Thermal Decomposition Chemistry of Amine Borane (U)

Ashley C. Stowe

Jordan Feigerle, Norm Smyrl, Jonathan Morrell

B&W Y-12 National Security Complex

Oak Ridge, Tennessee, USA

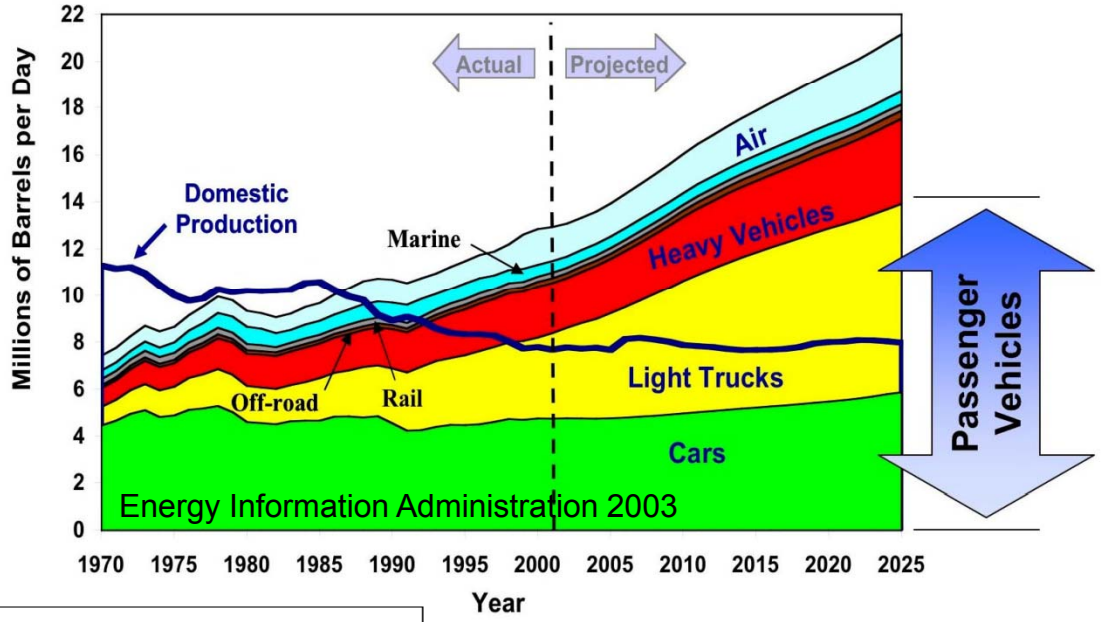
January 29, 2010

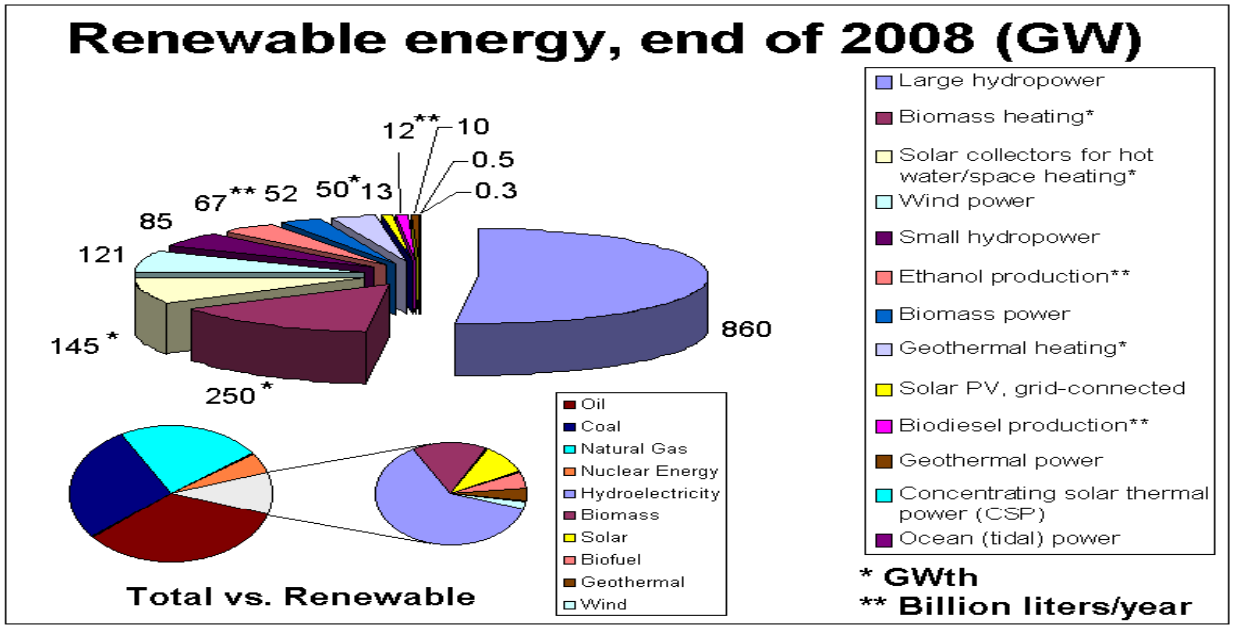
Prepared by the Y-12 National Security Complex
P.O. Box 2009, Oak Ridge, Tennessee 37831-8109
managed by B&W Y-12, L.L.C. for the U. S. Department
of Energy under contract DOE-AC05-00OR22800

Disclaimer

The Alternative Energy Landscape

- Replacing the fossil fuel based economy will take a varied portfolio of alternative energies.
- Vehicles are a primary focus for an initial transition with hydrogen fuel being a priority.



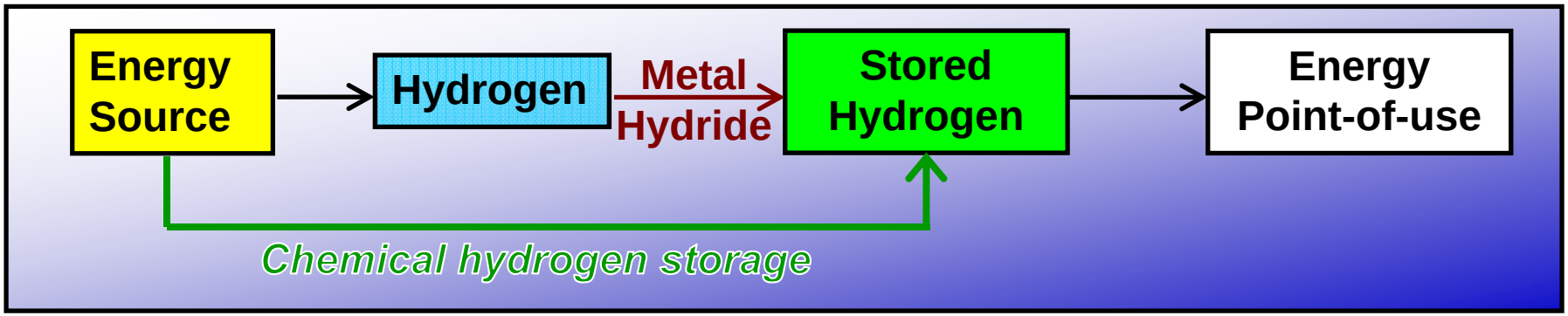


- Many sources will produce hydrogen gas as fuel but how should it effectively be stored until it is needed for energy conversion?

Hydrogen Storage Bottleneck

Ways to Store Hydrogen:

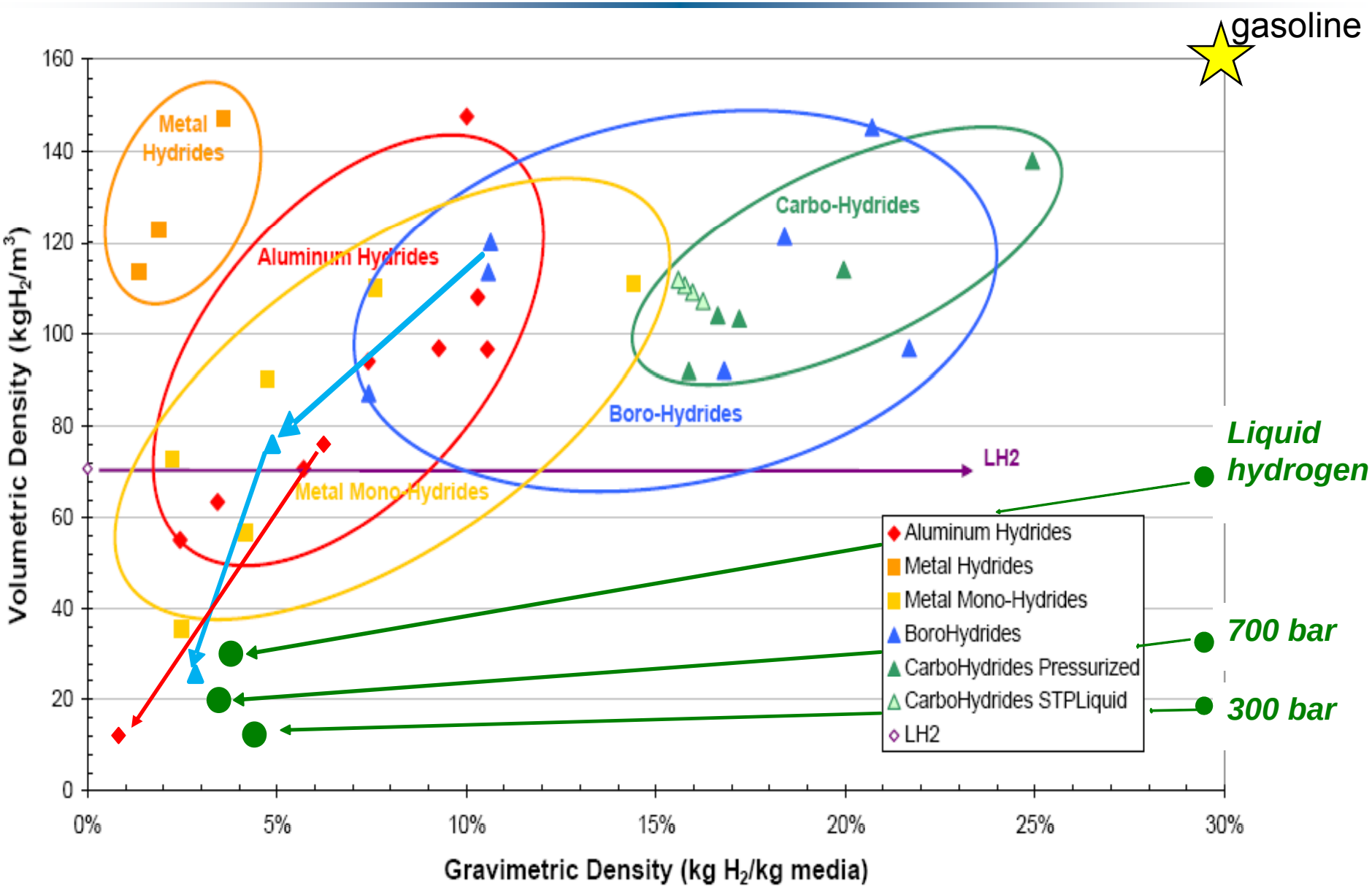
- Compressed H_2 gas
- Liquid H_2
- H_2 stored on substrate compound/surface



