Chemical Hydrogen Storage: Opportunities and Needs for Characterization and Rapid Throughput

Kevin Ott

Director, DOE Chemical Hydride Storage Center of Excellence

Team & Collaborators

Chemical Hydrogen Storage COE Partners

IPHE Partners

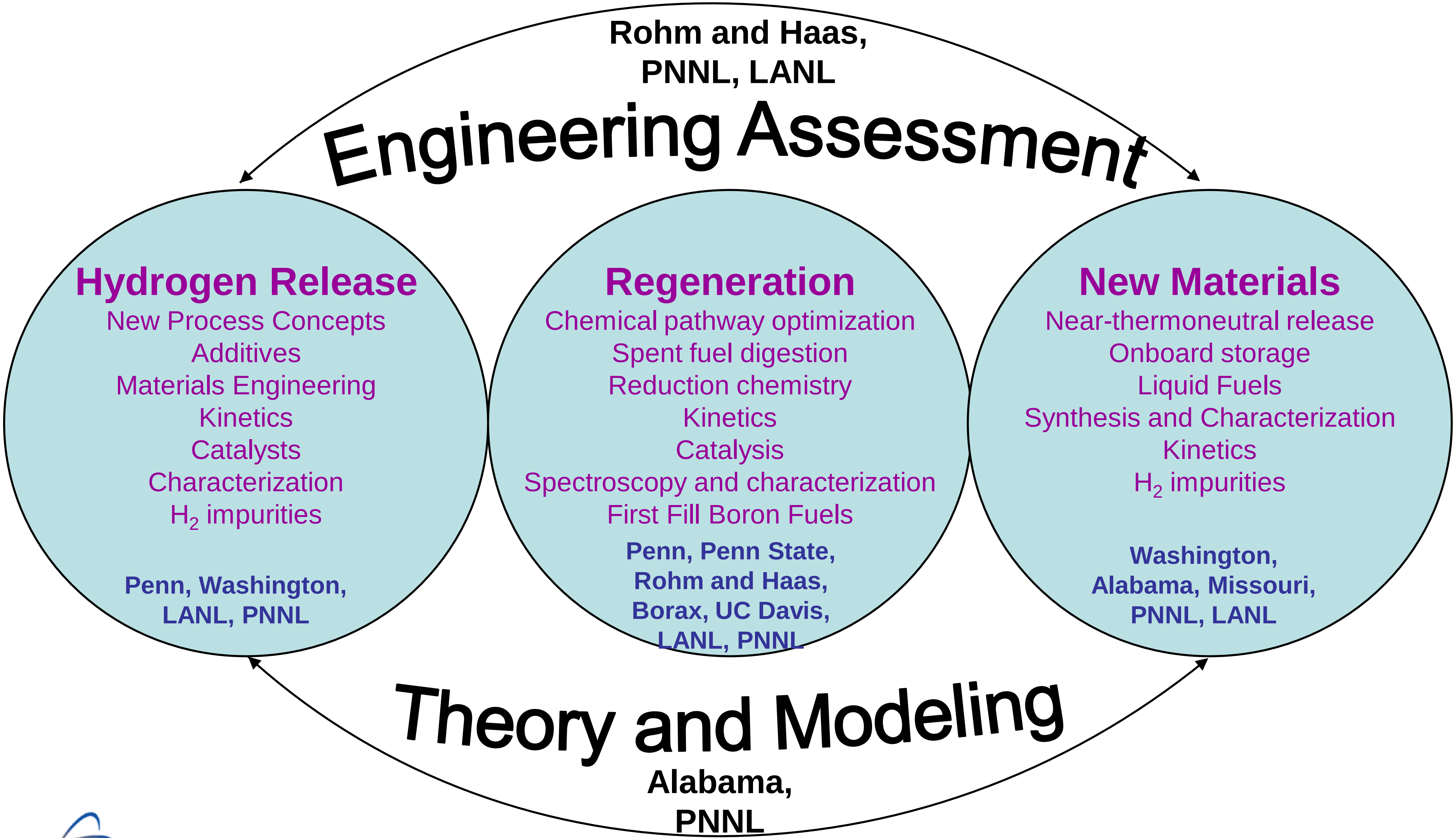
Discussion Topics

- Description of the chemical approach to hydrogen storage
- Examples of potentially viable chemical hydrogen storage compounds and - most critically – potential regeneration routes
- Suggestions of needs and potential opportunities in improved characterization and quantification of key chemical intermediates and products and
- Potential opportunities for enhancements of R&D output using high throughput approaches

Chemical Hydrogen Storage

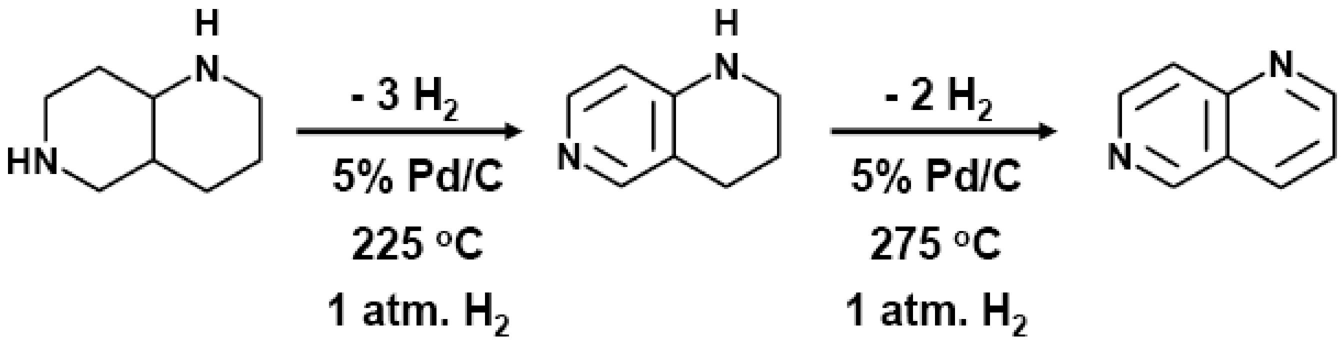
- Use of molecular, light element [E]-H_n compounds as a source of molecular hydrogen: [E]-$H_n \rightarrow$ [E] + n/2 H_2
  - Typically, strong and covalent bonds are involved
  - Variety of approaches to release of hydrogen from E-H_n
    - Thermolysis
    - Catalysis
    - Hydrolysis
    - Combinations
- Because the thermodynamics of many (most?) chemical hydrogen systems we are researching are more than a few kcal/mol downhill from thermoneutral,
- *Onboard regeneration is not feasible using hydrogen pressure* – Offboard chemical processing is required

Chemical Hydrogen Storage Center of Excellence



Examples of Chemical Hydrogen Storage Materials

- Prototypical chemical hydrogen storage (Millennium Cell)
  - $NaBH_4$ (aq) + $4H_2O \rightarrow NaB(OH)_4 + 4H_2$ [exothermic release]
- Amine boranes [exothermic release]:
  - $NH_3BH_3 \rightarrow$ "BHNH" + $2H_2$
  - $MeNH_2BH_3 \rightarrow$ "BHNMe" + $2H_2$
- Endothermic dehydrogenation of organic compounds (Air Products)



Amine Boranes as Storage Compounds

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes, ABs, are unique in their ability to store and release hydrogen while avoiding B-O formation

$$^{\delta-}H \quad H^{\delta+}$$

$$\text{AB: } H_2B\text{-}NH_2 \longrightarrow \text{--HB-NH--} + H_2$$

$$\text{AB: } H_3B\text{-}NH_3 \xrightarrow{-H_2} \text{cyclotriborazane} \xrightarrow{-H_2} \text{Borazine} \xrightarrow{-H_2} \text{Polyborazylene} \xrightarrow{-H_2} \text{‘BN’’}$$

