Hydrogen Release



- Up to 3 equivalents of H_2 can be released for complete dehydrogenation, though lesser extents are preferrable for regeneration purposes
- Early in the reactions, catalyzed reactions release more H_2 than uncatalyzed
- After 7h at 70°C, 1.3-1.7 equivalents of H_2 were released for all the catalysts. Release rate decreases as concentration of NH_3BH_3 decreases.

Summary

- Leads for NH_3BH_3 generated from library screening were confirmed on bulk scale
- Base metal catalysis observed
- Base metal/rhodium alloy catalysis observed
- Leads sent to partners for confirmation and further testing

Summary - DOE Targets

2010 DOE TARGET	Current Metric for NH_3BH_3	2010 Center 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 H2 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 *2.4kg active catalyst*	
Reactor volume under same conditions	*5000L*	

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

Collaborations

- Los Alamos National Lab – AB mechanisms, reaction conditions, follow-up testing of catalysts for gaseous products. Regeneration catalysis (planned)
- Pacific Northwest National Lab – AB mechanisms, reaction conditions, follow-up testing of catalysts for identification of B containing products (planned)
- University of Missouri (planned) – H_2 release from Polyhedral Borane

Future work

- High-throughput in-situ catalysts screening for heterogeneous catalysts
  - H_2 release from solution phase systems:
    - NH_3BH_3; polyhedral boranes
    - Mixed RNH_2BH_3/NH_3BH_3 liquid systems
    - Next generation materials
  - H_2 release from solid phase systems:
    - $NH_3BH_3^*$; $NH_3B_3H_7$ (Penn)
    - Next generation materials
- Bulk tests of catalyst leads on gram scale and bulk production of chosen catalyst leads

- Regeneration: Identification of step(s) where catalysis will aid process

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:

- Several leads for alloy catalysts, both precious metal and non-precious metal containing of H_2 release from NH_3BH_3 were identified
- Leads for NH_3BH_3 generated from library screening were confirmed on bulk scale
- Base metal catalysis and base metal/rhodium alloy catalysis were observed

Collaborations: PNNL and LANL on NH_3BH_3 H_2 release catalysis mechanisms. University of Missouri (Fred Hawthorne) on polyhedral borane H_2 release catalysis mechanisms.

Proposed Future Research:

- 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 Mizzou conditions
- Other systems – catalyst discovery for H_2 release and storage material regeneration