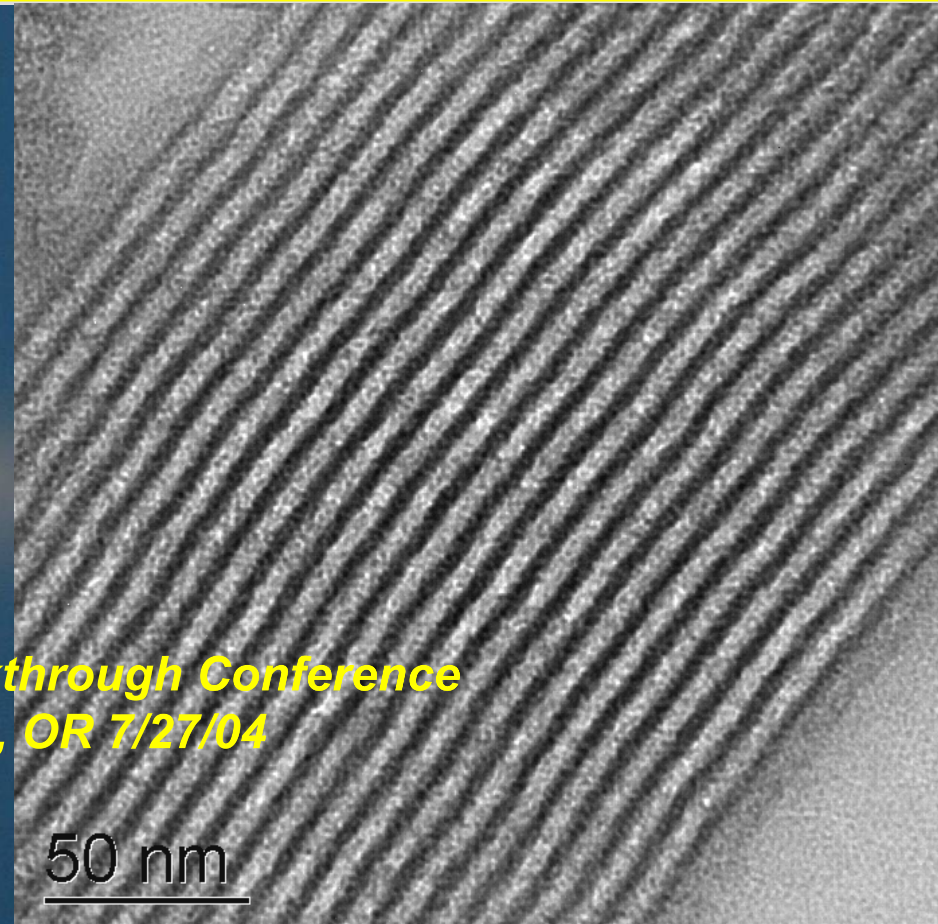
Enhancement of the Hydrogen Storage Properties of Ammonia Borane in the MicroNano Pores of Mesoporous Silica.



MicroNano Breakthrough Conference
Portland, OR 7/27/04

Office of Science
U.S. DEPARTMENT OF ENERGY

Pacific Northwest National Laboratory
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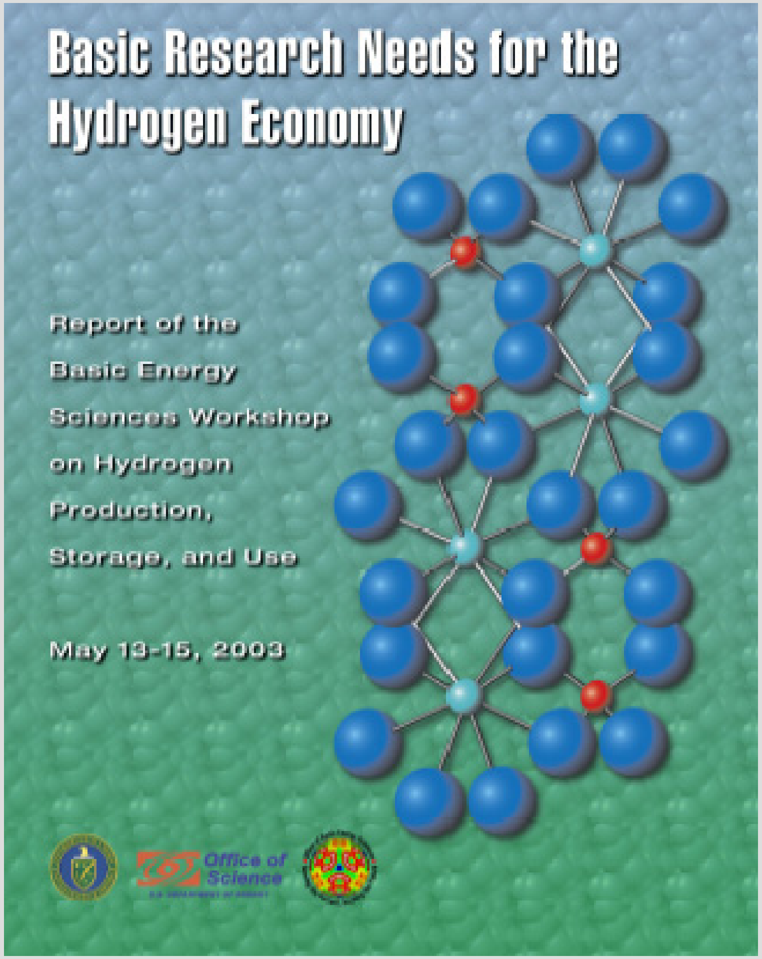
DOE (BES) Hydrogen Research Needs



ACS National Meeting Anaheim 3/30/04

The President's Hydrogen Fuel Initiative. *S. Santipal*

Energy-Related Research in the DOE Office of Basic Energy Science *W. Stevens*

Basic Research Needs for the Hydrogen Economy. *M. Dresselhaus*

Basic Research Needs in H_2 Production for a H_2 Energy Economy *T. Mallouk*

Hydrogen Storage issues in a new Hydrogen Economy. *P. Gena*

Fuel Cells: The Final Step in a Hydrogen Economy *F. DiSalvo*

Biggest Challenge: *on-Board Storage*

New ideas, new materials = Micro-Nano?

DOE (EERE) Hydrogen Storage Challenge

FreedomCAR On-board storage for FC vehicles
Call for "virtual centers" and advanced concepts

