Controlled Hydrogen Release From Ammonia Borane Using Mesoporous Scaffolds.

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Outline

- Background NH_xBH_x
  - Thermal decomposition pathways
- Approach
  - Mesoporous scaffolds
- Results
  - Thermodynamic and Kinetic Comparisons
- Future Work

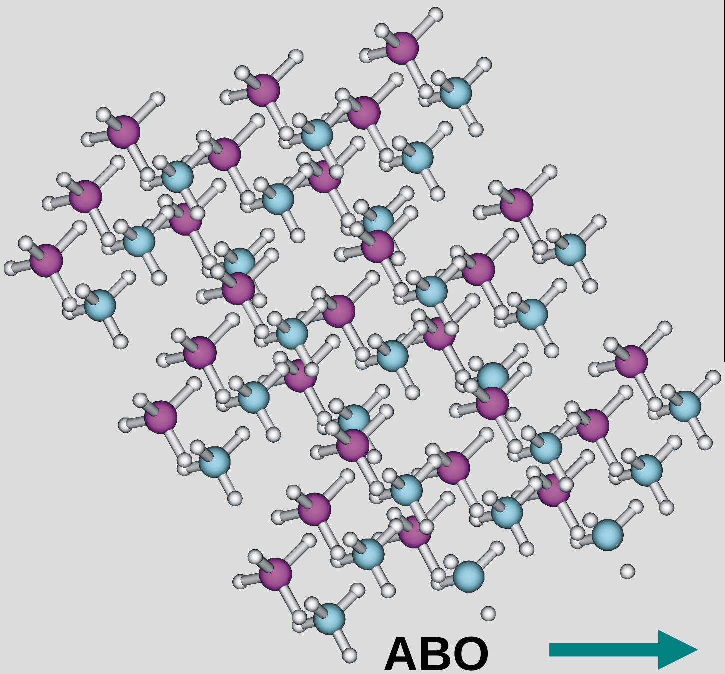
NH_xBH_x Store significant quantity of hydrogen (>6 wt%/step)

	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	<120
$NH_2BH_2 \rightarrow NHBH + H_2$	6.9	>120
$NHBH \rightarrow BN + H_2$	7.3	>500

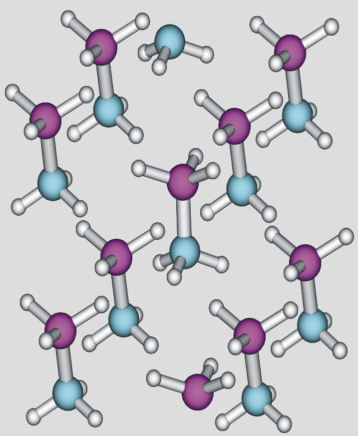
Two sequential steps > 12 wt% hydrogen

Favorable Thermodynamics?

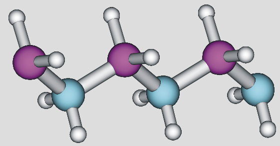
Reactants		Products	ΔE (kcal/mol)
$NH_4BH_4(s)$	$\rightarrow$	$NH_3BH_3(s) + H_2$	-2.3
$NH_3BH_3(s)$	$\rightarrow$	$(NH_2BH_2)_n + H_2$	+8.8
$(NH_2BH_2)_n$	$\rightarrow$	$(NHBH)_n + nH_2$	-3.2
$(NHBH)_n$	$\rightarrow$	$BN(s) + nH_2$	-9.2