Important aspects:

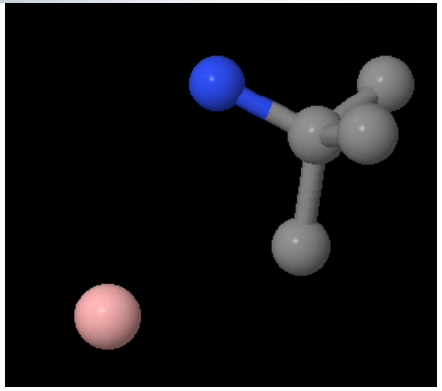
- ✓Safety
- ✓Cost
- ✓H_2 purity
- ✓H_2 capacity
- ✓H_2 kinetics
- ✓Reversibility

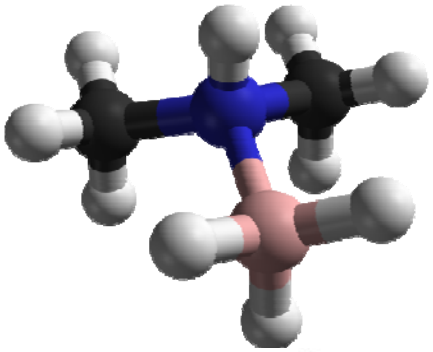
Hydrogen Storage Materials and Targets

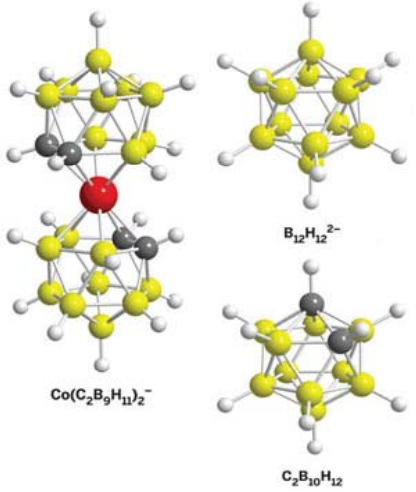


Chemical Hydrides : Amine Boranes

- Hydrogen release resultant of chemical reaction forming distinct chemical products.
- Amine Boranes: R_3NBH_3 (R = H, hydrocarbon)
- Inorganic hydrocarbon analogs which are mostly solids.
- Release hydrogen (3-15 wt %) at temperatures below 200 ^oC.
- Ammonia Borane (H_3NBH_3) releases 13 wt% fairly pure H_2 stream from dihydrogen bonding network in solid.
- Studied reaction mechanisms by “R” substitution of the amine
  - this weakens dihydrogen bonding network
- t-butylamine borane ($(H_3C)_3CNH_2BH_3$) has similar physical properties, but bulky hydrocarbon ligand replaces single proton.
- T-butylamine borane has 15.1 % theoretical H_2 capacity
  - 4.5 % if isobutane is released during decompositon.





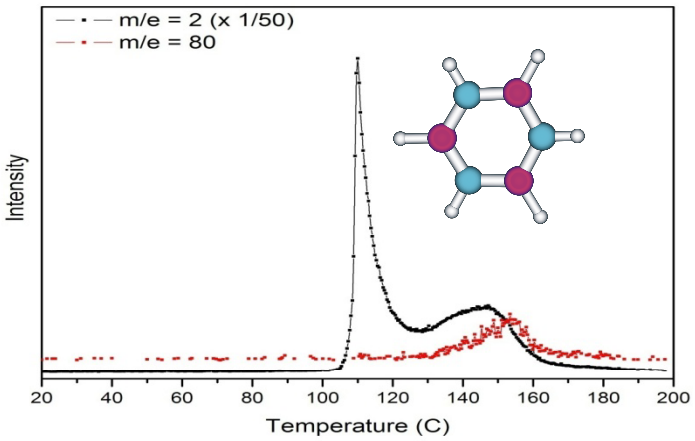


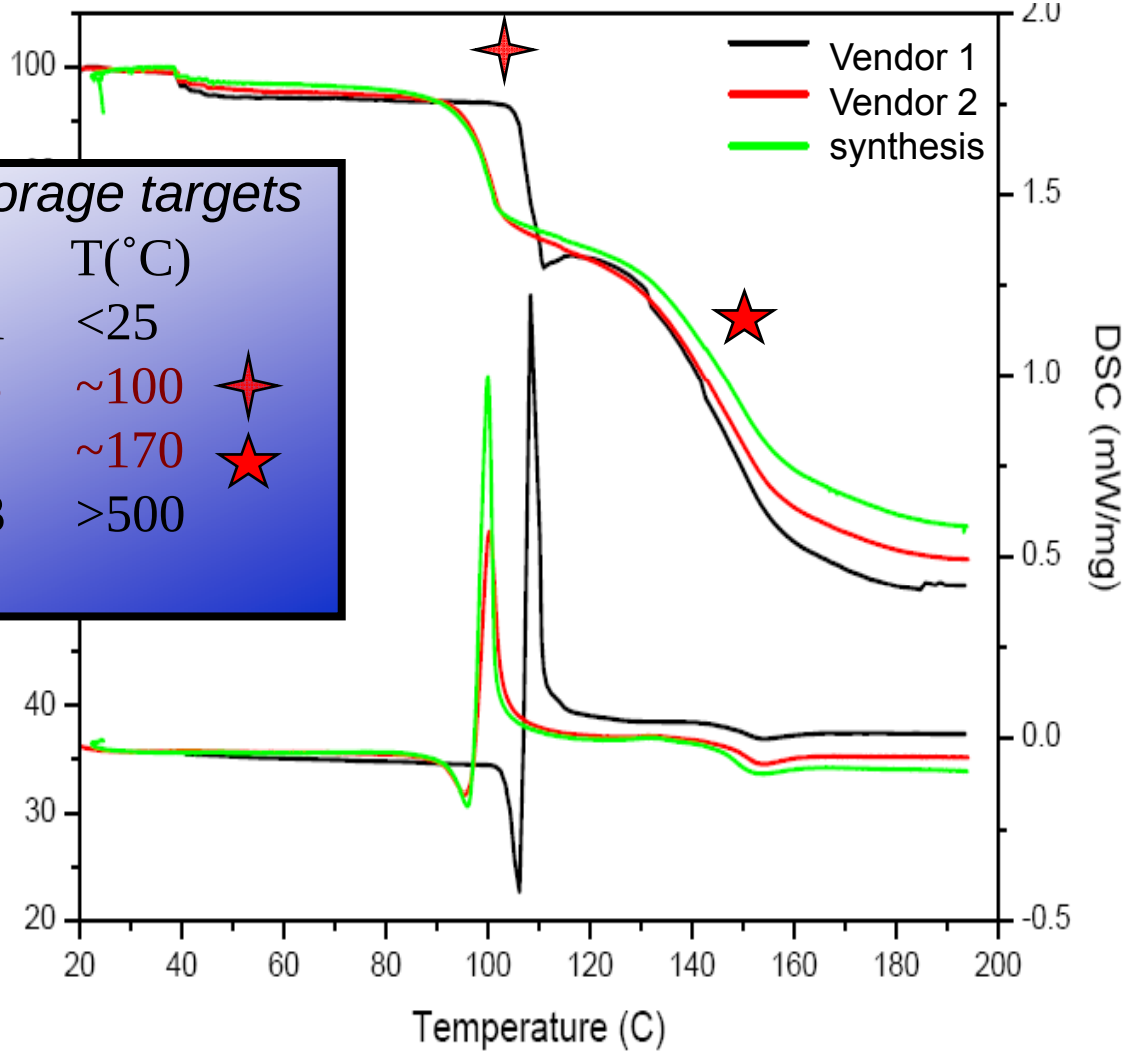
Thermochemistry of NH_3BH_3

- The purity of AB effects the onset of H_2 release.