Volumetric Density

year	2010	2015
KWh/liter	1.5	2.7
MJ/liter	5.4	9.7
gm/liter	45	81

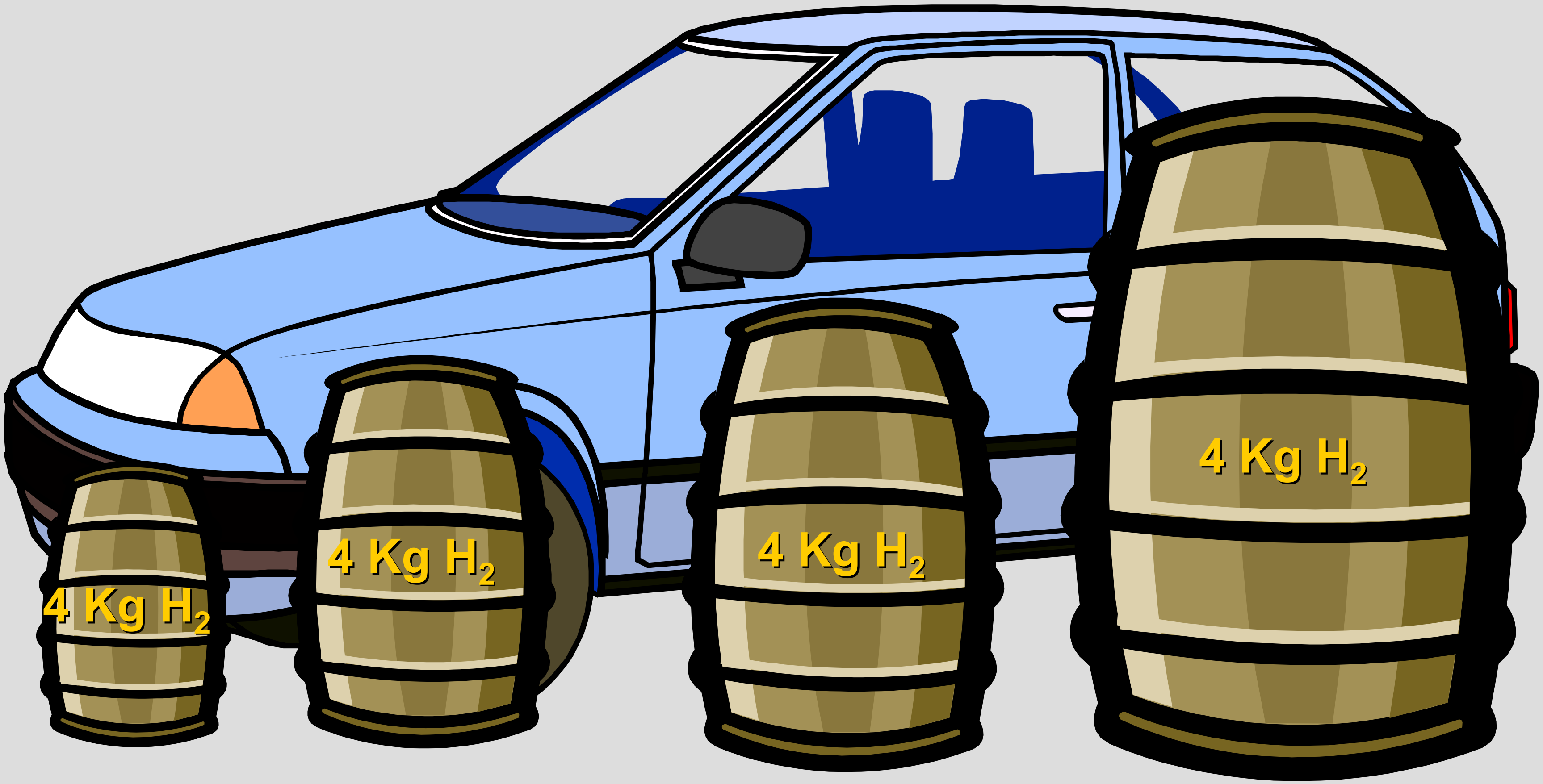
Gravimetric Density

year	2010	2015
KWh/kg	2	3
MJ/kg	7.2	10.8
gm/kg	60	90

Operational temperature: $-20 < {}^{\circ}C < 80$

Material with 9 wt% H_2 that releases $H_2 < 80^{\circ}$ C

Volumetric Challenges



MgH_2 32 liter

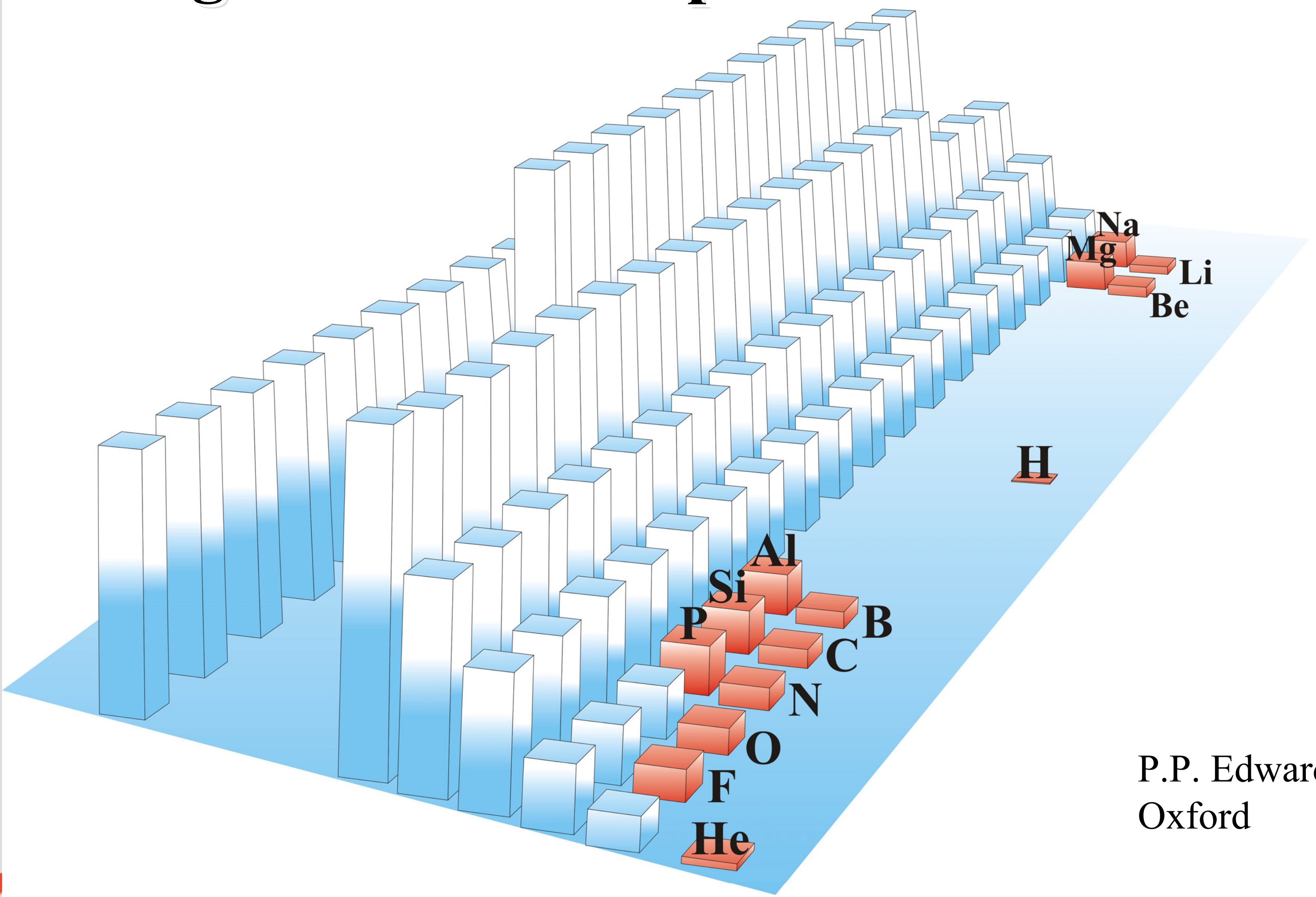
liquid H_2 (-250˚C) 56 liter

$NaAlH_4$ 69 liter

Compressed H_2 (200 bar) 225 liter

Gravimetric Challenges

Height of bar corresponds to mass of element



P.P. Edwards
Oxford

The Periodic Table of the Chemical Elements.
The mass of each element is indicated by its elevation above the plane.