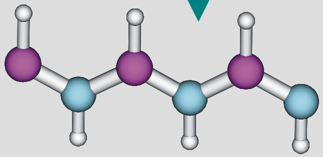
ABO



AB+ H_2



PAB+ H_2

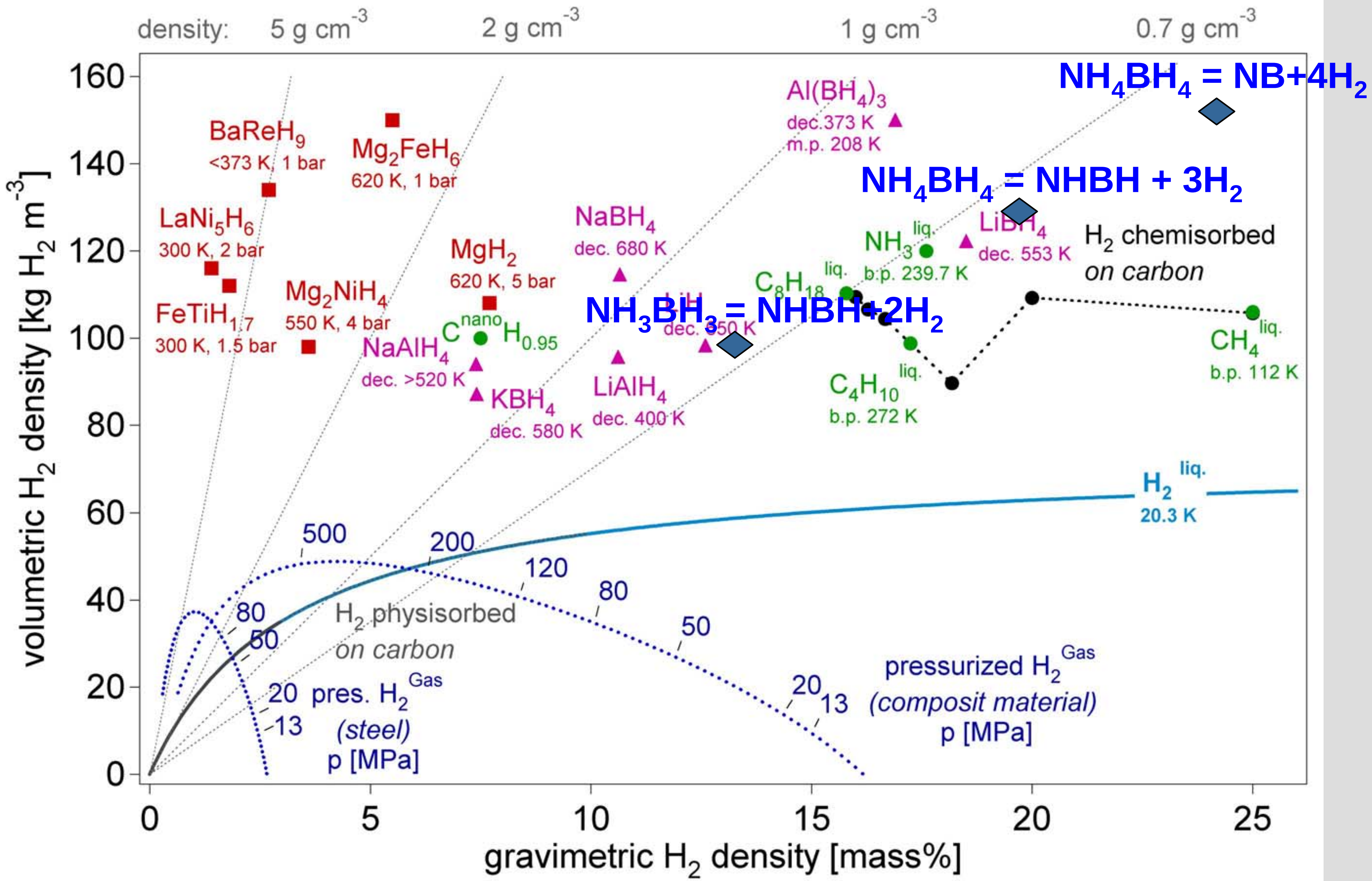


PIB+ H_2

ABO = NH_4BH_4
AB = NH_3BH_3
PAB = $(NH_2BH_2)_n$
PIB = $(NHBH)_n$

$$BH_4 + 4H_2O \rightarrow B(OH)_4 + 4H_2$$
$$\Delta H = -60 \text{ kcal/mol}$$

Materials for H_2 Storage



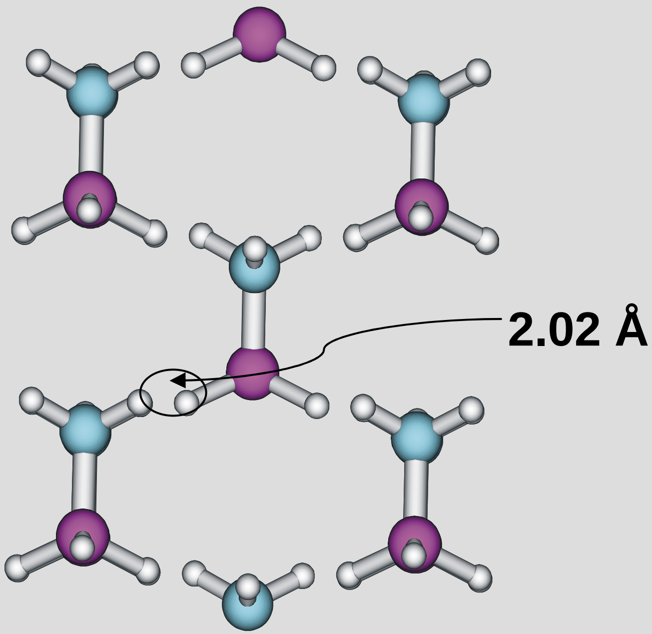