Potential for meeting DOE storage targets

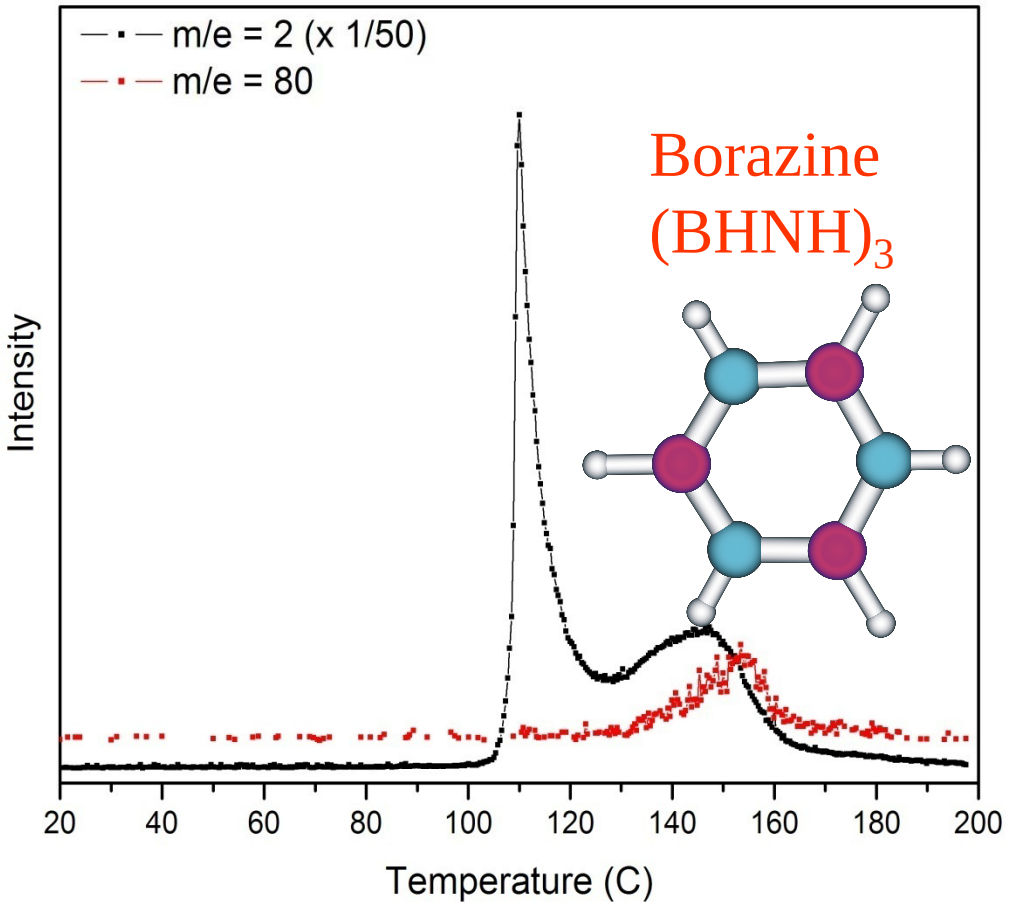
		wt%	T(˚C)
NH_4BH_4	→ $NH_3BH_3 + H_2$	6.1	<25
NH_3BH_3	→ $NH_2BH_2 + H_2$	6.5	~100
NH_2BH_2	→ NHBH $+ H_2$	6.9	~170
NHBH	→ BN $+ H_2$	7.3	>500





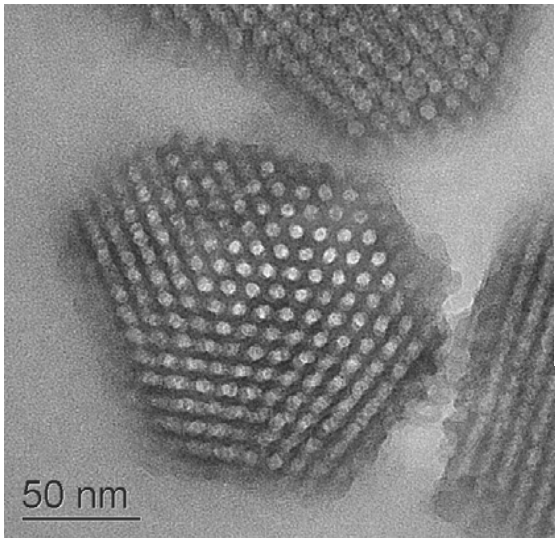
Volatile Species of Thermolysis

- H_2 is major species in 1st step
  - (note: scale 1/50)
- Other products observed in 2nd step
- Non-H_2 volatile products poison fuel cell
- Non-H_2 volatile products reduce reusable storage material



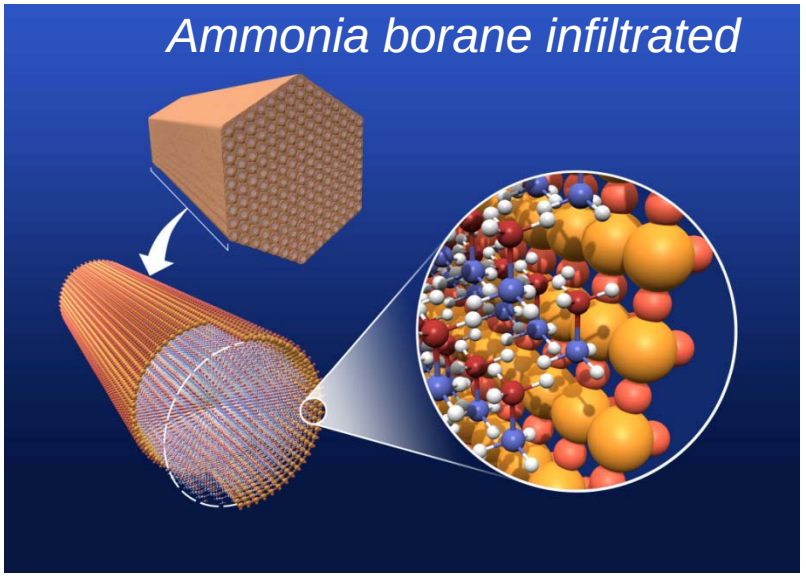
Nano-phase Ammonia Borane

- Can hydrogen storage properties be controlled?
  - Nano-phase NH_3BH_3 trapped in 6-7 nm wide channels of mesoporous substrates (silica, carbon)



NH_3BH_3

Add saturated solution of NH_3BH_3 to mesoporous substrate

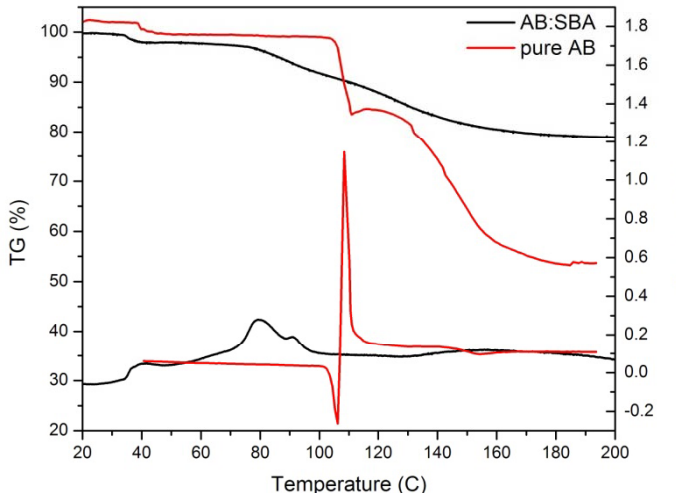


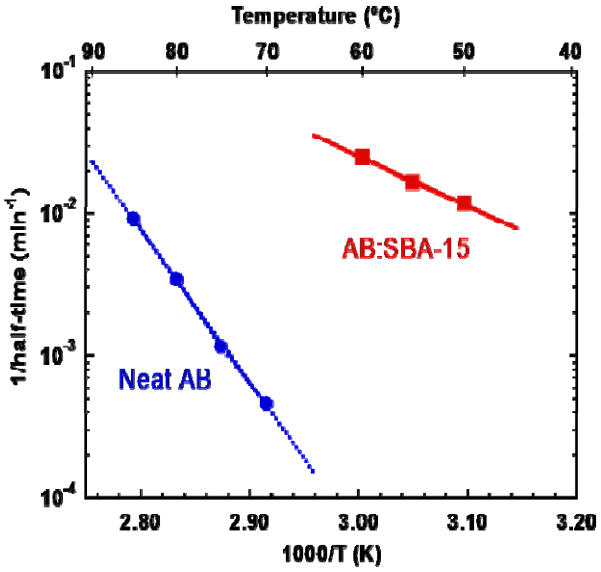
Gutowska *et al.*, *Angew. Chem.* (2005).