	H_2 wt%, H_2 density (assumes conv. to ‘BN’)	properties
NH_4BH_4	24.5%, 0.2 kg-H_2/L;	Unstable
AB: NH_3BH_3	19.6, 0.16	Crystalline solid
Cyclotriborazane: $B_3N_3H_{12}$	14.9, 0.11	Crystalline solid
Borazine: $B_3N_3H_6$	7.5, 0.06	Liquid, bp 55 °C
AT: $NH_3B_3H_7$	17.8, 0.14	Crystalline solid
MeAB: $MeNH_2BH_3$	8.9, 0.08 (assuming $2H_2$/MeAB)	Solid, mp 55 °C

Release of H_2 from AB

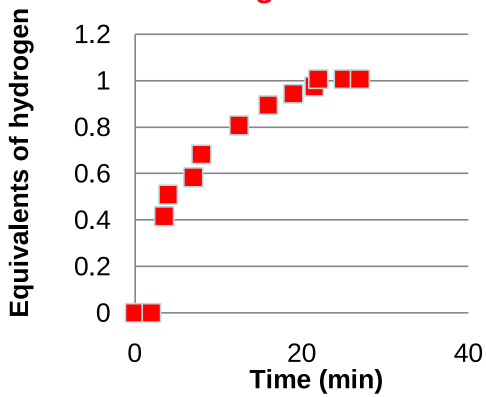
- Hydrolysis – but makes very stable B-O bonds = borates
- Thermolytic – proceeds rapidly and exothermically above ca. 90 °C; rapid to 2 mol H_2 at ca. 130 °C
- Desire is to reduce the temperature of release to better match fuel cell operating conditions [ca. 80 °C]
- Catalytic release of hydrogen
  - Homogeneous catalysts
  - Heterogeneous catalysts
- For solid AB – thermolysis
- For catalytic release – need a liquid fuel!
  - But cannot afford the weight penalty of a large quantity of an inert solvent

To complete the fuel cycle, must regenerate the fuel: onboard vs. offboard

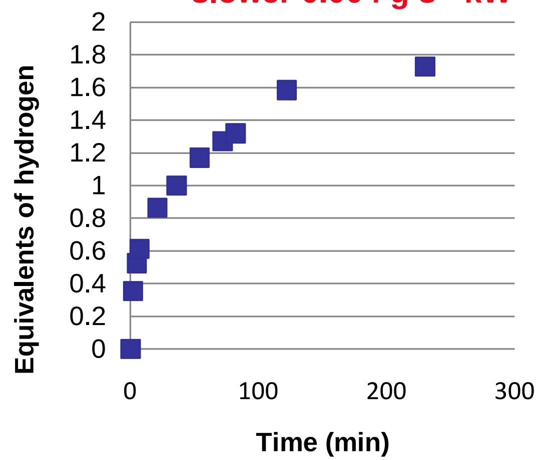
- Conventional reversible rehydrogenation of unsaturated organic compounds
  - Known catalytic processes, favorable energetics, etc.
  - Some potential for onboard regeneration
- Systems that are > 1kcal/mol H_2 exothermic on release cannot be regenerated with reasonable hydrogen pressures – offboard chemical processes are required
- $Na(BOH)_4 \rightarrow NaBH_4$
  - Energy intensive processes (e.g. Schlesinger)
- Regeneration of BNH_x – inventions are required
  - 6-8 kcal/mol uphill to ammonia borane (AB)

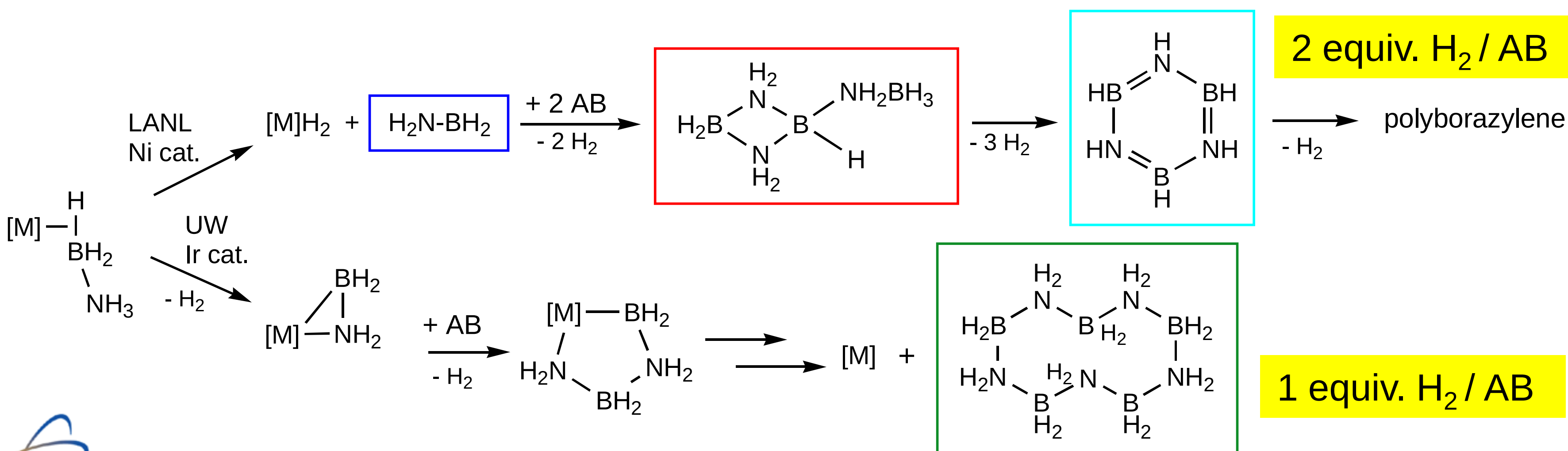
Subtle Changes in Catalyst Lead to Dramatic Change in Mechanism(s) of Release

$(dcpe)(dpen)Fe[N(SiMe_3)_2]$
Fast but only 1 Equiv. H_2
0.026 g s^{-1} kW^{-1}



$(PCy_3)_2Fe[N(SiMe_3)_2]_2$ > 1 H_2 but slower 0.004 g s^{-1} kW^{-1}



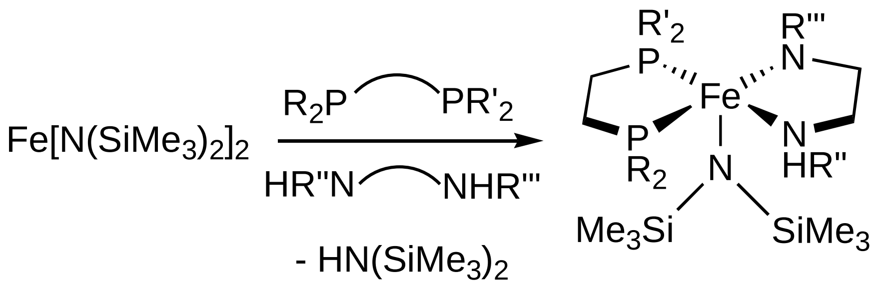


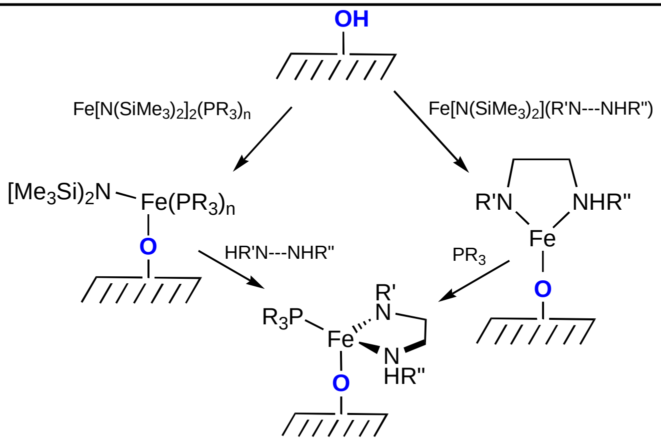
2 equiv. H_2 / AB

1 equiv. H_2 / AB

Baker, *et al* LANL

Potential for High Throughput Catalyst Discovery to Increase Rates, Extent of H_2 Release