Ref: A. Züttel, "Materials for hydrogen storage", materials today, Septemper (2003), pp. 18-27

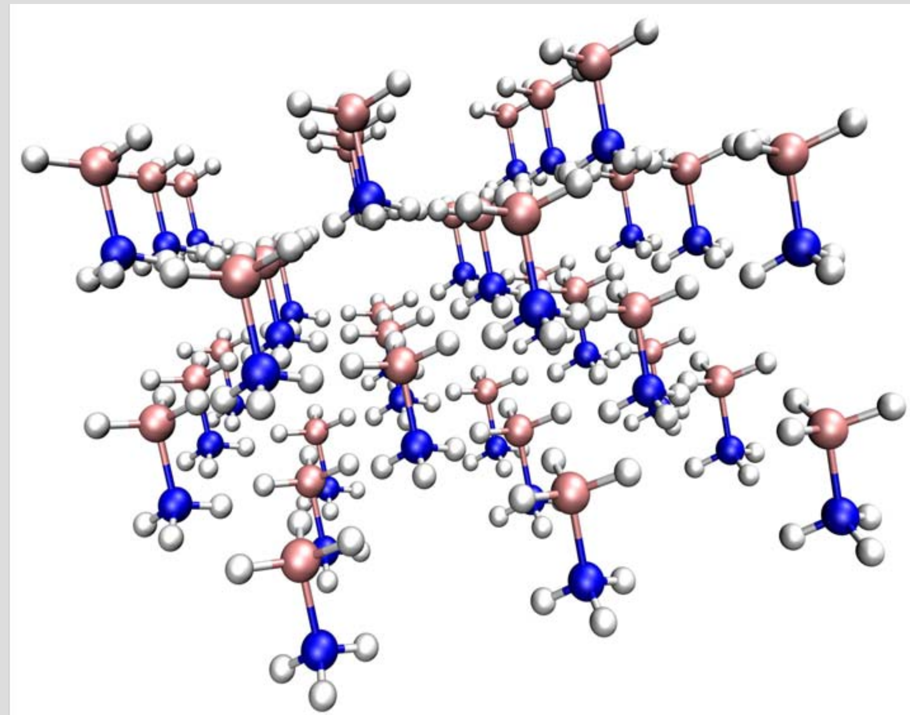
Ammonia Borane vs Ethane
Any similarities?

Isoelectronic Isomers

	$H_3N \rightarrow BH_3$	H_3C—CH_3
MW	30.81	30.07
Mp[°C]	114	-172
bonding	dative	covalent
*D*H°[kcal/m]	31	90
M[D]	5.2	0
R[A]	1.66	1.53
Wt% H2	19%	19%

How is hydrogen released?