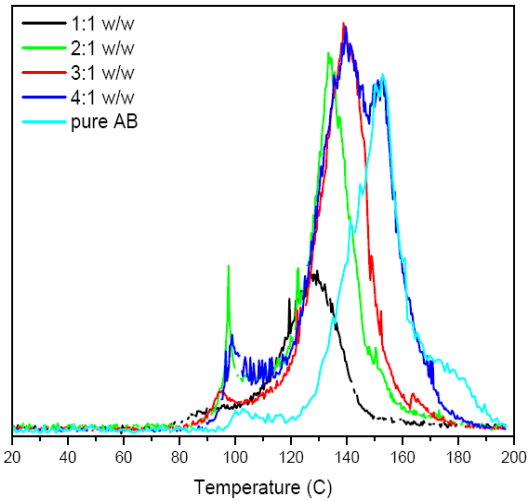
Nano-phase Ammonia Borane

Ammonia borane:mesoporous silica substrate (SBA-15):

- Improves thermodynamics, ΔH = -1 kcal/mol
- Improves kinetics, >1000x
- Prevents formation of non-H_2 volatiles, 70% less borazine





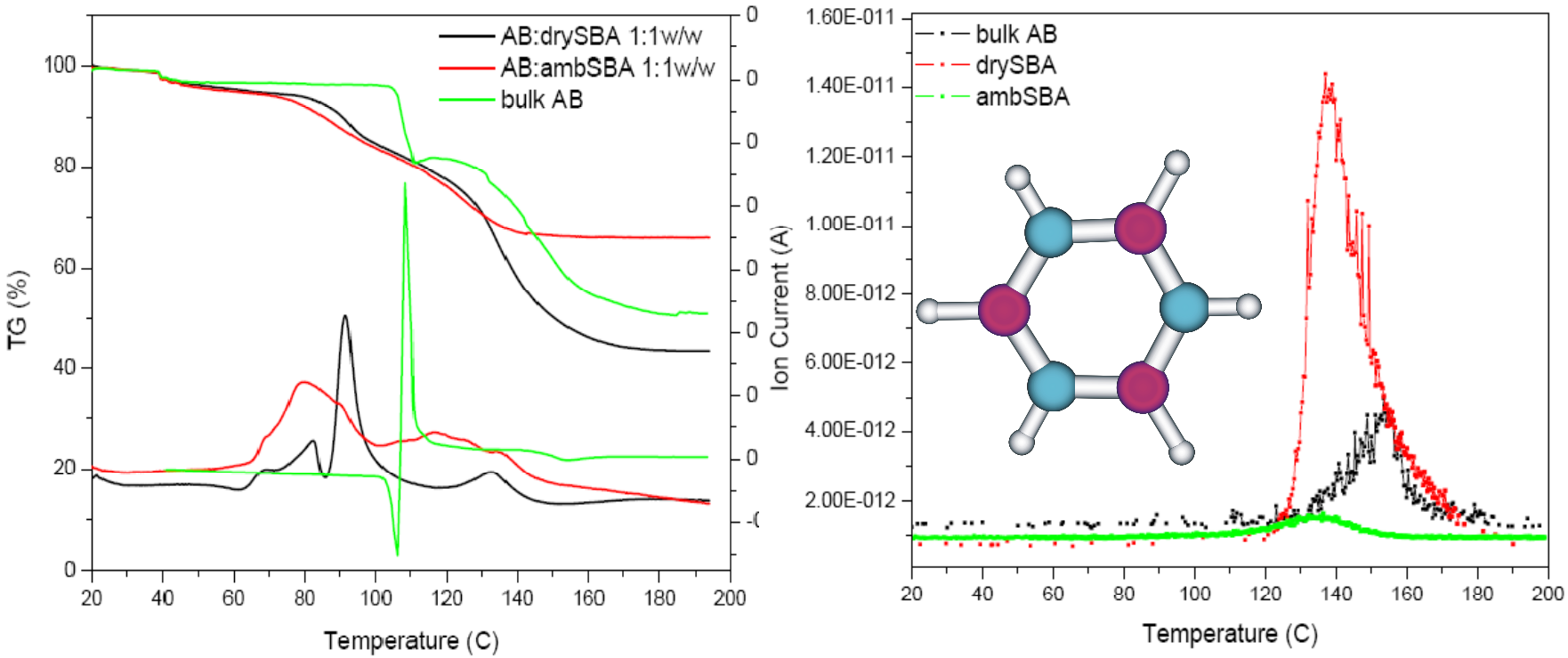


Gutowska *et al.*, *Angew. Chem.* (2005).

Stowe *et al., J. Materials* (submitted)

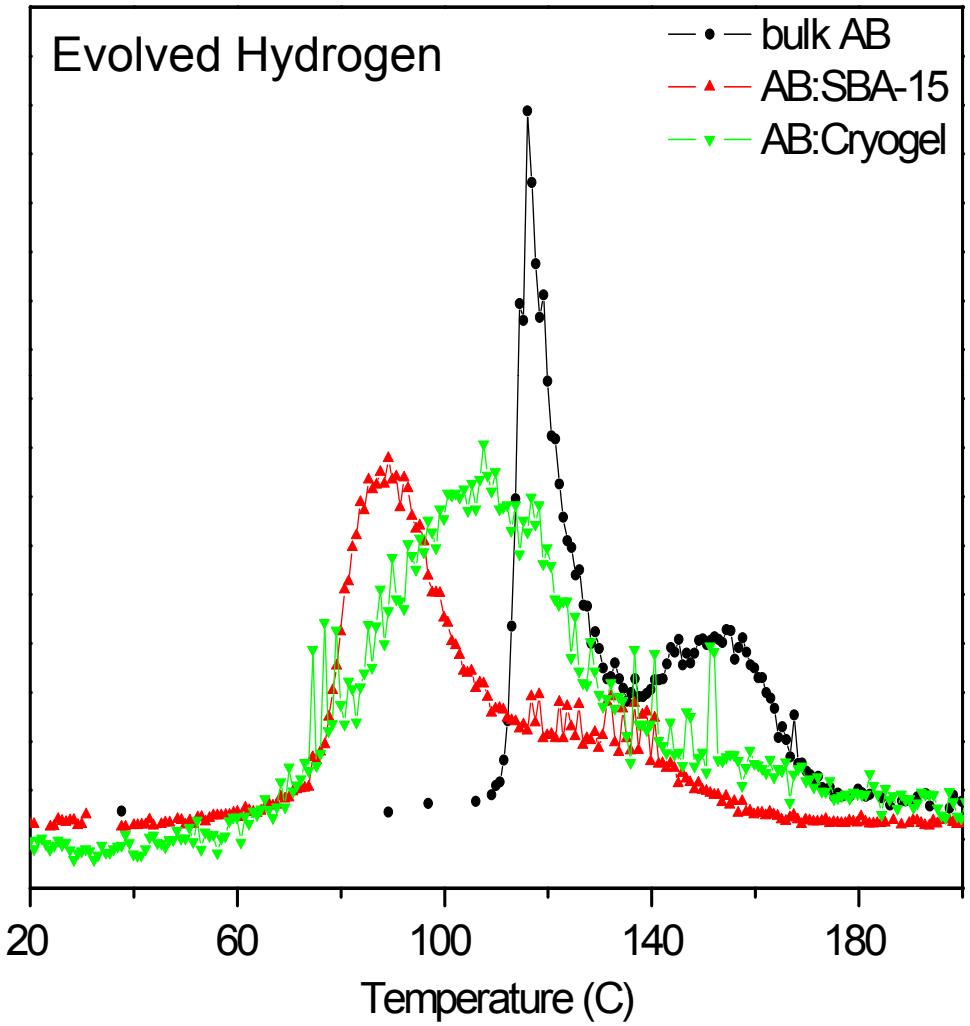
Effect of Water in SBA-15

- Noticed that H_2O content in SBA-15 effected chemistry of NH_3BH_3



H_2O content reacts with borane bond to form borate

NH3BH3 in Carbon Cryogels

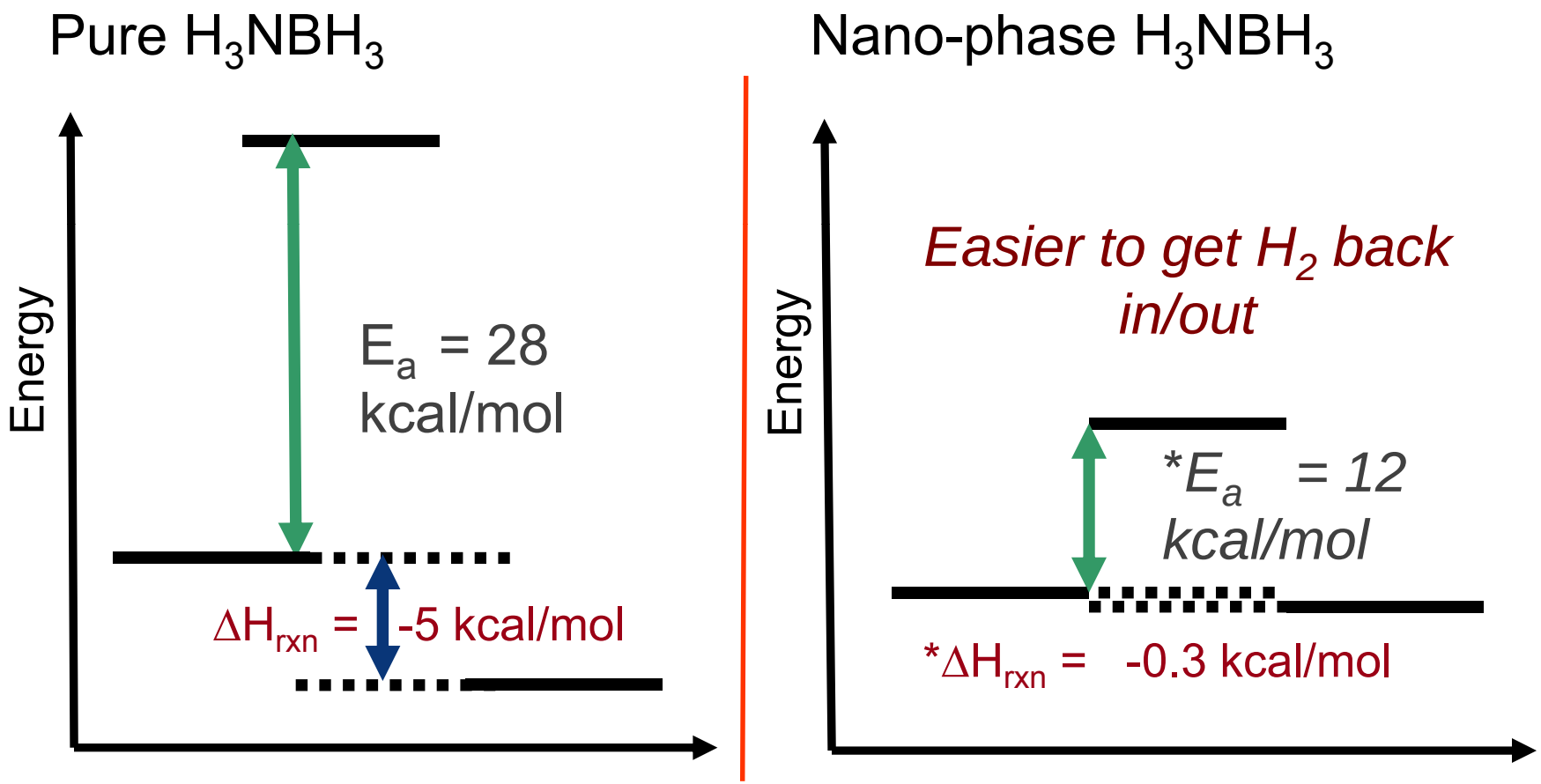


- Surface area
  - ~800 m2/g
- Pore diameter
  - macropore: 80-110 nm
  - micropore: ~5 nm