NH_xBH_x stores significant quantity of hydrogen

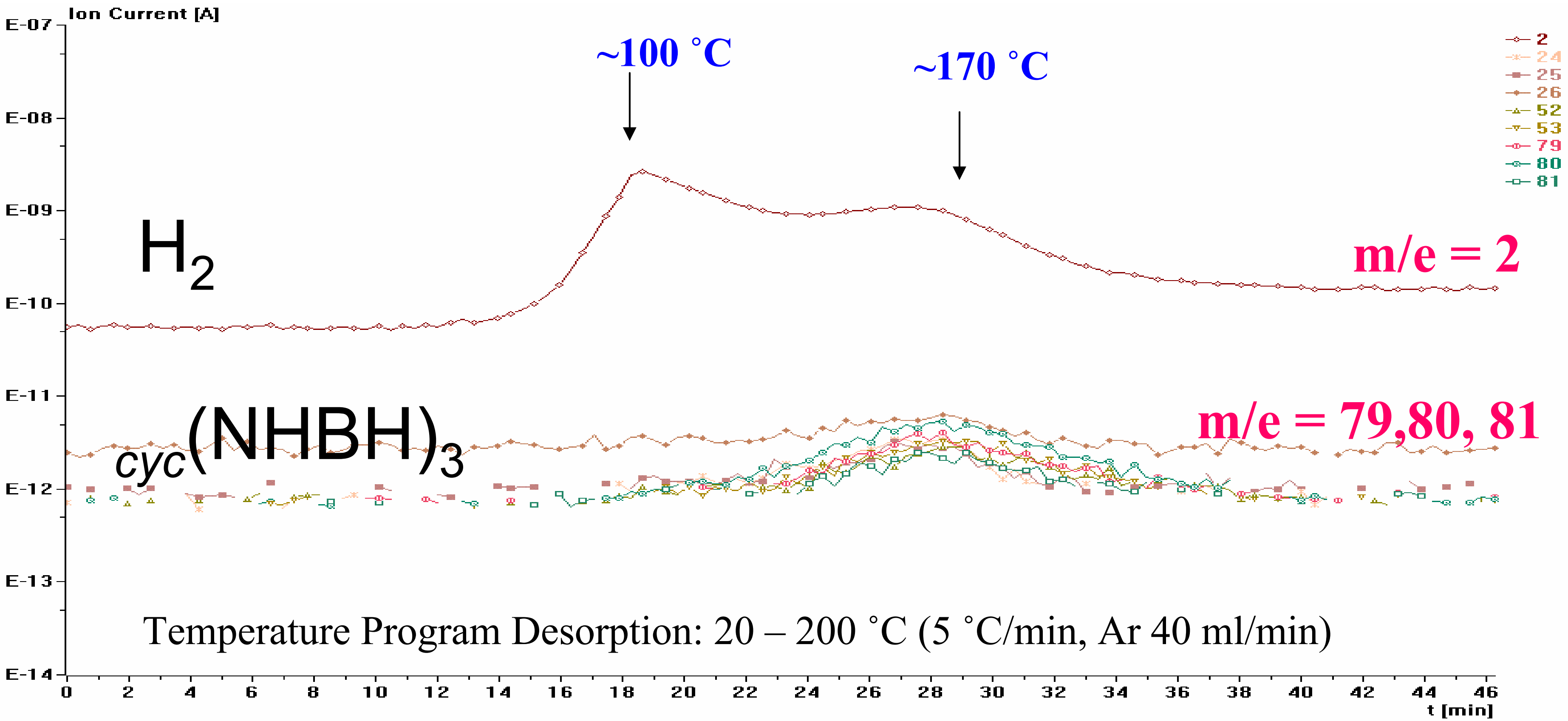
	Wt% H_2	T (°C)
$NH_4BH_4 \rightarrow NH_3BH_3 + H_2$	6.1	<25
$NH_3BH_3 \rightarrow NH_2BH_2 + H_2$	6.5	<100
$NH_2BH_2 \rightarrow NHBH + H_2$	6.9	>100
$NHBH \rightarrow BN + H_2$	7.3	>500

- Hydrogen Storage potential Between 6 and 24 wt% H_2
- NH_3BH_3 isoelectronic with ethane yet is a solid, mp 115 C

- Computational: Enthalpy (each step) near thermoneutral (reversible?) Borohydride hydrolysis –60 kcal/mol (B-O very stable).

Volatile Products from NH_3BH_3

$$NH_3BH_3 \rightarrow \text{Products} + H_2 \rightarrow \text{Products} + H_2$$



Get H_2, but temperature still a bit high and volatile borazine not good for FC

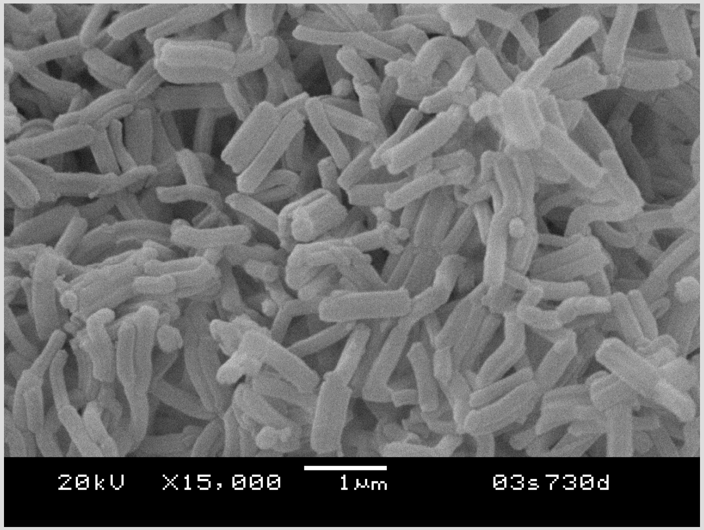
How does nano science improve the efficiency of hydrogen storage?

- Hypothesis: Nano phase hydrogen storage materials will have different thermodynamic and kinetic properties compared to bulk hydrogen storage materials.

- Nano particles of Hydrogen Storage material
  - Control Reactivity (enhanced rate of hydrogen release)
  - Control Selectivity (prevent Borazine formation)
  - Can we prevent fusion of the nanoparticles as the reaction proceeds? (Don't want to lose nano properties)

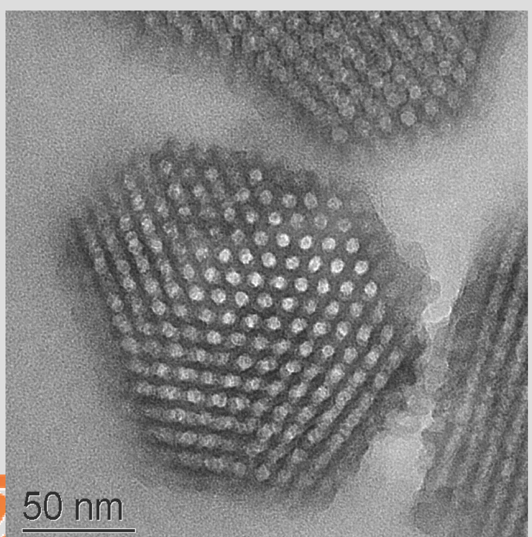
- Use Mesoporous Scaffolds

Synthesis of Nano-phase Ammonia Borane



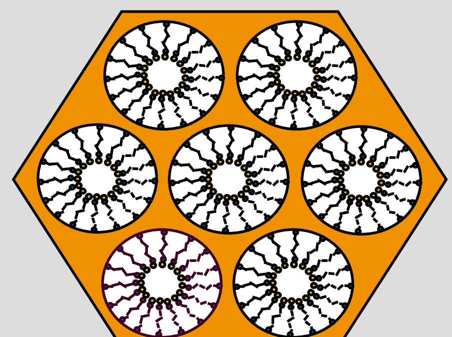
Mesoporous silica (SBA-15)
100-200 micron particles
High surface area (900 m^2/gm)
High porosity (1.3 cc/gm)

Use as a scaffold 6-7 nm wide channels to *hold* Ammonia Borane (NH_3BH_3) in the nano-phase