δ-　　δ+

BH ----- HN　　　Dihydrogen bond

Hydride atoms act as Proton acceptor

Thermolysis of Ammonia Borane

	T (˚C)
$NH_3BH_3 \rightarrow (NH_2BH_2)_n + H_2 + ?$	<120
$(NH_2BH_2)_n \rightarrow (NHBH)_n + H_2 + ?$	>120

Are there other ‘products’?

is the hydrogen clean? (*borazine*)

How is the H_2 released?

mechanism (*solid state*)

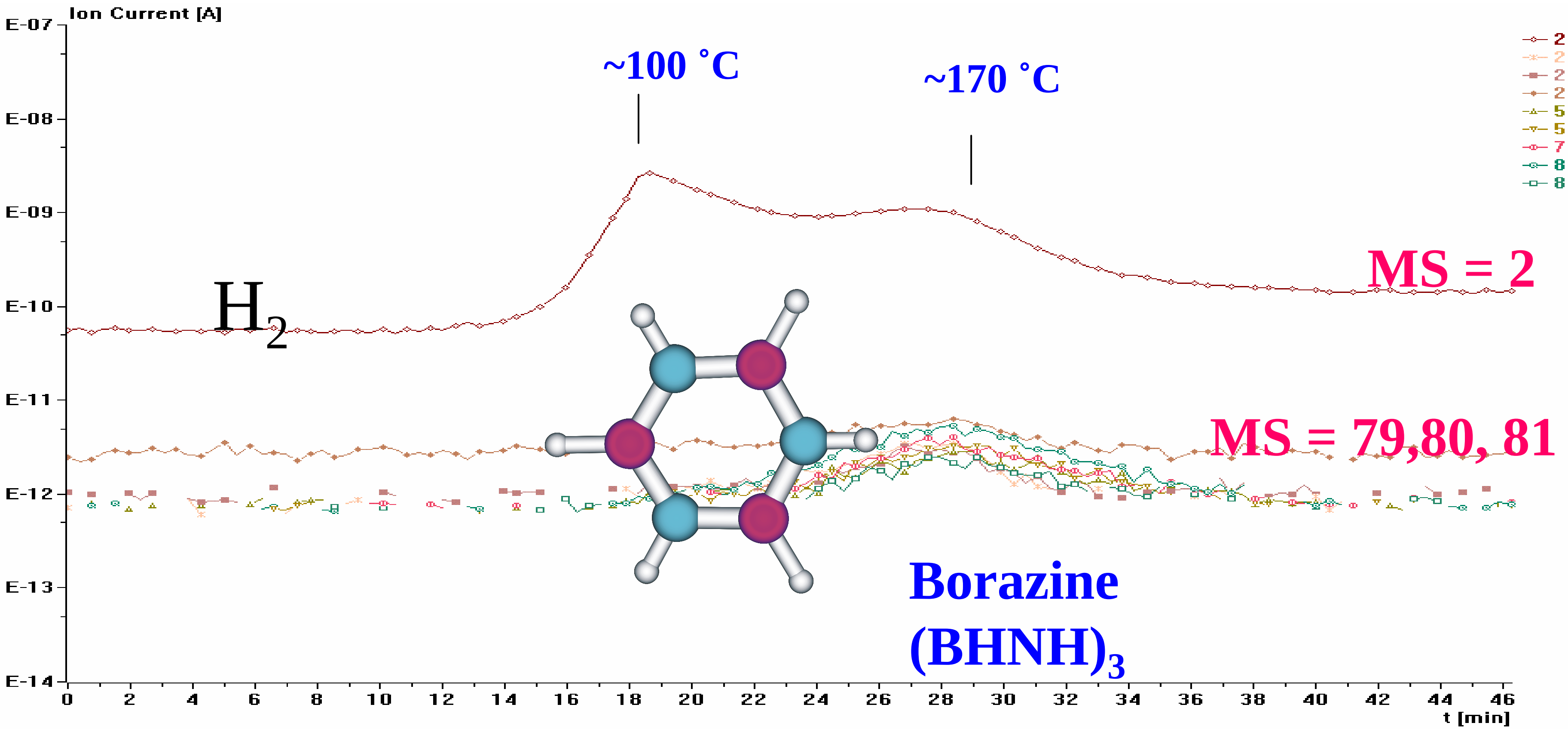
What is the activation barrier?

can we change it with catalysis, (*other*)

Can the reaction be reversible?