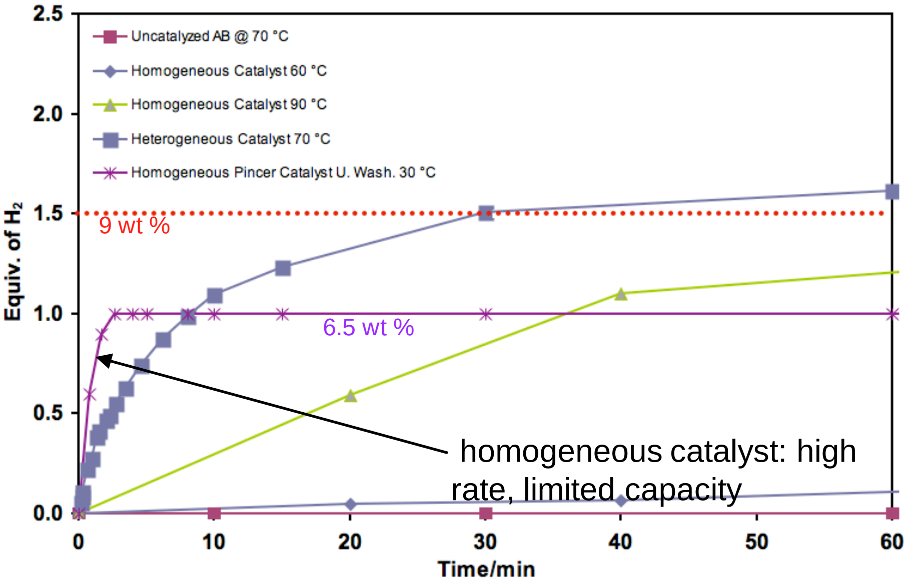


Route to Supported Iron Dehydrogenation Catalysts

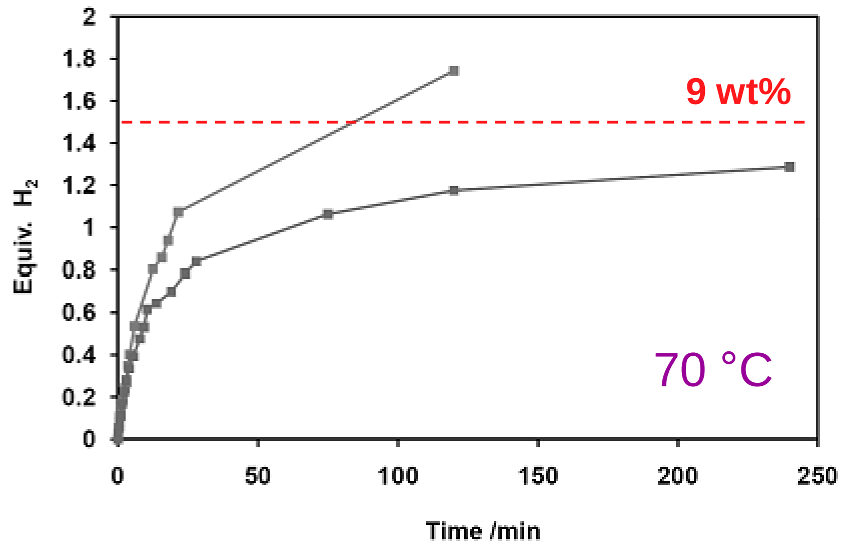
- Potential of improved rates of hydrogen release from new supported catalysts employing high throughput techniques

Charles Hamilton LANL

Identified Effective Heterogeneous Catalysis for the Release of H_2 with cleaner hydrogen stream



Non-precious metal catalyst identified!



- Potential to find additional non-precious metal catalysts with high rates and stability under continuous flow reaction conditions:
- Metal cation(s)
- Support properties

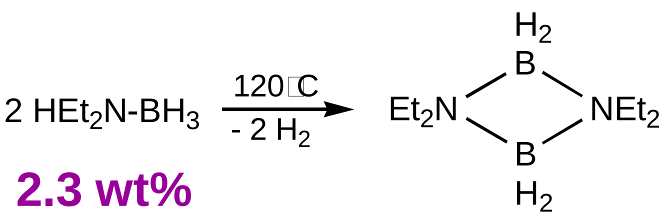
titanium	vanadium	chromium	manganese	iron	cobalt	nickel	copper	zinc
22	23	24	25	26	27	28	29	30
Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.39

Roshan Shrestha, LANL

New AB Fuels that are Liquid Down to -30 °C Have Been Found

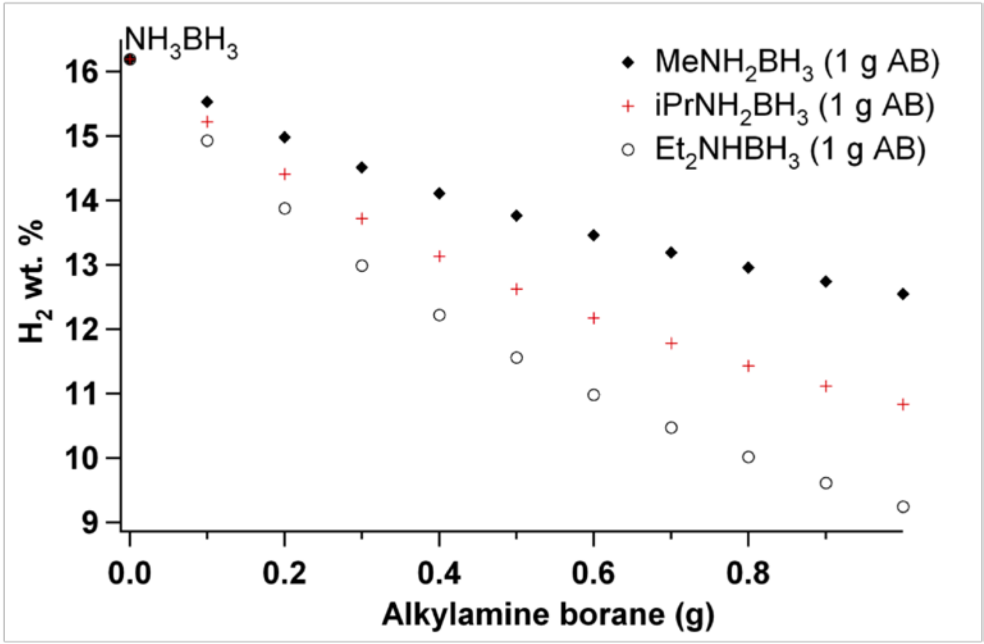
- Need to find good solvent systems for AB that may also contribute to hydrogen release

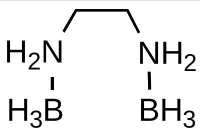
- Initial work using methylamine-borane was terminated due to volatility and instability of MeAB/AB containing liquid mixtures