Feaver *et al.* JPCB (2007)

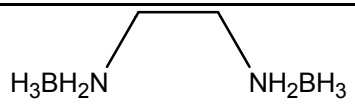
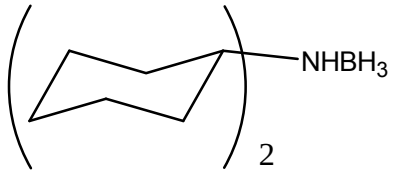
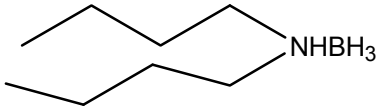
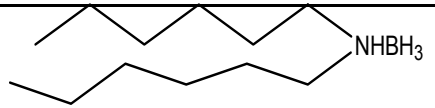
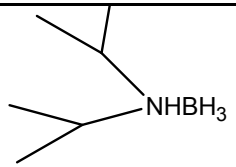
Nano-phase Enhancement

- Dehydrogenation Enthalpy (ΔH) nearly thermoneutral.



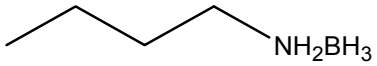
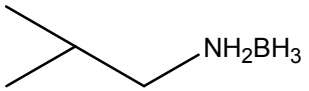
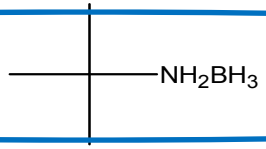
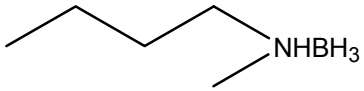
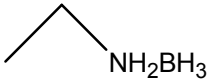
Controlling Chemistry without Encapsulation?

- Decompose a substituted amine borane with NH_3BH_3 to alter the reaction products.
  - Carbon addition to (BNH)x species destabilizes them making it potentially easier to regenerate hydrogenated material. *JPC A 113 (2009) 6121.*

Abbreviation	Actual Name	Structure	^{11}B {^{1}H} Chemical Shift (ppm)	Melting Point (°C)
ENAB	Ethylene diamine *N,N'*-diborane		-15.3	116 dec
DCAB	Dicyclohexylamine borane		-15.3	101-104 dec
DnBAB	Di-*n*-butylamine borane		-11.3	< 25
DHAB	Dihexylamine borane		-11.2	32-36 dec
DiPrAB	Di-*iso*-propylamine borane		-17.0	< 25

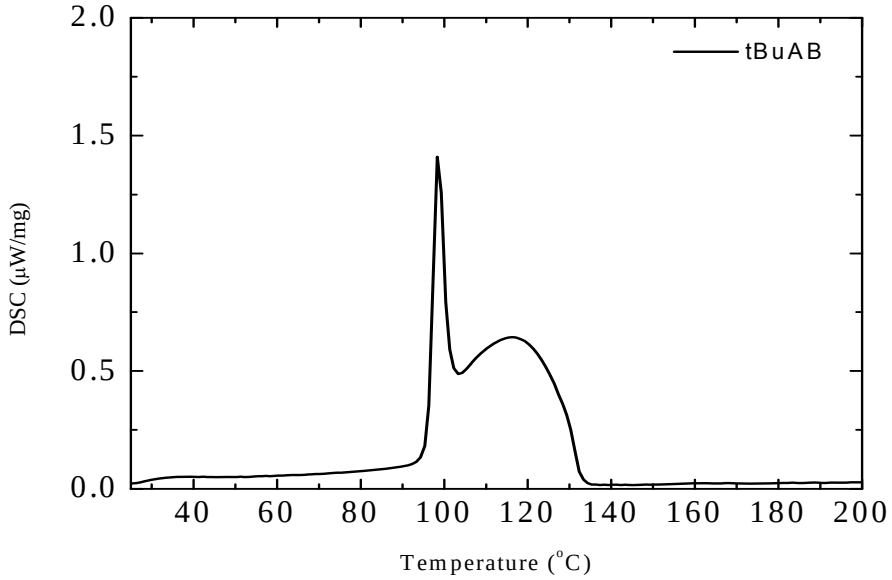
Controlling Chemistry without Encapsulation?

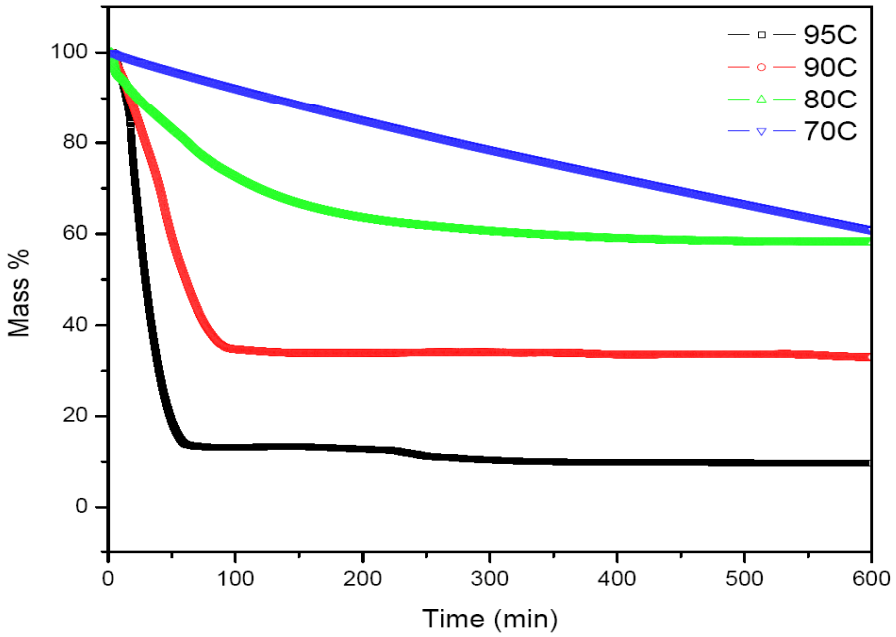
- Decompose a substituted amine borane with NH3BH3 to alter the reaction products.
  - Carbon addition to (BNH)x species destabilizes them making it potentially easier to regenerate hydrogenated material. *JPC A 113 (2009) 6121.*

Abbreviation	Actual Name	Structure	^{11}B {^{1}H} Chemical Shift (ppm)	Melting Point (^{o}C)
nBuAB	*n*-Butylamine borane		-14.9	<25
iBuAB	*iso*-Butylamine borane		-14.8	88-90 dec
tBuAB	*tert*-Butylamine borane		-14.8	96-97 dec
MBuAB	Methyl-Butylamine borane		-10.5	nm
CAB	Cyclohexylamine borane		-16.0	82-87 dec.
EAB	Ethylamine borane		-20.0	< 25

tBuAB Thermochemistry

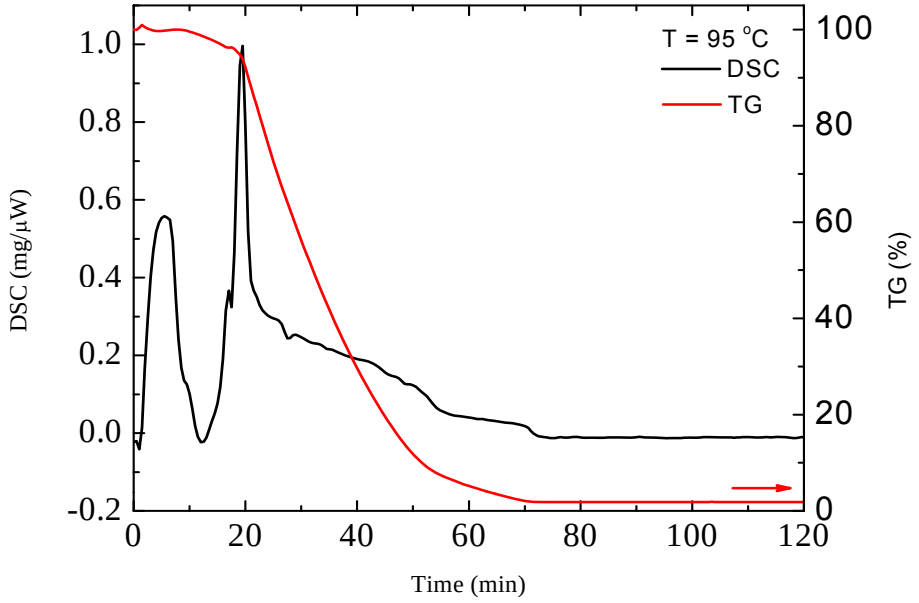
- t-butylamine borane ($(H_3C)_3CNH_2BH_3$) has similar physical properties
- Bulky hydrocarbon ligand replaces single proton.
- T-butylamine borane has 15.1 % theoretical H_2 capacity
  - 4.5 % if isobutane is released during decompositon.
- Strong transition occurs at melting point (96 ^oC).
- Decomposition quickly occurs with nearly complete volatilization of products.
- Isotherms below the melting point still result in significant gas evolution.