Volatile Products from NH_3BH_3

$NH_3BH_3 \rightarrow$ Products + $H_2 \rightarrow$ Products + H_2



DSC: 20 – 200 ˚C (5 ˚C/min, Ar 40 ml/min)

NH_3BH_3 Challenges

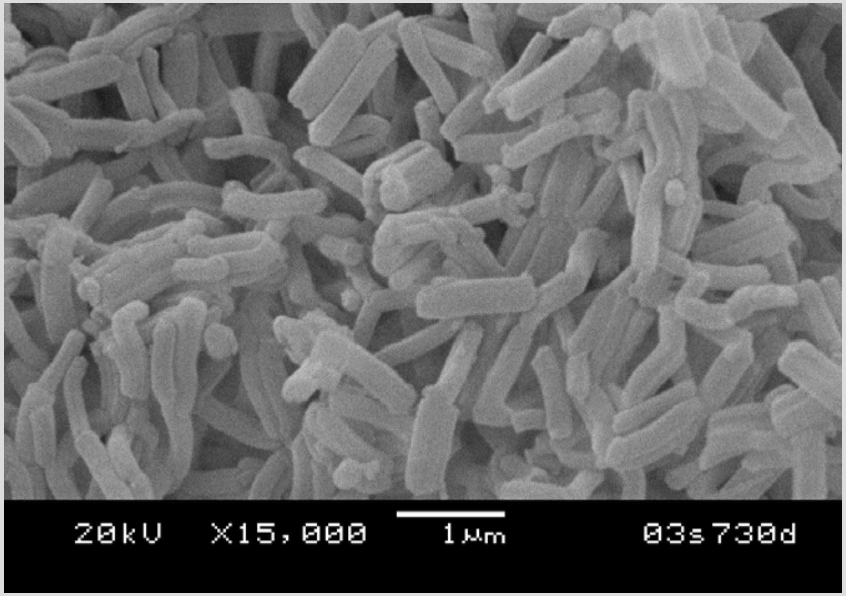
- Meets and exceeds DOE gravimetric & volumetric targets
- Need to lower temperature (or increase rates)
- Minimize volatile (borazine)
- Can this be reversible?
  - Not making B-O bonds (ΔH = -60 kcal/mol)
  - Release of H_2 near thermoneutral (ΔH = -5 kcal/mol)

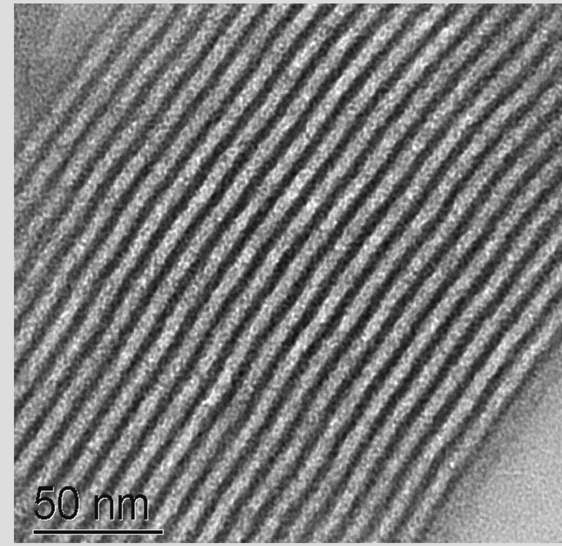
How does nano science improve the efficiency of hydrogen storage?

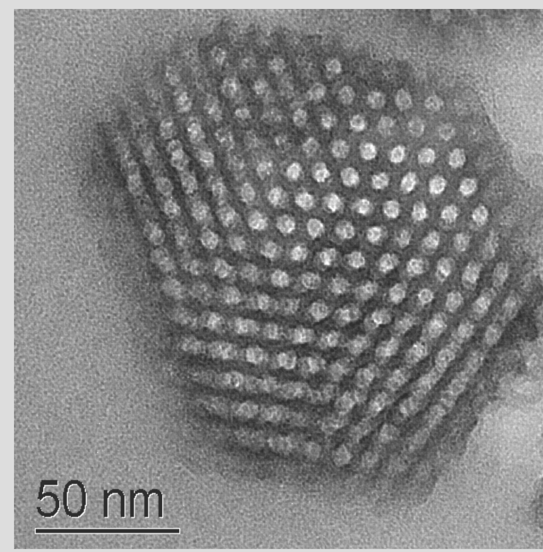
- **Hypothesis:** Nano phase hydrogen storage materials can have different thermodynamic and kinetic properties compared to bulk hydrogen storage materials.