NH_3BH_3

Add saturated solution of NH_3BH_3 to SBA-15



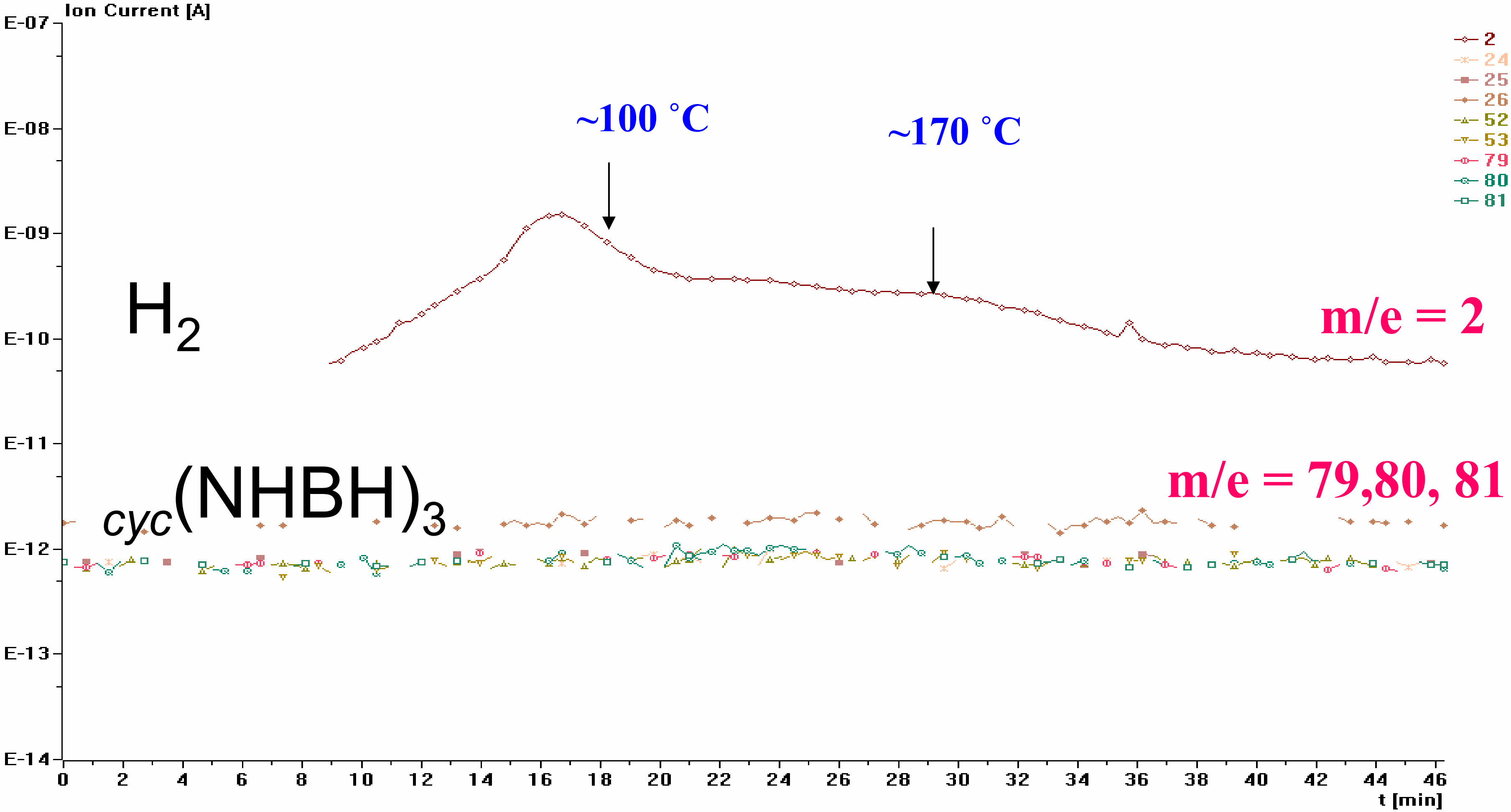
Ammonia borane infiltrated

How does NH_3BH_3 embedded in a mesoporous scaffold compare to bulk NH_3BH_3?

- Minimize borazine formation?
- Change thermochemistry?
- Change kinetics?

- TEM/BET/EDX
  - Material Characterization (Surface area, porosity)
- DSC/MS (differential scanning calorimetry/mass spec)
  - Volatile products
  - Thermodynamics
  - Kinetics
- Solid State NMR ^{11}B
  - Product identity
  - Kinetics

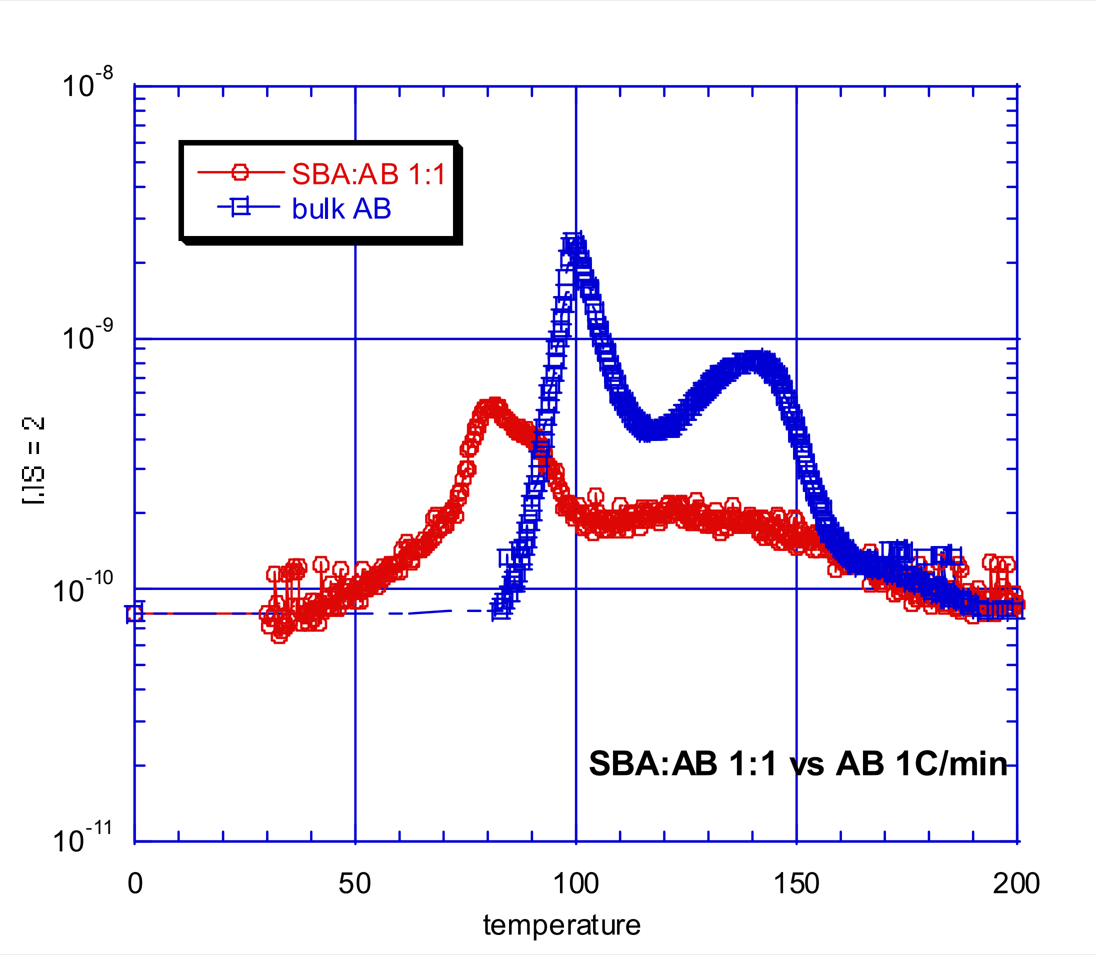
Volatile Products from NH_3BH_3 in SBA-15 mesoporous scaffold



H$_2$ at lower temperature!

No Borazine!