2.3 wt%

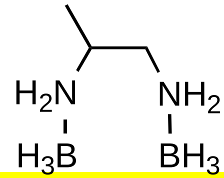
liquid **liquid**

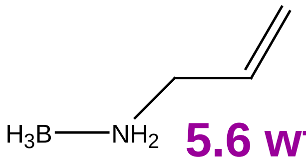




9.1 wt%

7.8 wt%



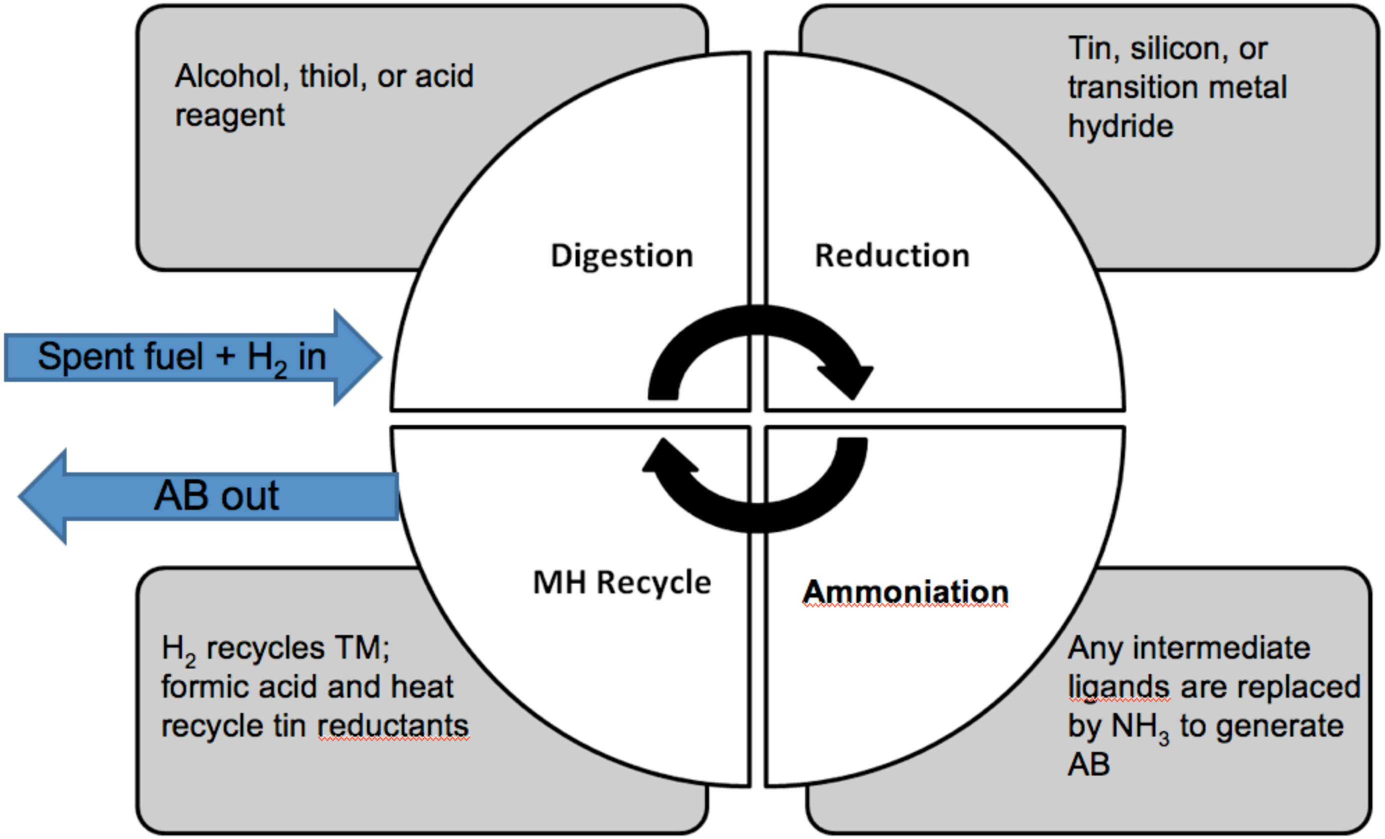


5.6 wt%

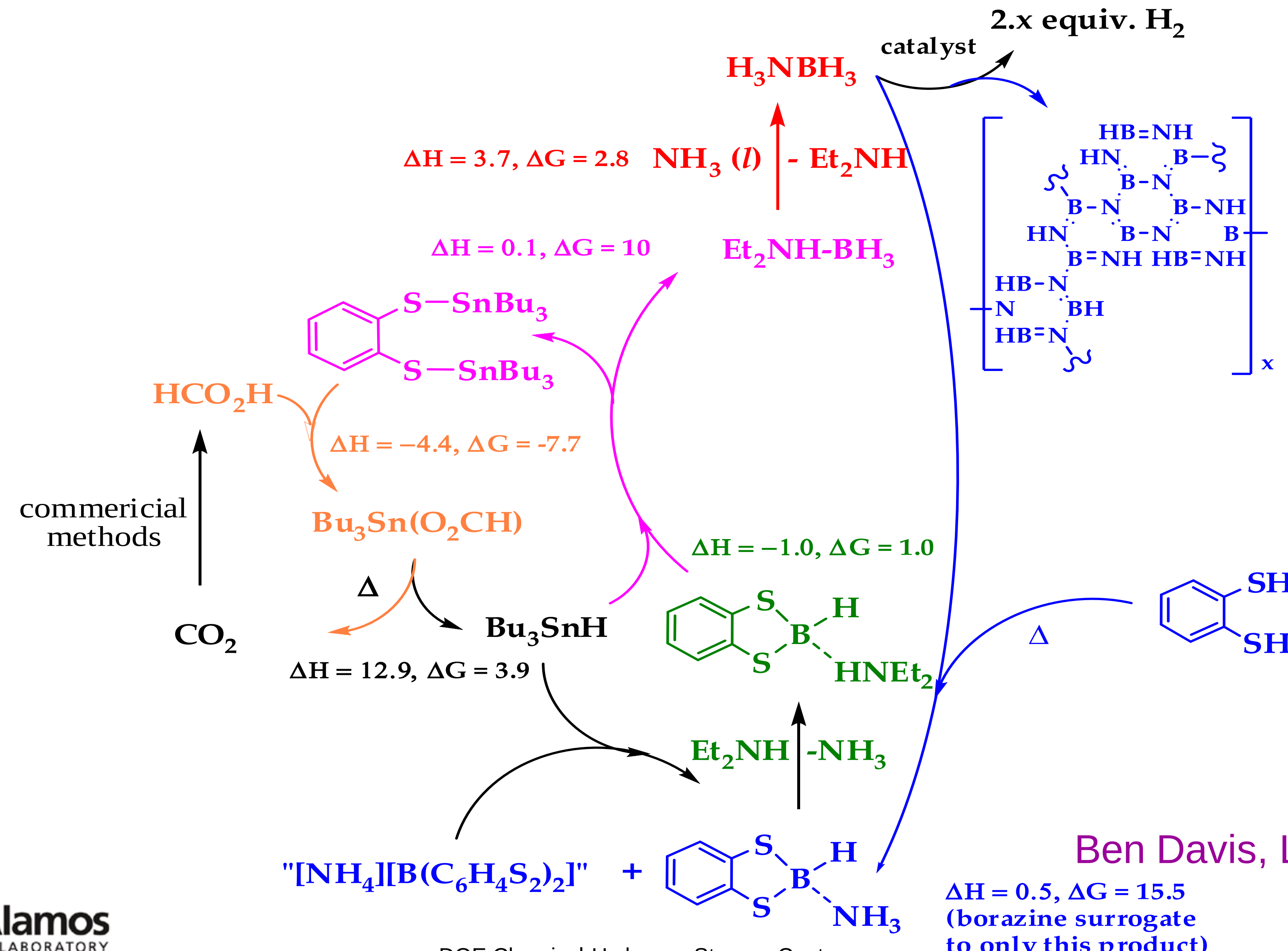
- Potential to optimize fuel mixture for highest wt% H_2 and target liquid range for fuel AND spent fuel using high throughput approaches