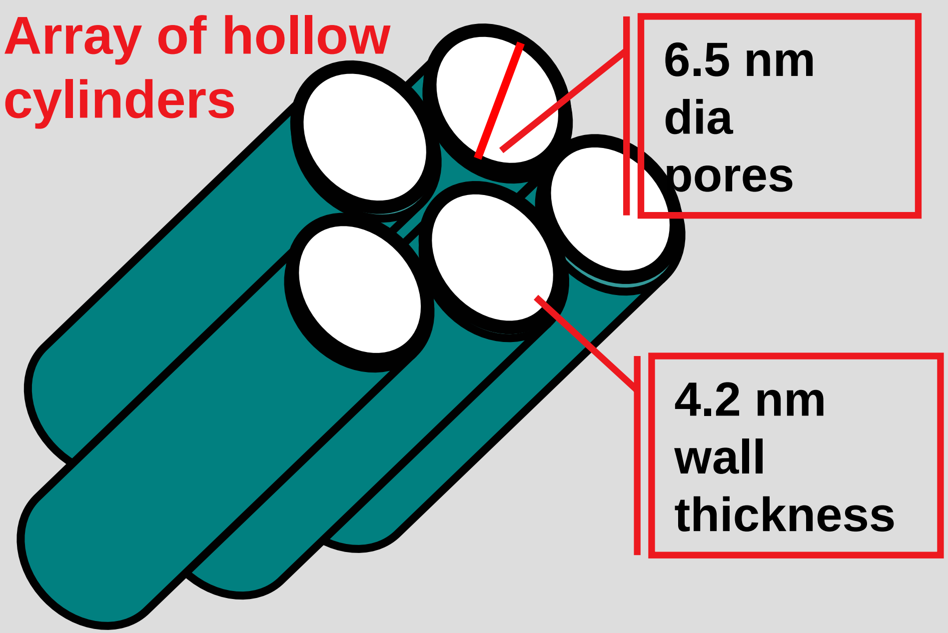
- Nano particles of Hydrogen Storage material
  - Control Reactivity (enhanced rate of hydrogen release)
  - Control Selectivity (prevent borazine formation)
  - Can we prevent fusion of the nanoparticles as the reaction proceeds? (Don't want to lose nano properties)

Approach: Nano-scale Scaffolds



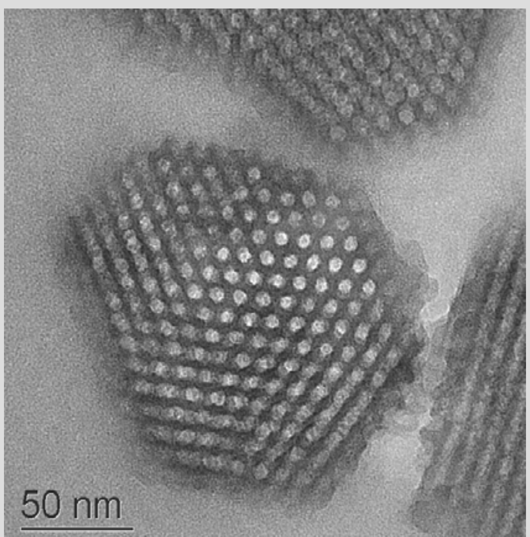






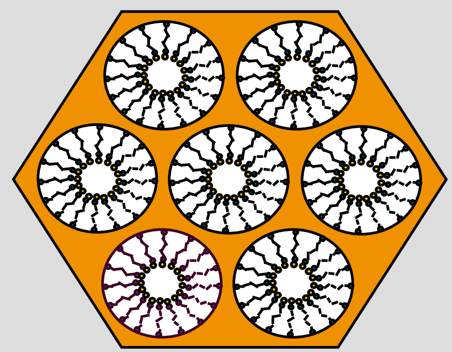
Nano-phase Ammonia Borane

Use mesoporous silica (SBA-15) as a scaffold 6-7 nm wide channels to *hold* Ammonia Borane (NH_3BH_3) in the nano-phase. Should also preserve nanophase. Trap borazine in pores?