Hydrogen data Bulk AB vs Scaffold AB



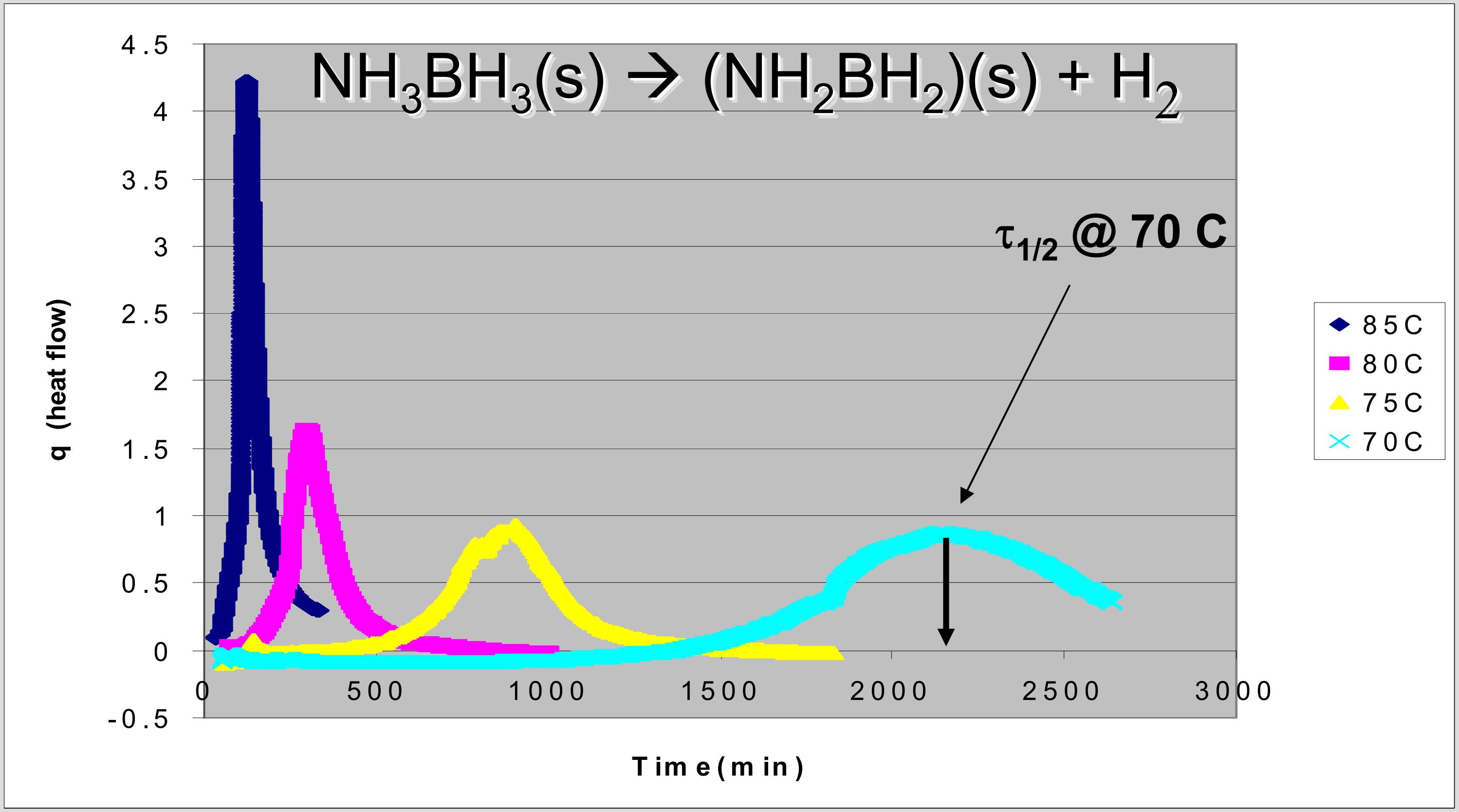
DSC temperature ramp 1 ºC/min

Hydrogen released from NH_3BH_3 at lower temperature when it is embedded in scaffold

Enhanced kinetics!

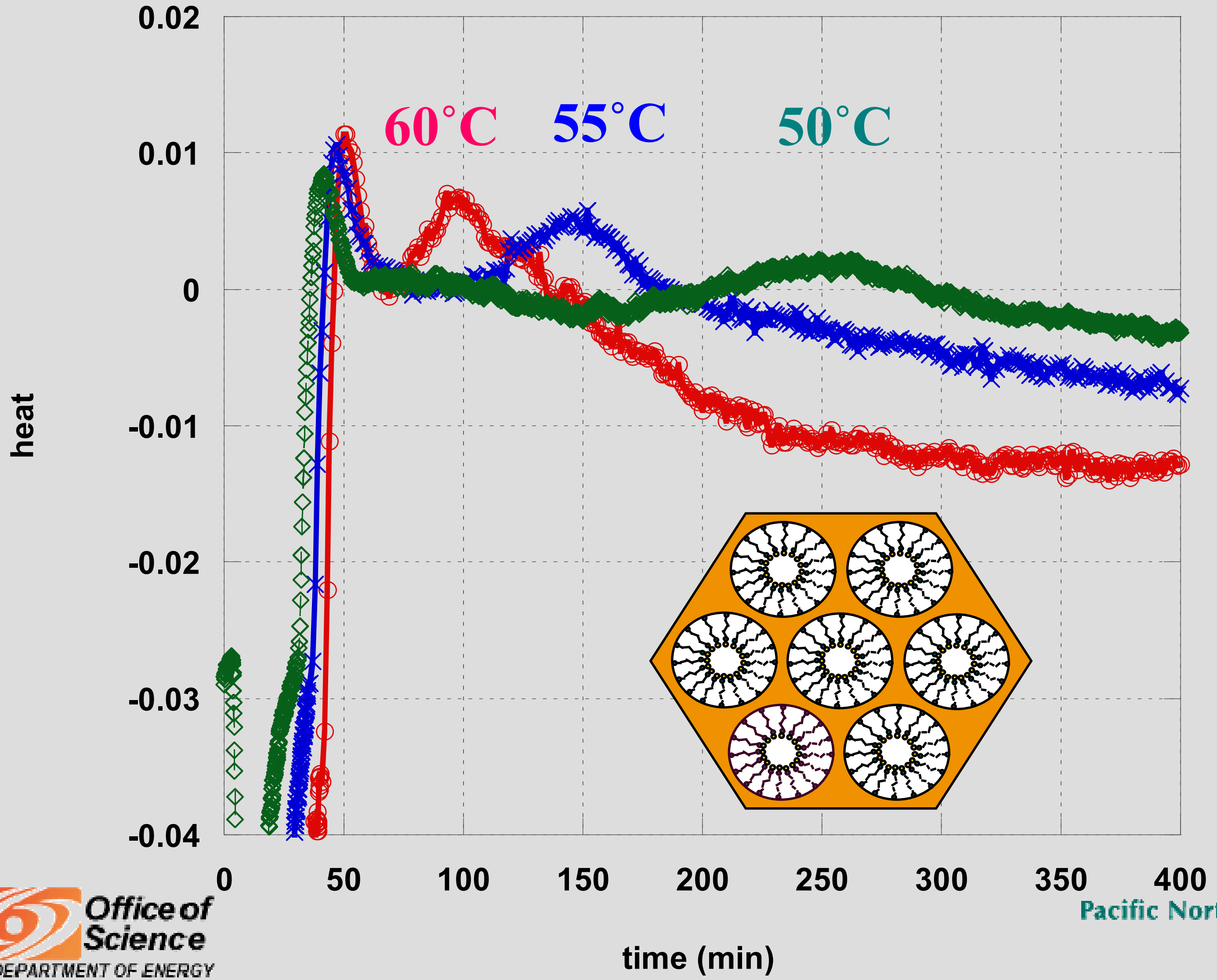
Can we quantify a difference in the barrier for hydrogen release from NH_3BH_3?

Quantitative Kinetic Comparison bulk vs scaffold (isothermal DSC)