Spent Fuel Regeneration

- Chemical reprocessing of spent fuel is likely to be comprised of multiple steps. Using AB as an example:



One Route to Regeneration of AB Spent Fuel



Ben Davis, LANL

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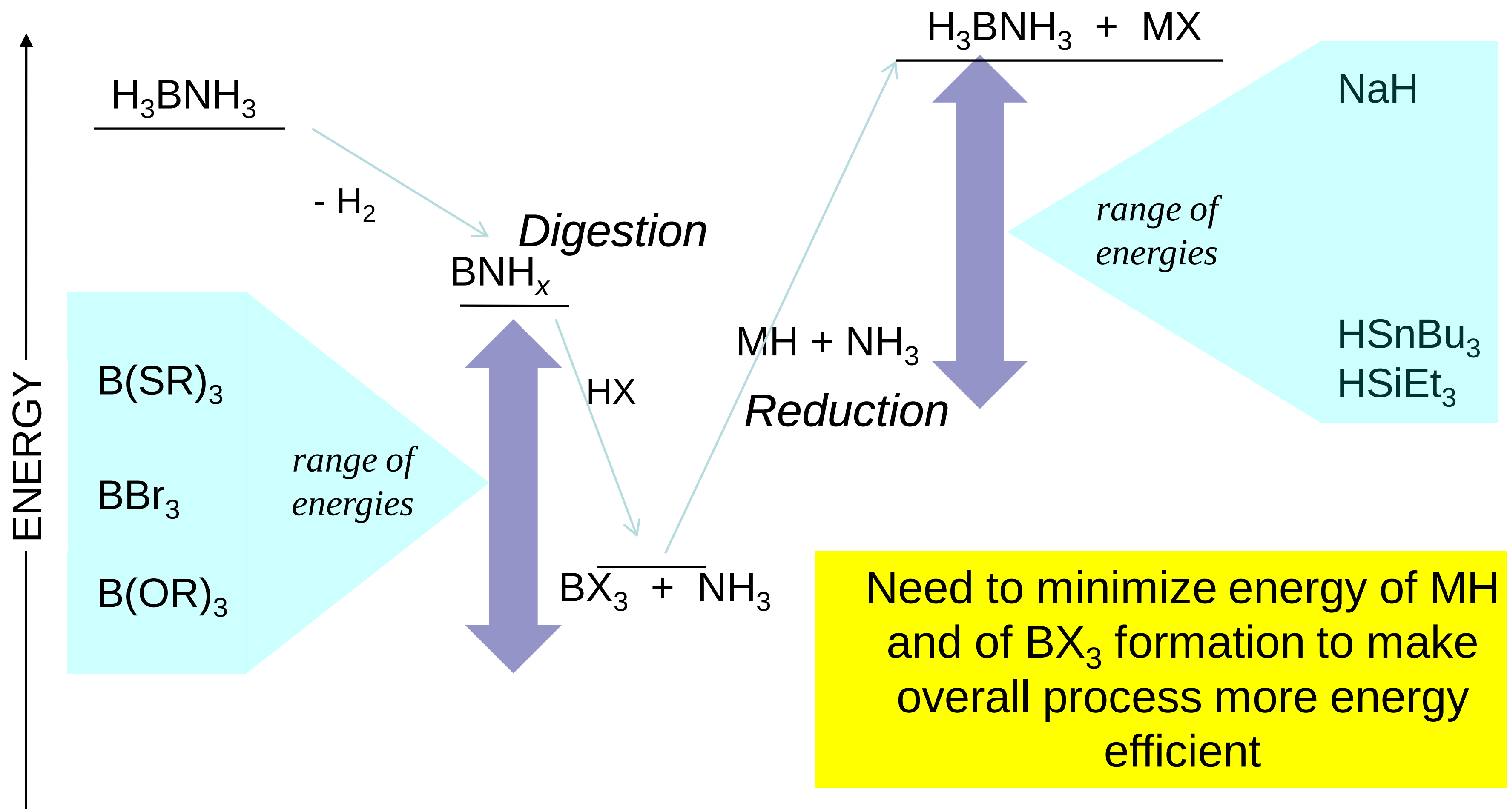
Matching Digestion/Reduction Energetics



Need to minimize energy of MH and of BX_3 formation to make overall process more energy efficient

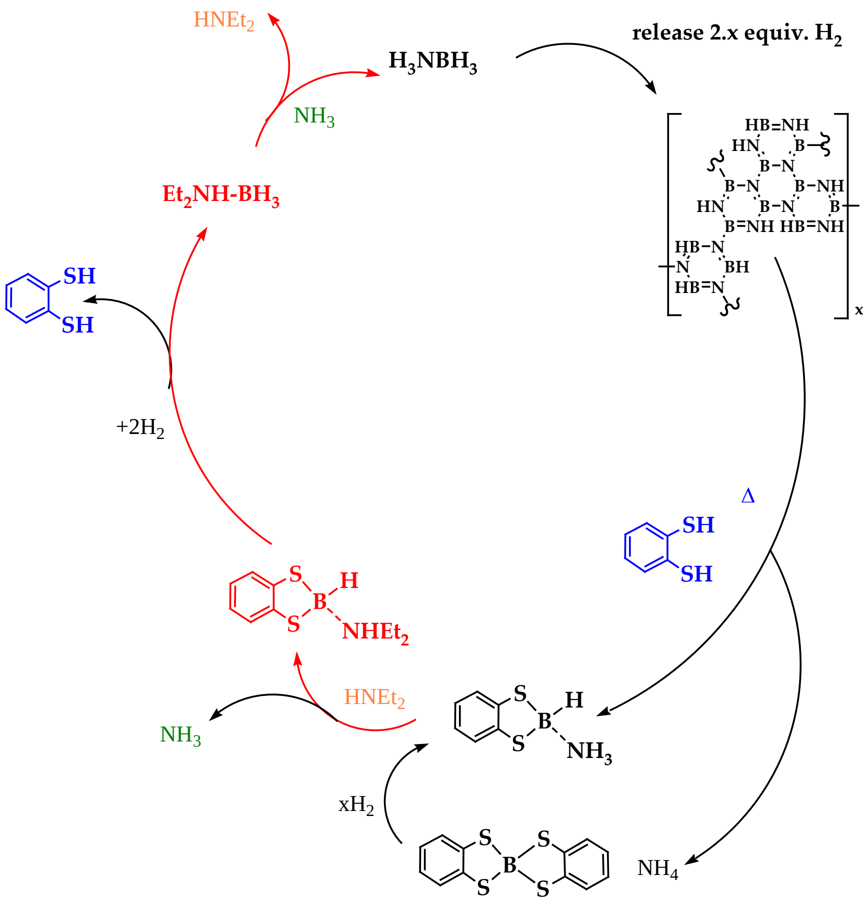
Rely on Computation to Screen Potential Reactions to Find 'Optimal' Thermodynamics

Reduction Reactions:

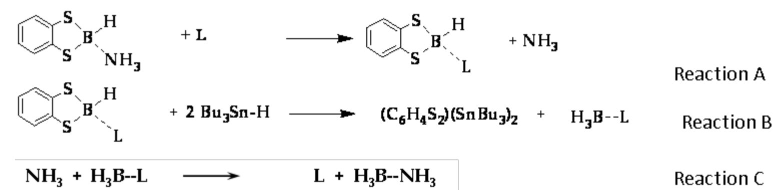
Reaction	ΔH (298K)	ΔG
$HSi(CH_3)_3 + BF_3 \rightarrow FSi(CH_3)_3 + HBF_2$	-2.0	-2.8
$HSi(CH_3)_3 + BCl_3 \rightarrow ClSi(CH_3)_3 + HBCl_2$	-7.6	-8.4
$HSi(CH_3)_3 + BBr_3 \rightarrow BrSi(CH_3)_3 + HBBr_2$	-10.4	-11.2
$HSi(CH_3)_3 + B(OH)_3 \rightarrow (OH)Si(CH_3)_3 + HB(OH)_2$	8.3	6.6
$HSi(CH_3)_3 + B(OCH_3)_3 \rightarrow (OCH_3)Si(CH_3)_3 + HB(OCH_3)_2$	7.9	7.5
$HSi(CH_3)_3 + B(SPh)_3 \rightarrow (SPh)Si(CH_3)_3 + HB(SPh)_2$	-2.0	-3.4
$HSn(CH_3)_3 + BF_3 \rightarrow FSn(CH_3)_3 + HBF_2$	12.9	11.6
$HSn(CH_3)_3 + BCl_3 \rightarrow ClSn(CH_3)_3 + HBCl_2$	-8.8	-9.5
$HSn(CH_3)_3 + BBr_3 \rightarrow BrSn(CH_3)_3 + HBBr_2$	-15.5	-16.4
$HSn(CH_3)_3 + B(OH)_3 \rightarrow (HO)Sn(CH_3)_3 + HB(OH)_2$	23.4	22.7
$HSn(CH_3)_3 + B(OCH_3)_3 \rightarrow (CH_3O)Sn(CH_3)_3 + HB(OCH_3)_2$	23.4	22.9

Dave Dixon

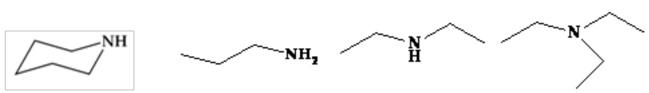
Choosing the Best Ligand for Reduction and Ammoniation by Matching Energetics



- Exchange of NH_3 for NEt_3 permits reduction of $HB(C_6H_4S_2)\cdot L$ at lower temperature
- Now energy balance required for Rxns A-C: $HNEt_2$ (ongoing work)



L =



Reaction A	ΔH	-5.5	-4.5	-1.0	6.2
	ΔG	-3.7	-3.3	1.0	9.2
Reaction B	ΔH	1.5	2.7	0.1	-4.7
	ΔG	11.6	13.0	10.0	5.6
Reaction C	ΔH	6.8	4.6	3.7	1.3
	ΔG	5.9	4.1	2.8	-1.0

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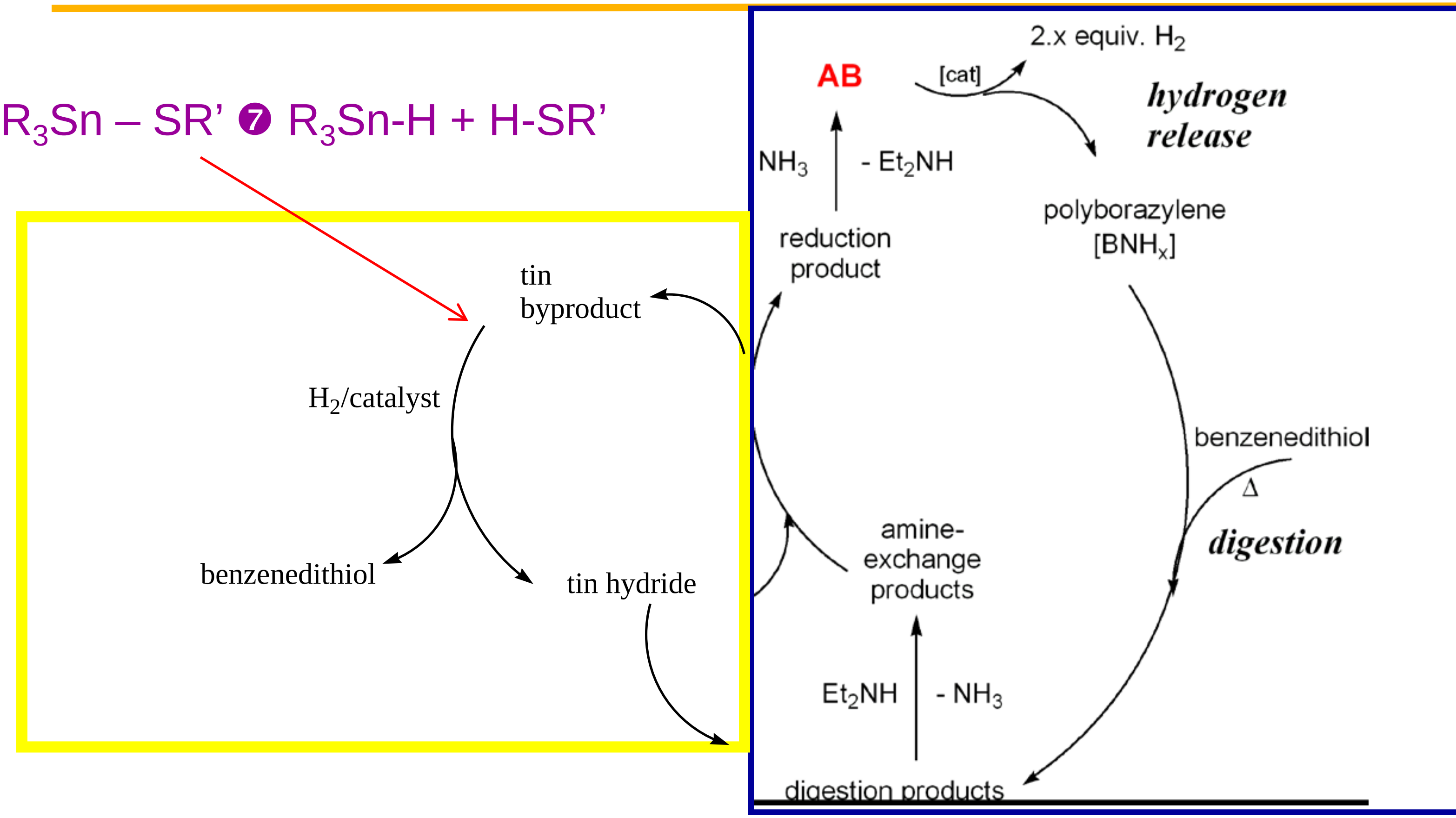
Metal Hydride Recycle a Current Focus: Discovery of Sn-S hydrogenolysis catalysts

R_3Sn – SR’ ❼ R_3Sn-H + H-SR’



Potential to use rapid throughput approaches to optimize the Sn-X identity and the catalyst to most optimally recycle the M-H reagent

New solution routes to new AB derivatives

Extensive portfolio of storage materials with lower exothermicity, higher rates and extent of release, with reduced impurities in H_2 stream

Metal Amidoborane Derivatives

$MgCl_2 + 2NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)_2 + 2NaCl$
$MgCl_2 + NaNH_2BH_3 \rightarrow Mg(NH_2BH_3)Cl + NaCl$
$ZnCl_2 + 2NaNH_2BH_3 \rightarrow Zn(NH_2BH_3)_2 + 2NaCl$
$TiCl_4 + 4NaNH_2BH_3 \rightarrow Ti(NH_2BH_3)_4 + 4NaCl$
$LiNH_2 + NH_3BH_3 \rightarrow LiNH_2BH_3 + NH_3$