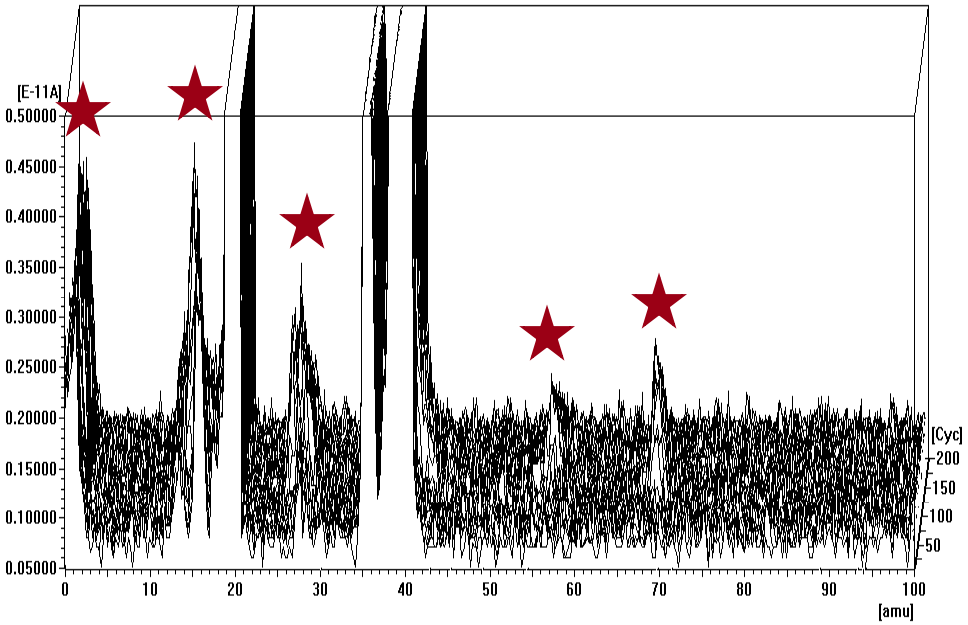


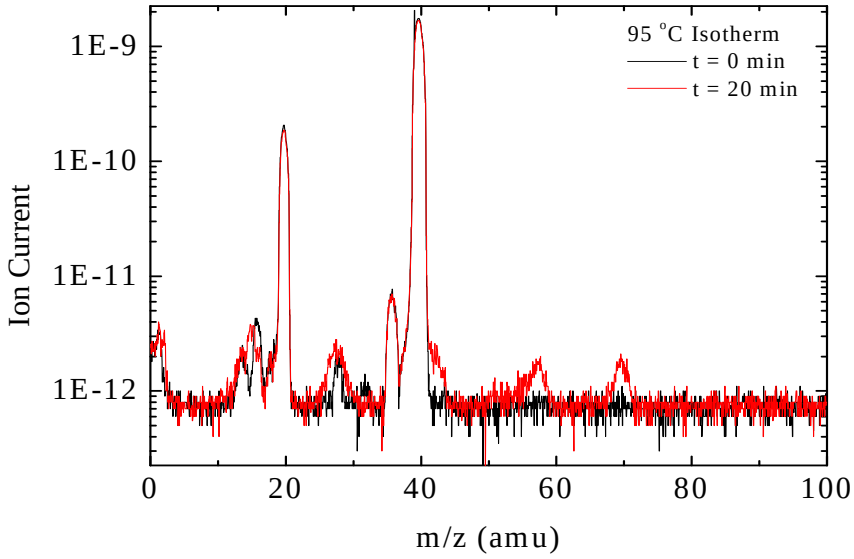


tBuAB Thermochemistry

- Evolved gas measured with mass spectrometer during DSC isotherm.
- Decomposition to evolve H_2 and other volatile species is observed.
- A small quantity of BH_3 is observed indicating dissociation of tBuAB.
  - No t-butylamine gas (m/z = 74 amu) is observed.