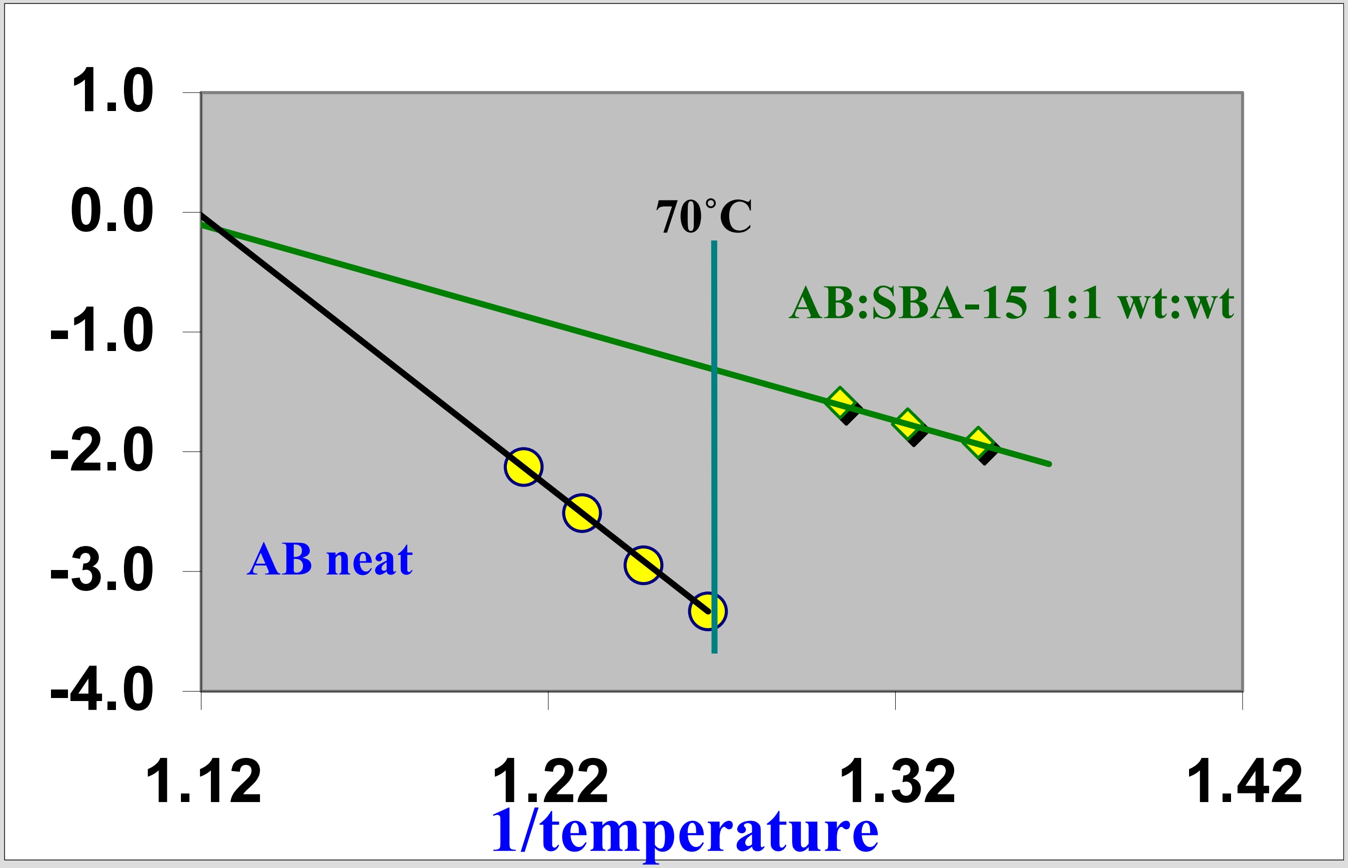


If peak max is ~ half-life than we can get semi-quantitative rate comparison between AB in the scaffold vs. neat AB.

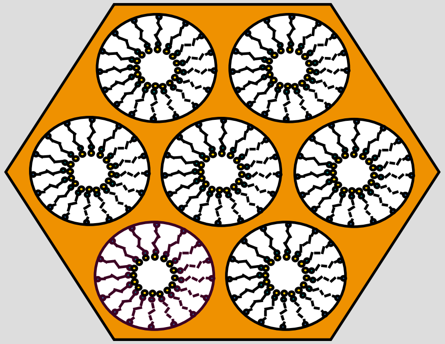
Ammonia Borane in Mesoporous Scaffold (isothermal DSC)



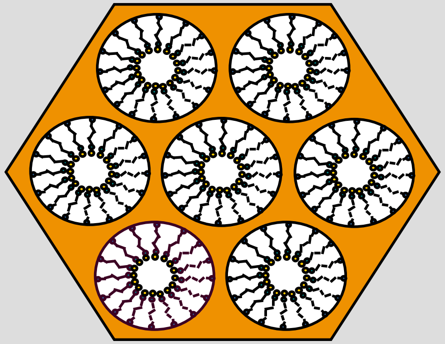
Comparison of H_2 Release: Ammonia Borane versus mesoporous Ammonia Borane



Rate of hydrogen release is 1 to 2 orders of magnitude faster with mesoporous scaffold



Summary

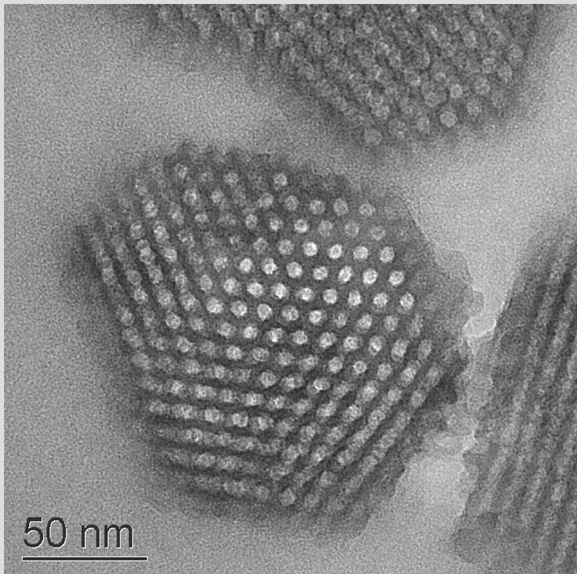


►H_2 release from NH_3BH_3 in Mesoporous scaffolds:

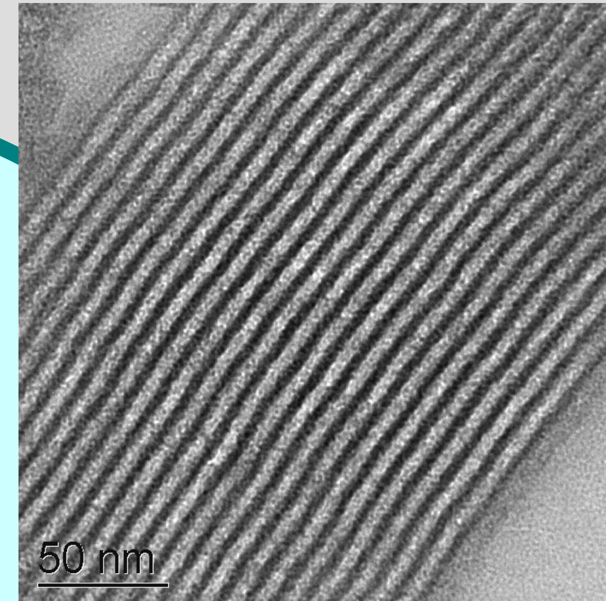
- *Control* of reactivity for H_2 release from AB
  - 1-2 orders of magnitude faster!

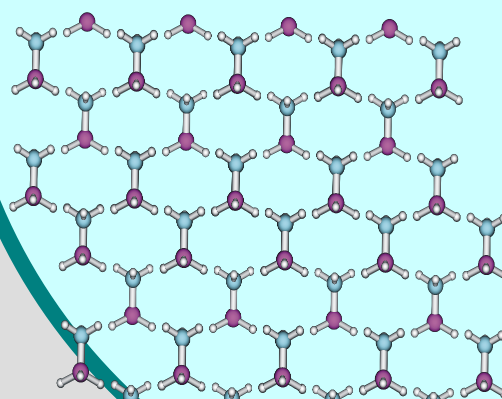
- *Control* of selectivity of H_2 release from AB
- SBA-15 appears to guide NH_3BH_3 towards linear polymer formation.
  - No borazine seen in volatile products or left behind in scaffold.
  - No cyclized products observed in NMR and DSC data show process is less exothermic

Future Efforts



65 Å





Vary pore diameter (60-300 nm)
Coat nano particles (in vs. out)
Thin films (curvature)
Cover Si-OH (alkane)
More detailed kinetic studies

Surface interactions?
Curvature?
Changes in structure?