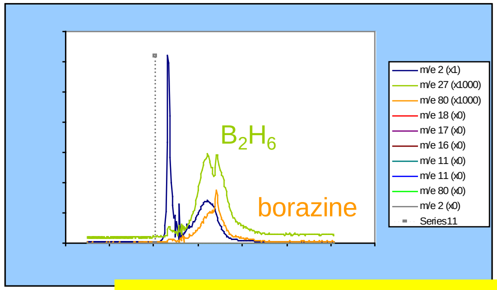
$NaH + NH_3BH_3 \rightarrow NaNH_2BH_3 + H_2$
$CaH_2 + 2NH_3BH_3 \rightarrow Ca(NH_2BH_3)_2 + 2H_2$
$AlH_3 + 3NH_3BH_3 \rightarrow Al(NH_2BH_3)_3 + 3H_2$
$LiAlH_4 + 4NH_3BH_3 \rightarrow LiAl(NH_2BH_3)_4 + 4H_2$
$Li_2(ZnH_4) + 4NH_3BH_3 \rightarrow Li_2Zn(NH_2BH_3)_4 + 4H_2$
$Li(ZnH_3) + 3NH_3BH_3 \rightarrow LiZn(NH_2BH_3)_3 + 3H_2$

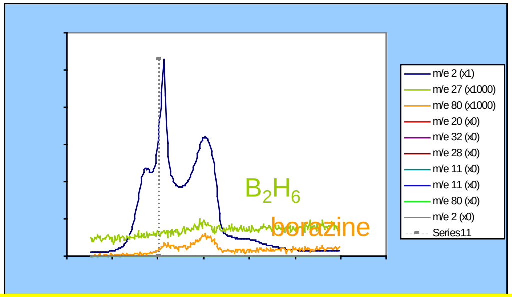
Example
$W(NH_2BH_3)_6 = 8.3$ wt%

e.g. $Ca(NH_2BH_3)_2$ has greater thermal stability than AB but undergoes faster catalytic release of H_2 at room temperature

Fluoride systems

$$NH_3BH_3 + MF_n \rightarrow NH_3BH_2F + M + ½H_2$$



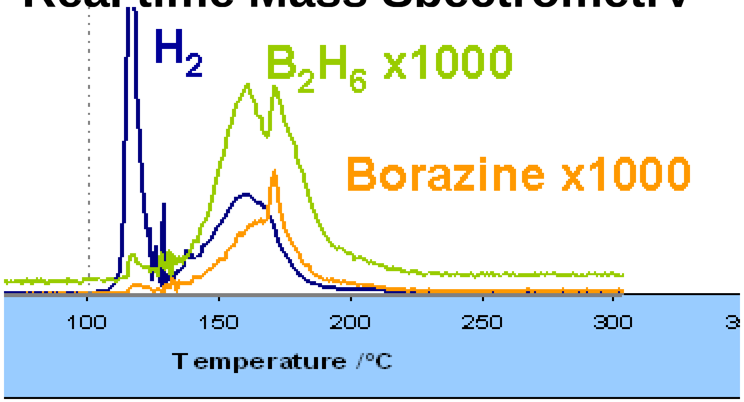


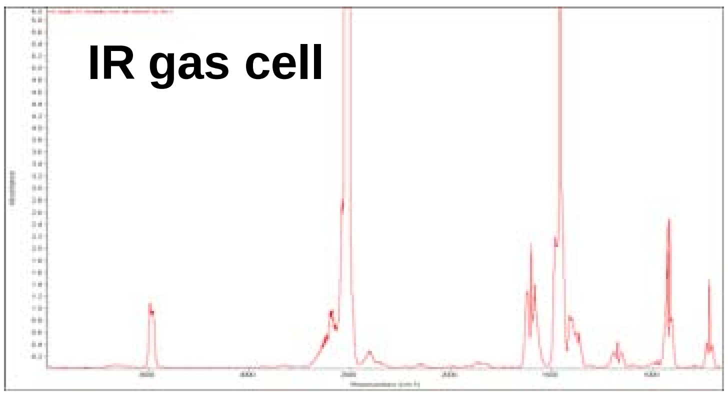
- Potential for high throughput synthesis of complex compounds containing multiple cations to tailor hydrogen release and hopefully, direct rehydrogenation

Himashinie Diyabalanage, LANL

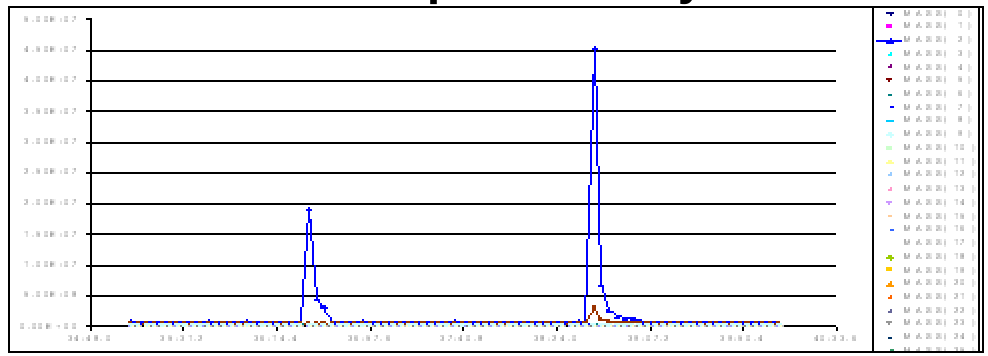
A Final Word on Measurements: Hydrogen Stream Purity from Storage Systems Crucial to Fuel Cell Performance