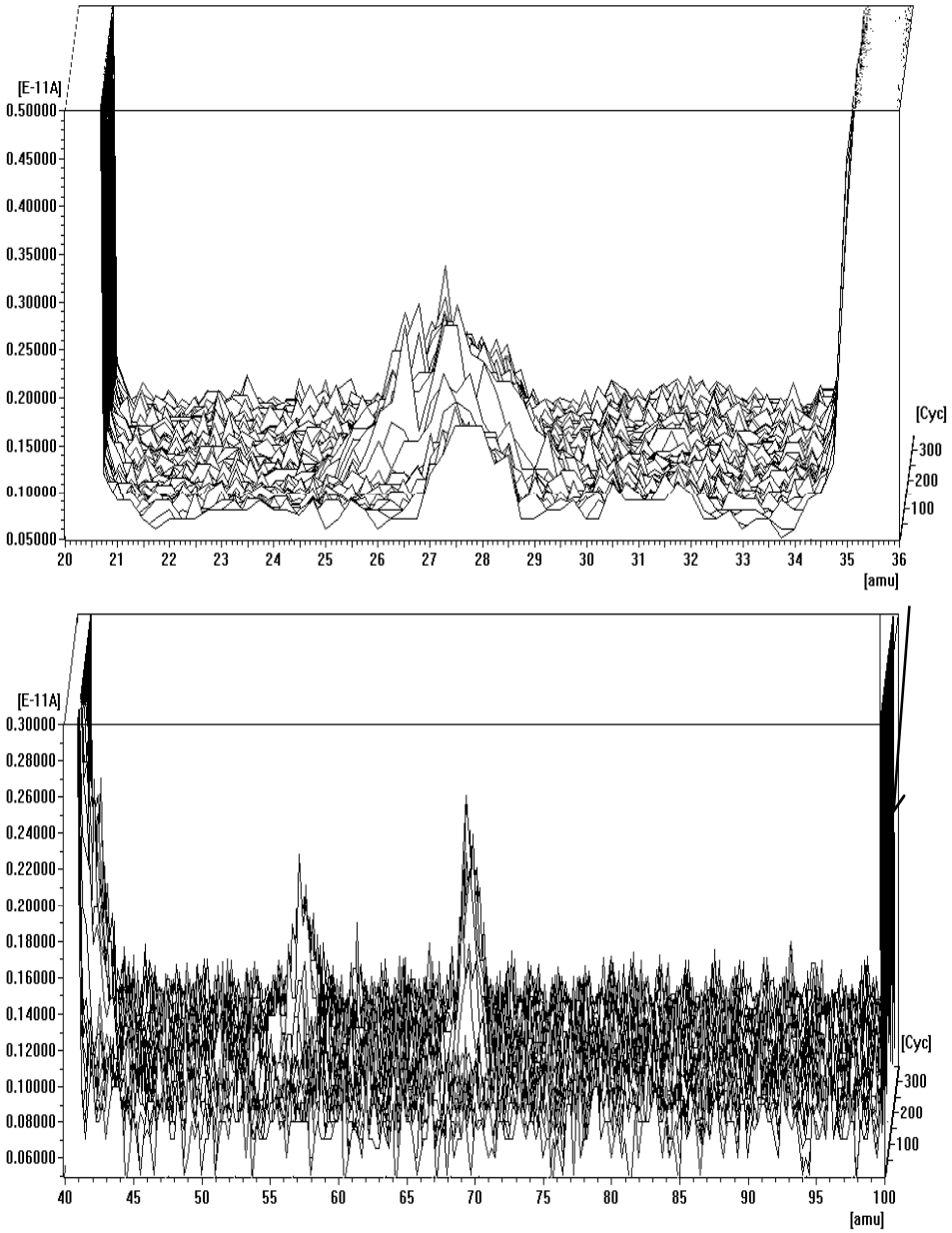






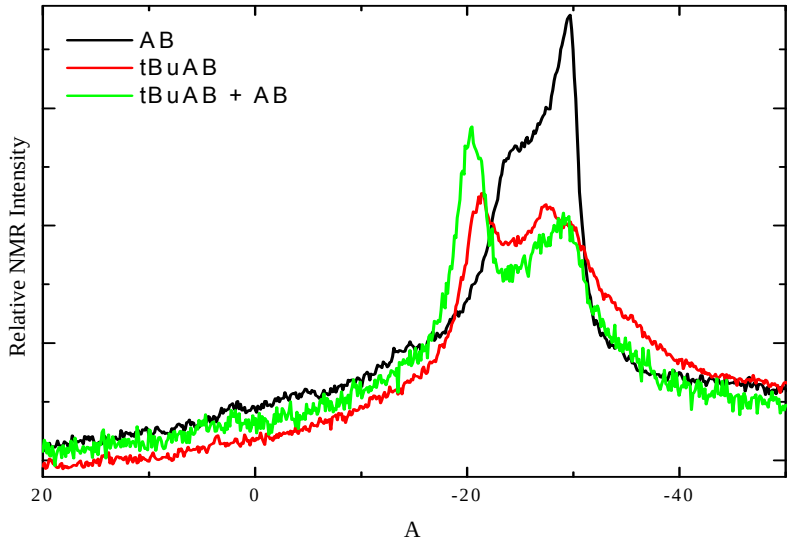
tBuAB Thermochemistry

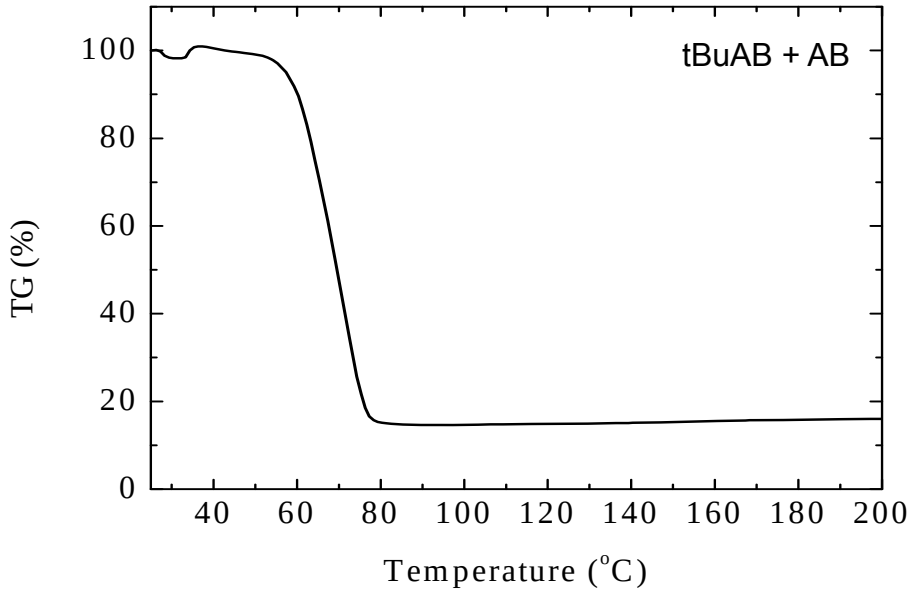
- m/z = 27, 28, 58, and 70 grow in as intermediates (15-50 min rxn)
  - m/z = 27,28 could be:
    - $NH_2{}^{10,11}BH_2$
      - Result of C_4H_{10} evolution.
    - B_2H_6
      - unlikely since the transfer capillary is at 250 ^oC.
  - m/z = 58
    - observed with m/z 27,28
    - C_4H_{10} evolved.
    - Confirms NH_2BH_2 evolution.
  - m/z = 70
    - tBuN=BH (tert-butylimido borane)
    - Evolved by tBuAB - $2H_2$



Mixtures of tBuAB and AB: *in situ* NMR

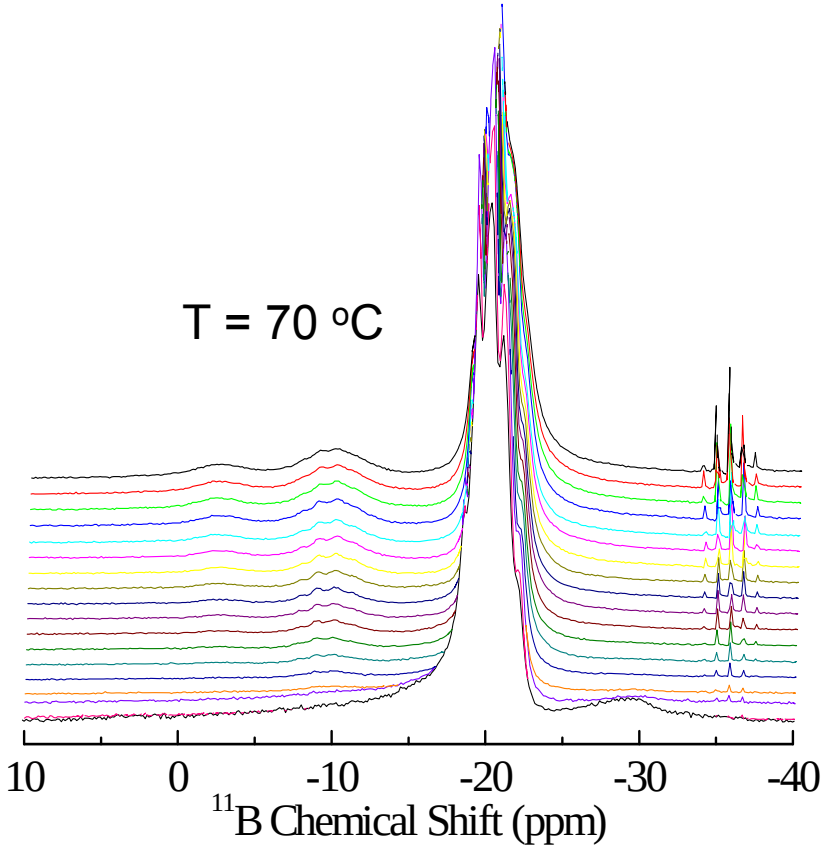
- Addition of tBuAB to AB could potentially alter the H_2 release pathway
  - More favorable $CBNH_x$ products may be formed promoting hydrogen regeneration.
- tBuAB and AB were weighed to specific molar proportions and hand ground for mixing.
  - 10 wt% tBuAB:AB
  - 50 wt% tBuAB:AB
  - tBuAB:10 wt% AB
- No reaction was observed prior to heating.
- Mass loss occurs ~30 °C lower than for pure tBuAB or AB.