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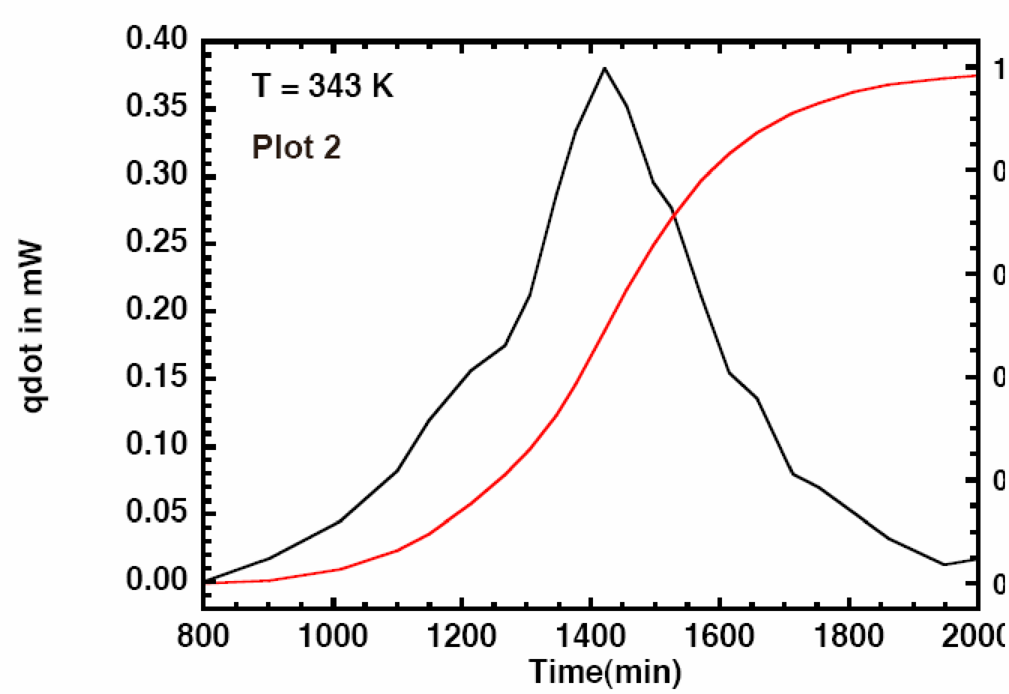
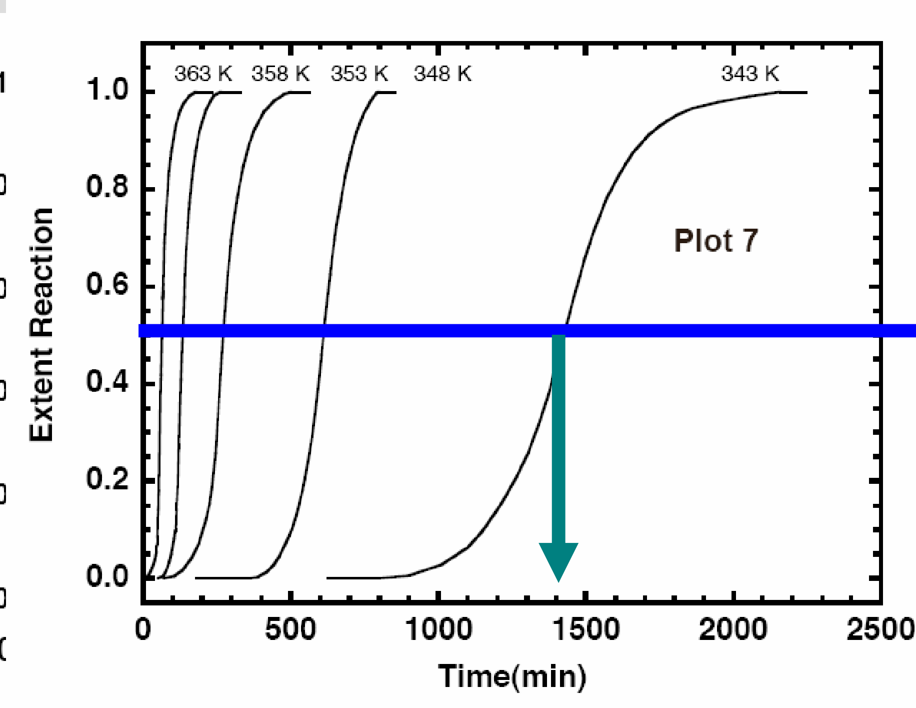
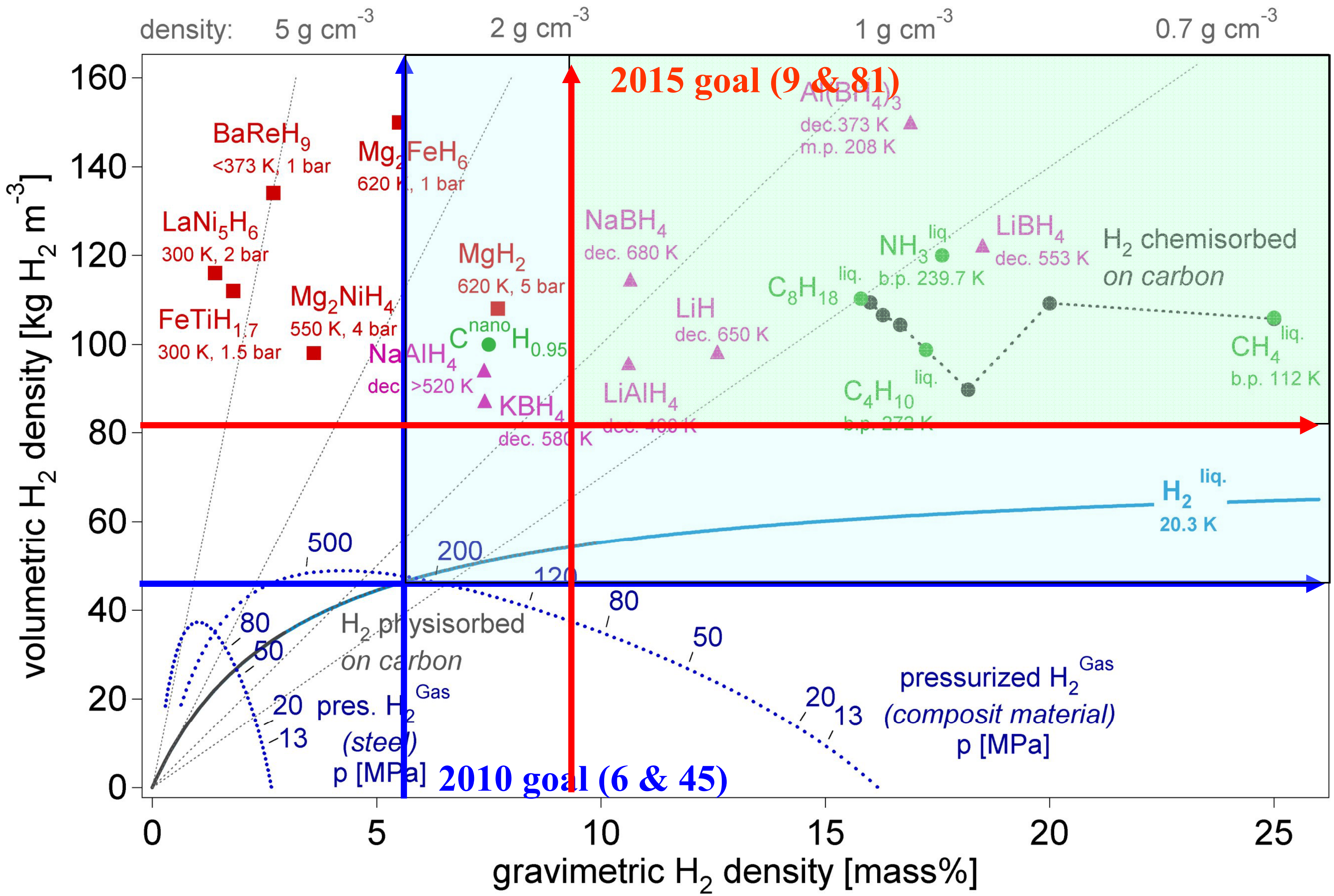
Kinetic Analysis