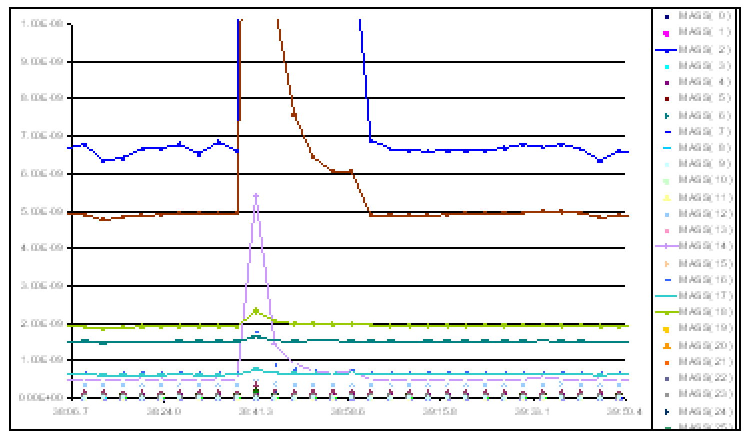
Real time Mass Spectrometry





Mass Spectrometry

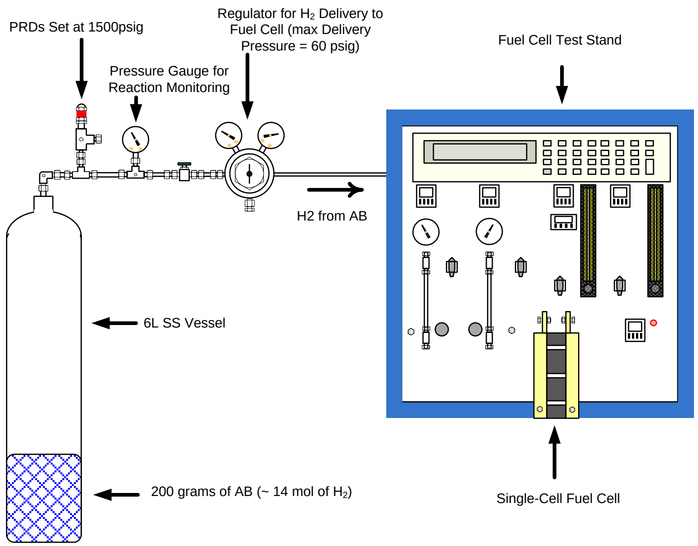


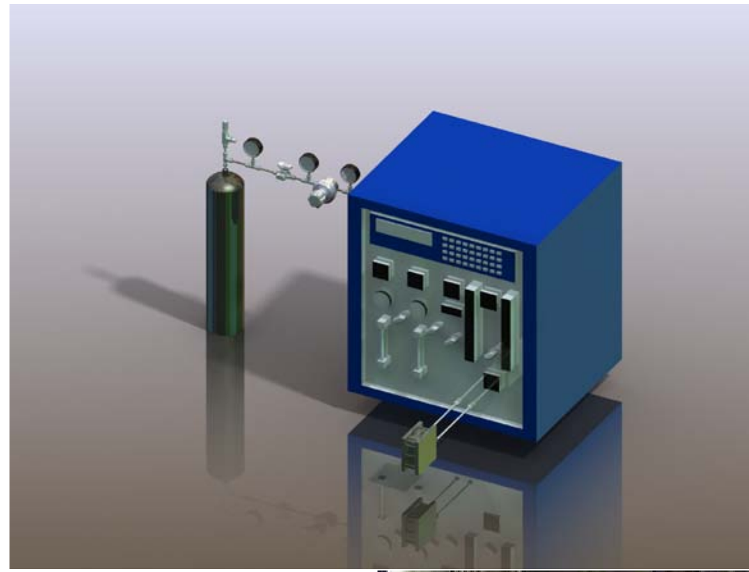


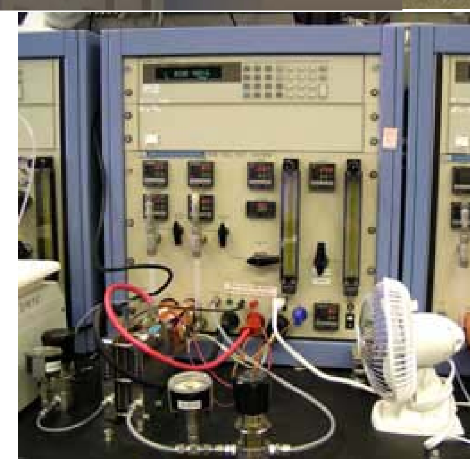
We can use spectroscopy and spectrometry for determining H_2 purity at perhaps sub ppm levels for some impurities.

But what about effects of very small, perhaps undetectable contaminants over long operating times?

PEM Fuel Cell Provides the Final Word On H_2 Purity







Small surface area fuel cell (1 cm^2) is used as a sensitive detector of hydrogen purity -- and acts as a dosimeter

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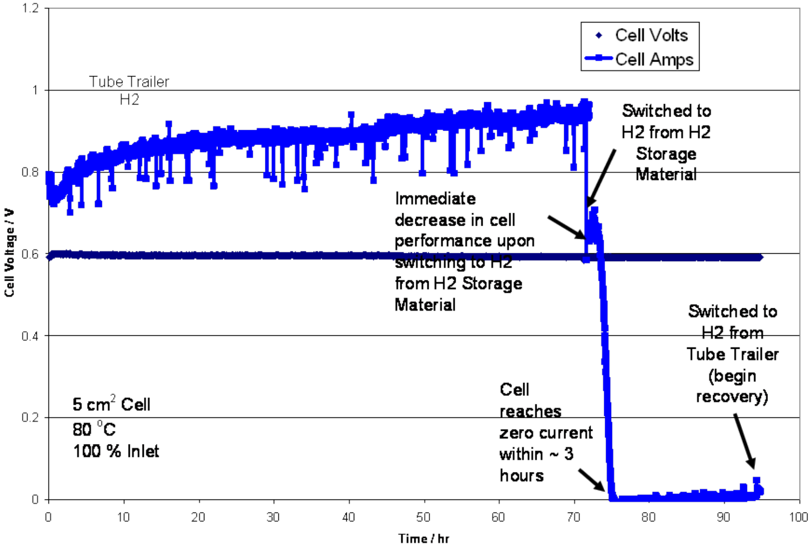
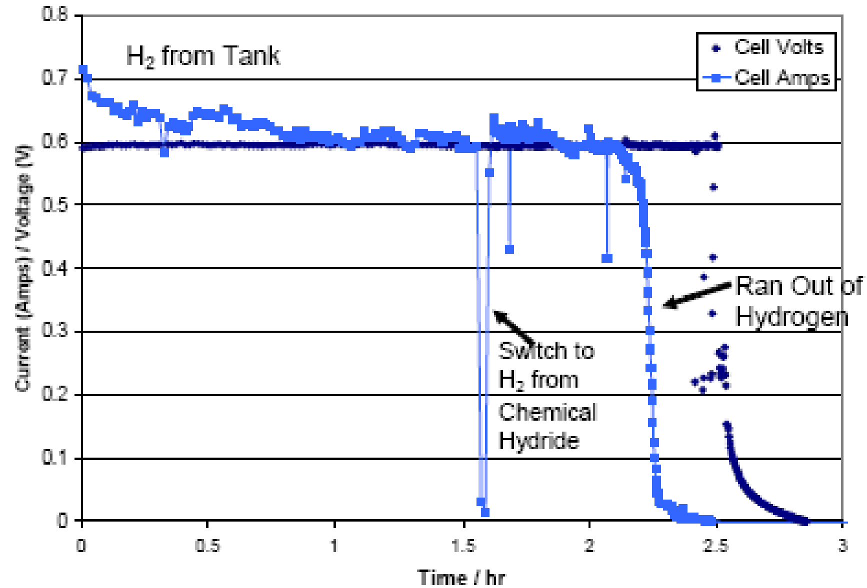
Worst Case Scenario Experiment: Impacts from the H_2 Stream on Fuel Cell Operation can be determined





Raw H_2 from thermal treatment of AB contains borazine, which is known to poison Pt fuel cell catalyst

Simple inline filter removes borazine, FC performance unaffected

Fuel cell recovered under clean hydrogen and analysis indicates catalysis was poisoned, not the membrane.

Collaboration with Rod Borup of the LANL Fuel Cell Durability Team

Conclusions

- Chemical hydrogen storage, if it is shown to be a viable long term approach, will rely upon a series of highly integrated, complex chemical transformations
- This will require both discovery and optimization of
  - Catalysts for hydrogen release
  - Liquid fuels
  - Catalysts for spent fuel regeneration, among others
  - New compositions of matter as storage compounds
- High throughput approaches may be practical for some or all of these needs
- Real time, low limits of detection measurements of potential contaminants in H_2 streams from all storage systems will likely be required to qualify systems prior to long term fuel cell operation

Chemical Hydrogen Storage Center of Excellence

- LANL – Tony Burrell, John Gordon, Kevin John, Troy Semelsberger, Charles Hamilton, Roshan Shrestha, Ben Davis, Himashinie Diyabalanage, Neil Henson, Mike Inbody, Fran Stephens
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- Rohm and Haas – Sue Linehan, Frank Lipiecki, Artie Chin
- U. Alabama – Dave Dixon and students
- U. Pennsylvania – Larry Sneddon and students
- U. Missouri – Fred Hawthorne, Satish Jalisatgi
- U. C. Davis – Susan Kauzlarich, Phil Power and students
- Penn State – Digby McDonald and students
- US Borax – Dave Schubert, Jonathan Owen
- And last, but way not least – Grace Ordaz, DOE