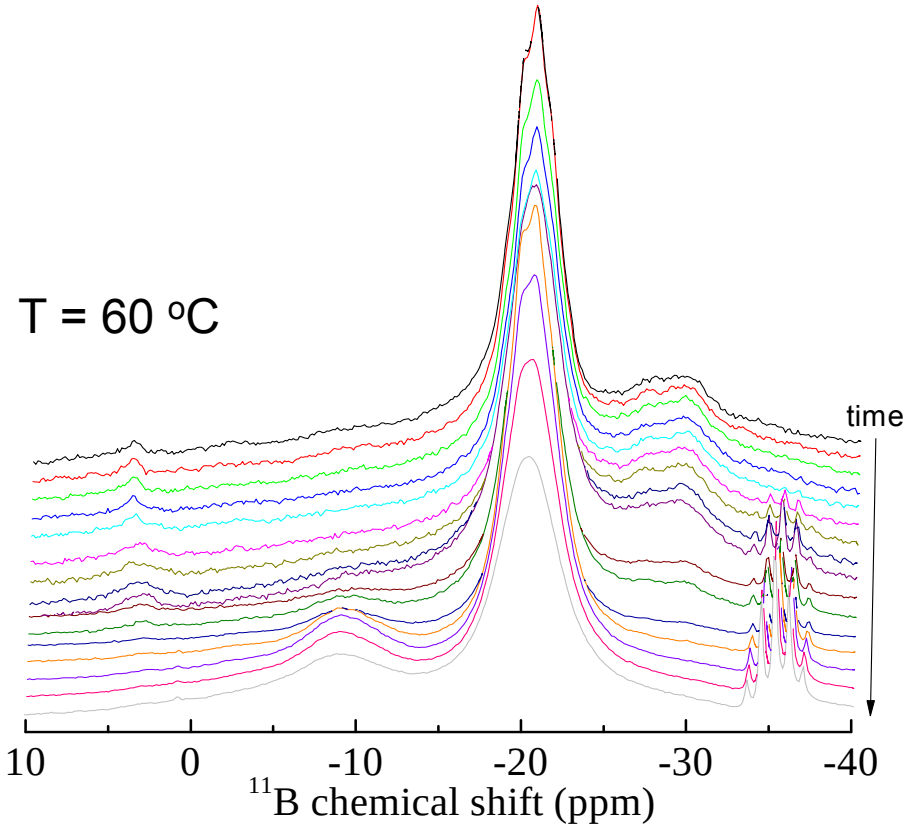




Mixtures of tBuAB and AB: *in situ* NMR

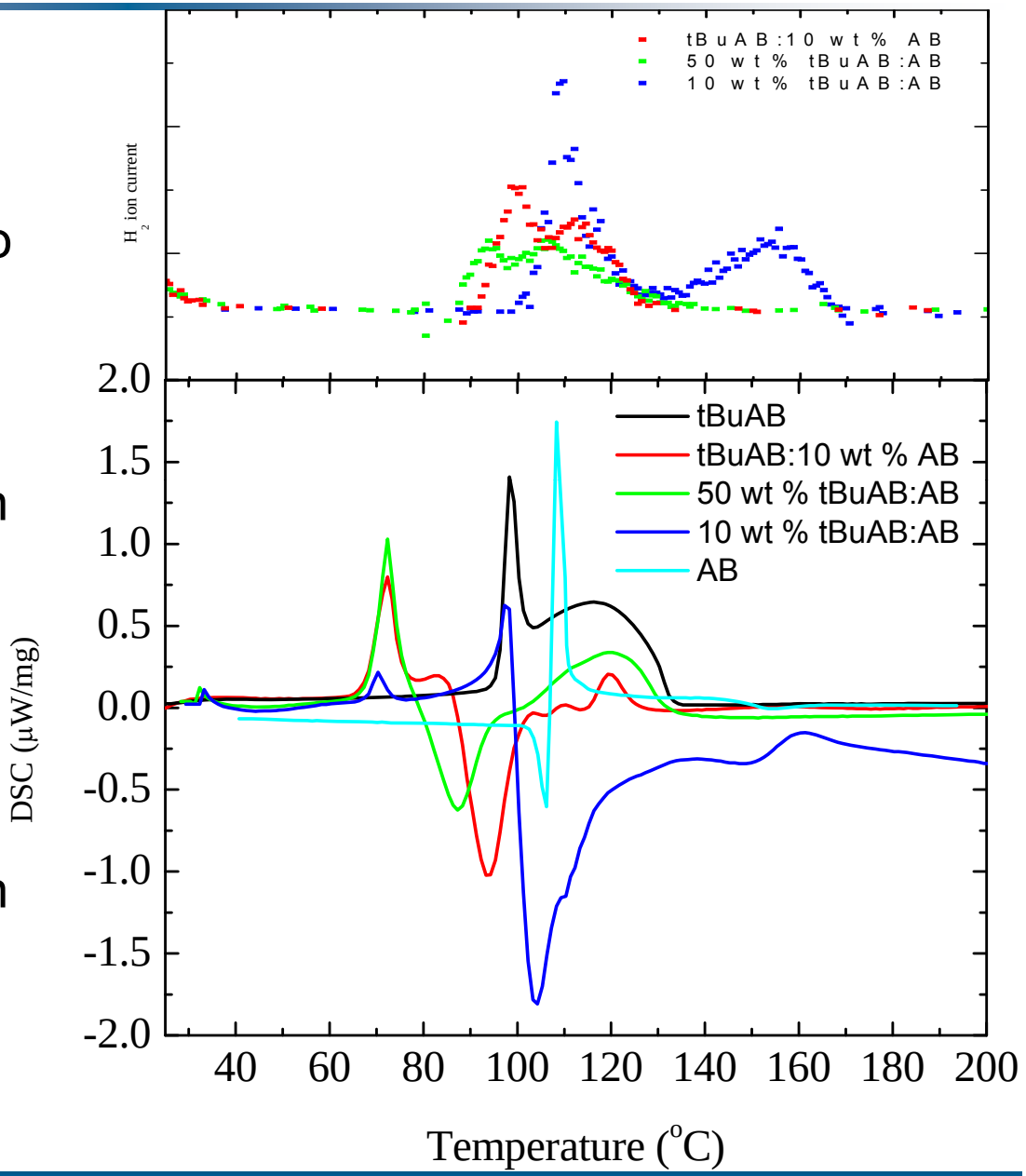
- For the 50 wt % tBuAB:AB sample, the decomposition appears to follow the typical amine borane decomposition pathway.
  - Isomerize to ionic dimer ($[BH_4]^-$; δ = -36 ppm), initiating decomposition.
  - AB is primarily consumed (δ = -30 ppm).
  - Decomposition continues as $–BH_2$ and -BH species are observed.





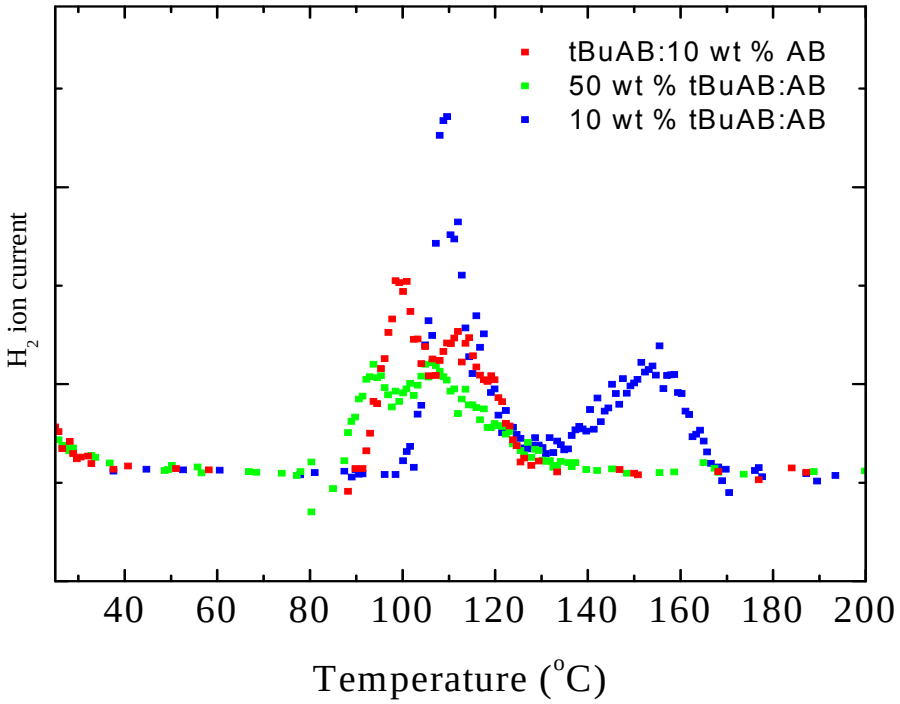
Mixtures of tBuAB and AB: Thermochemistry

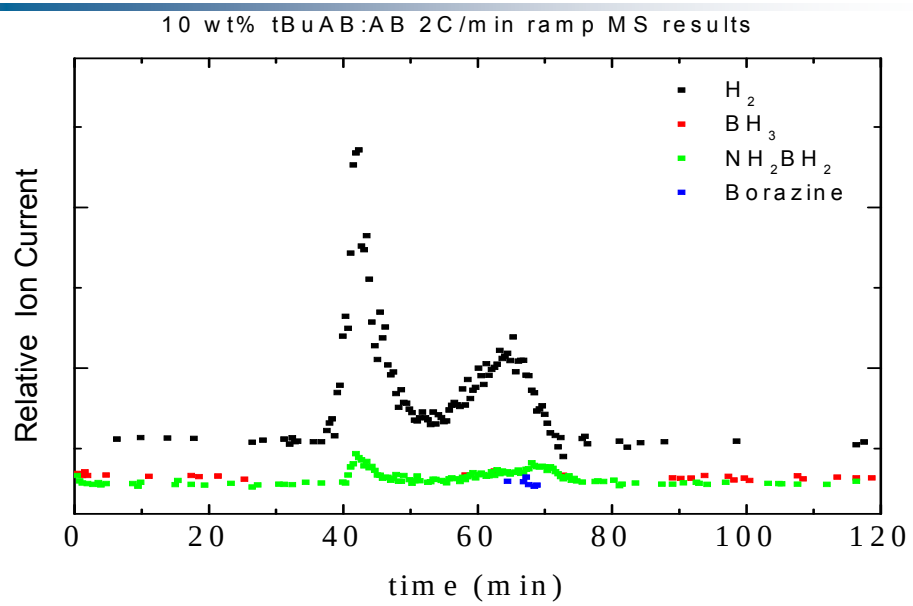
- DSC-MS ramps show significant changes to the chemistry of the mixed tBuAB:AB system compared to the pure components.
  - T ramp is 2 °C/min
- Addition of hydrocarbon complicates the decomposition thermochemistry.
- Multiple reaction paths are competing. To release H_2 and non-H_2 species.
- Ratio of tBuAB to AB is important and optimal between 10-50 wt %.

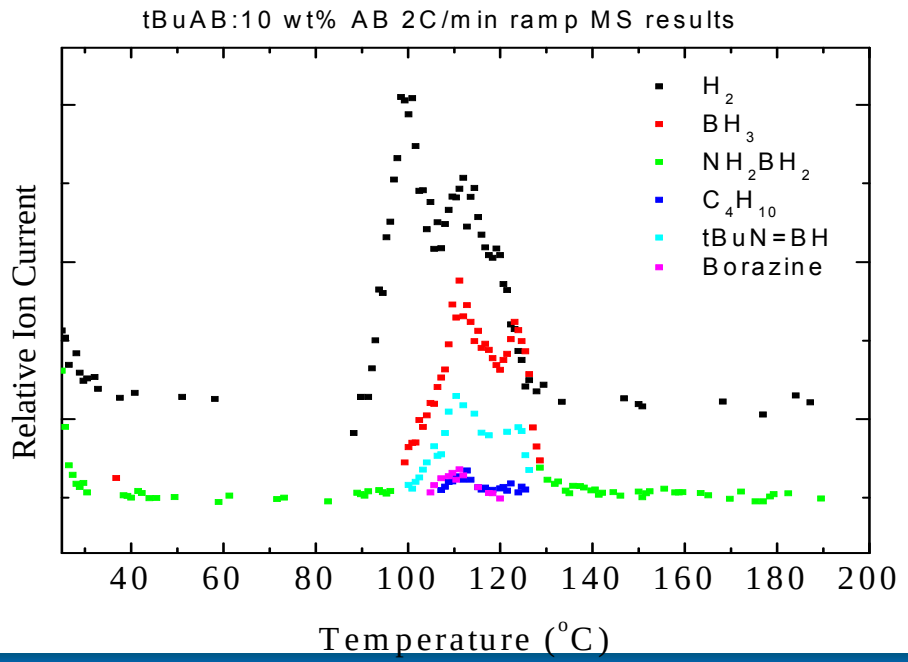


Evolved Gas Analysis

- Addition of tBuAB initiates decomposition at lower temperatures.
- H_2 stream is not pure, containing C_4H_{10}.
- 10-50 wt% tBuAB required to suppress borazine formation.







Conclusions

- Amine boranes potentially can be used as a vehicular hydrogen storage material.
- Purity of the hydrogen stream is critical for use with a fuel cell.
  - Pure H_2 can be provided by carefully conditioning the fuel (encapsulation, drying, heating rate, impurities).
- Thermodynamics and kinetics can be controlled by conditioning as well.
- Regeneration of the spent amine borane fuel is still the greatest challenge to its potential use.
- Addition of hydrocarbon-substituted amine boranes alter the chemistry dramatically.
- Decomposition of the substituted amine borane mixed system favors reaction products that are more potentially easier to regenerate the hydrogenated fuel.
- t-butylamine borane is not the best substituted amine borane to use since it releases isobutane; however, formation of $CNBH_x$ products does occur.

Acknowledgements

- Tom Autrey
- John Linehan
- Q Grindstaff
- Daniel Brasfield
- Karl Gross

- Y-12 Plant Directed Research and Development funding.