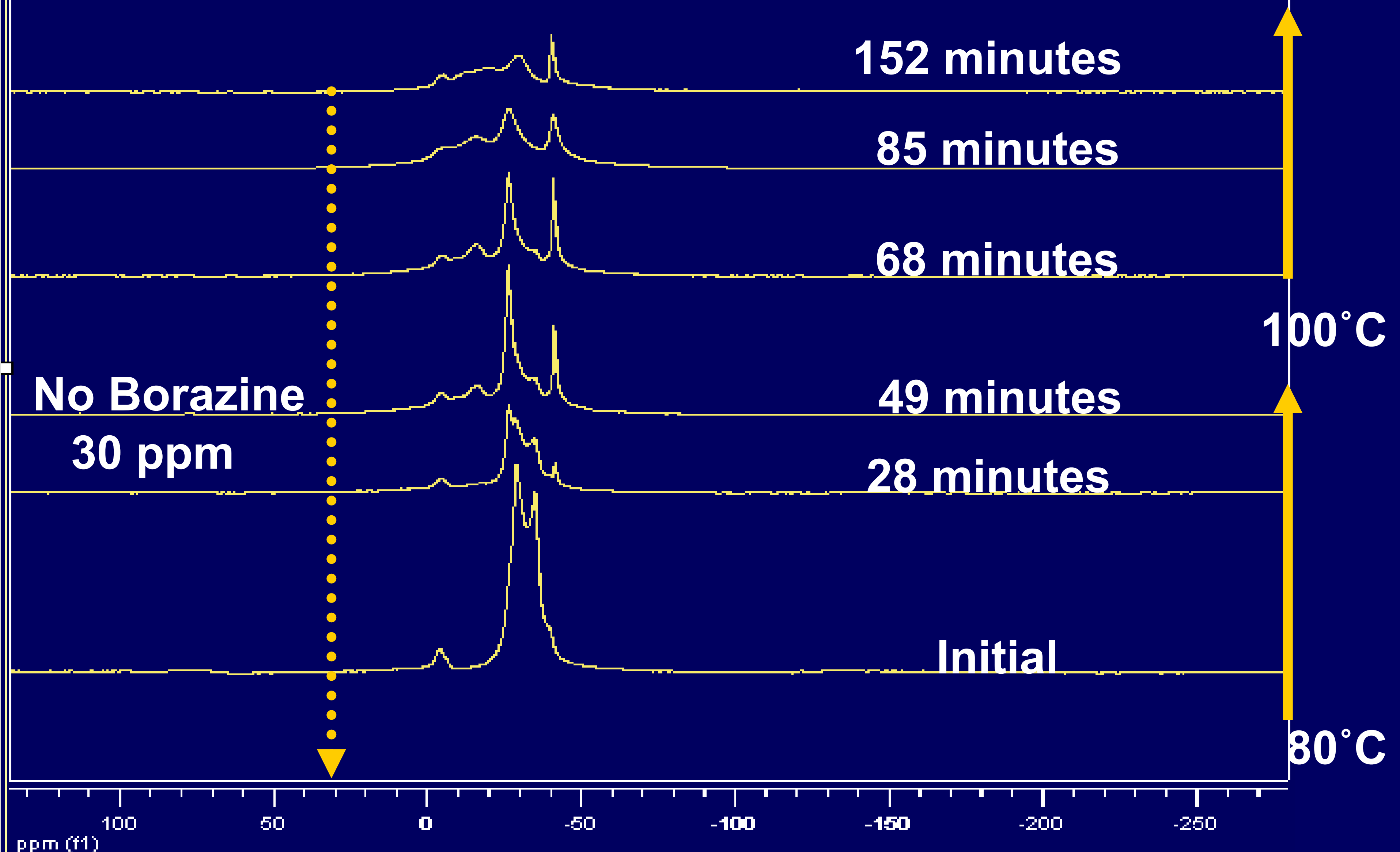
Integrate the DSC curve as a function of temperature to get half-life

Materials for H_2 Storage



Ref: A. Züttel, “Materials for hydrogen storage”, materials today, Septemper (2003), pp. 18-27

Borazine not in volatiles nor stuck in scaffold(?)



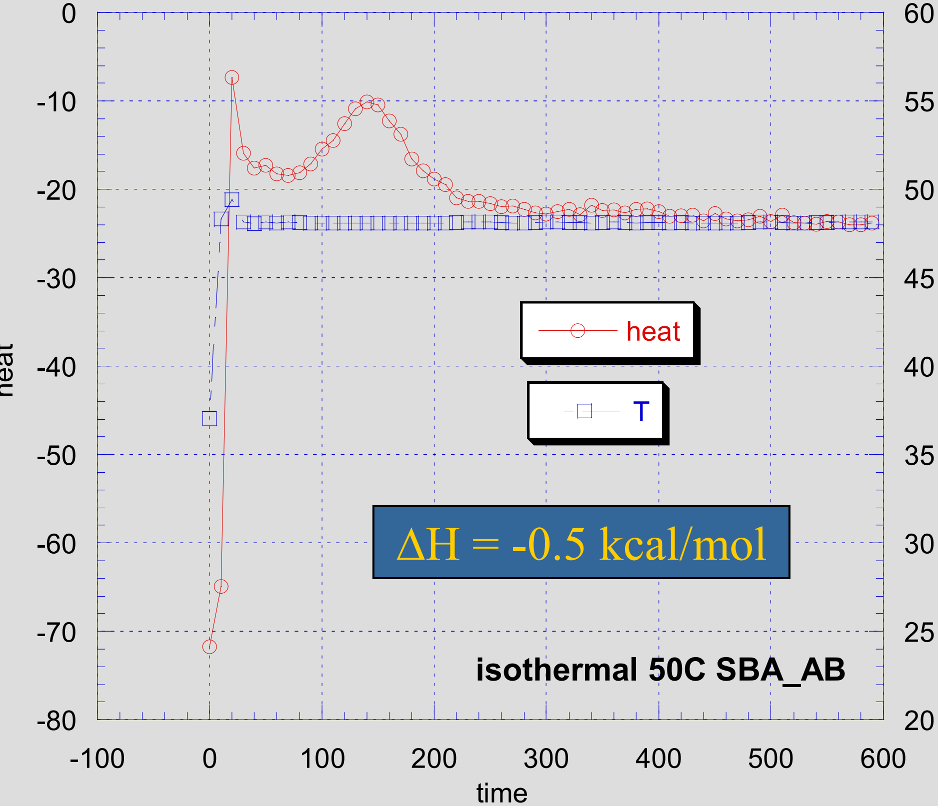
Solid ^{11}B NMR (9.6 KHz) of NH_3BH_3 on SBA-15

NH_3BH_3 in Scaffold

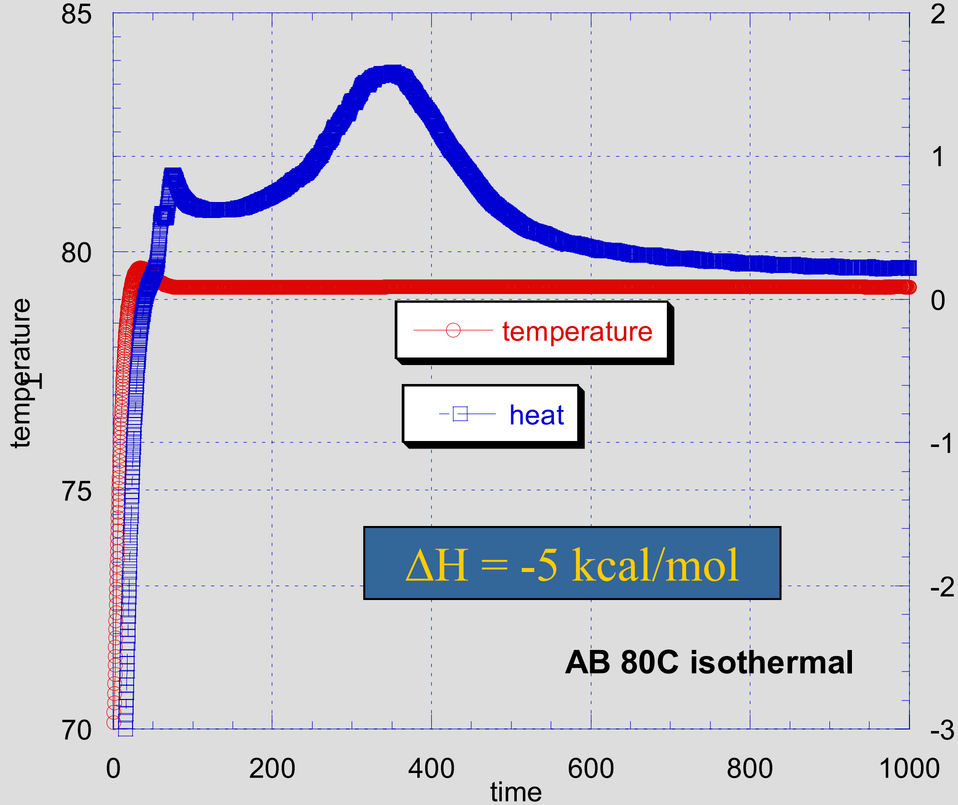
- Borazine not released to the gas phase and it is not stuck in the scaffold. Unlike the bulk reaction, borazine is not formed from the ammonia borane in the scaffold.
- Look closer at the DSC/MS data. Are there any hints?
- If cyclized products are not formed in nano-pores of SBA-15 reaction should be less exothermic.

Isothermal DSC

AB:SBA-15



AB bulk



(1) H_2 release from AB embedded in SBA-15 comes off faster at lower temperatures!

(2) H_2 release from AB embedded in SBA-15 is not as exothermic!

Why are we interested in H_2 storage?

Fuel Cells

H_2 Production

W

H_2 Storage

Hydrogen Economy

State of the Union 2003