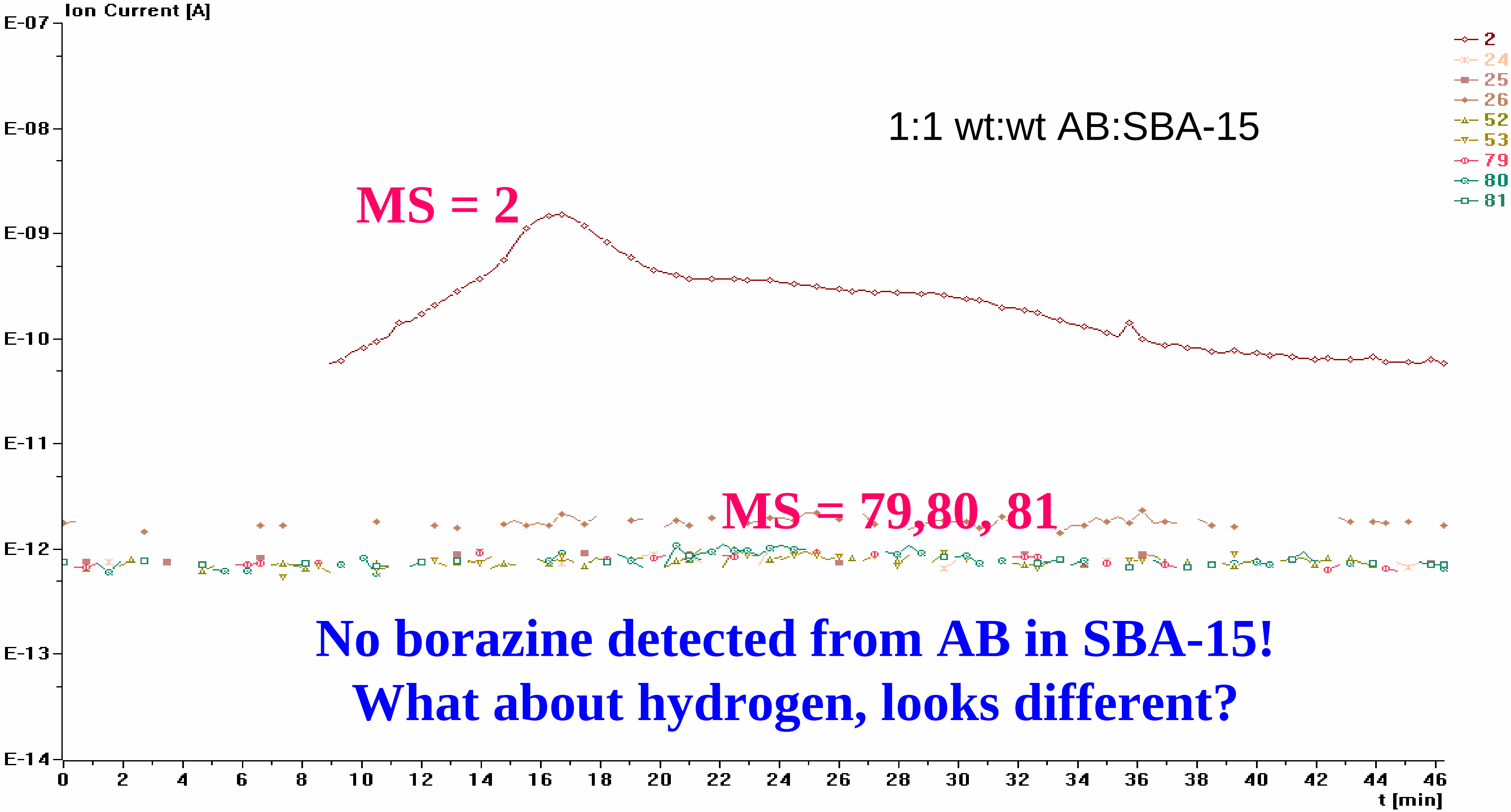
NH_3BH_3

Add saturated solution of NH_3BH_3 to SBA-15

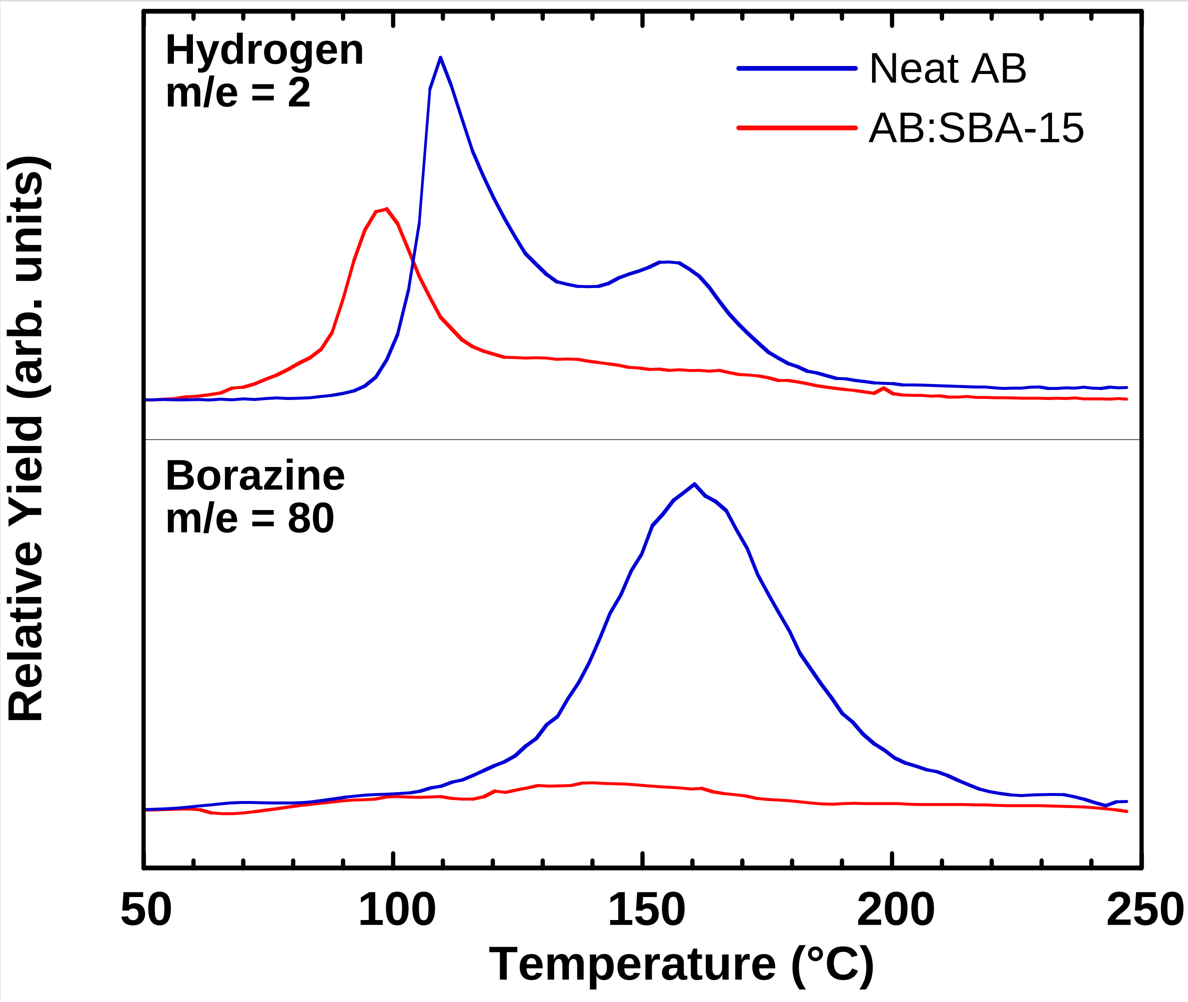


Ammonia borane infiltrated

Volatile Products from NH_3BH_3 in SBA-15 mesoporous scaffold



Hydrogen at lower temperature



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

Little borazine!

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

What is ΔH_{rxn}?

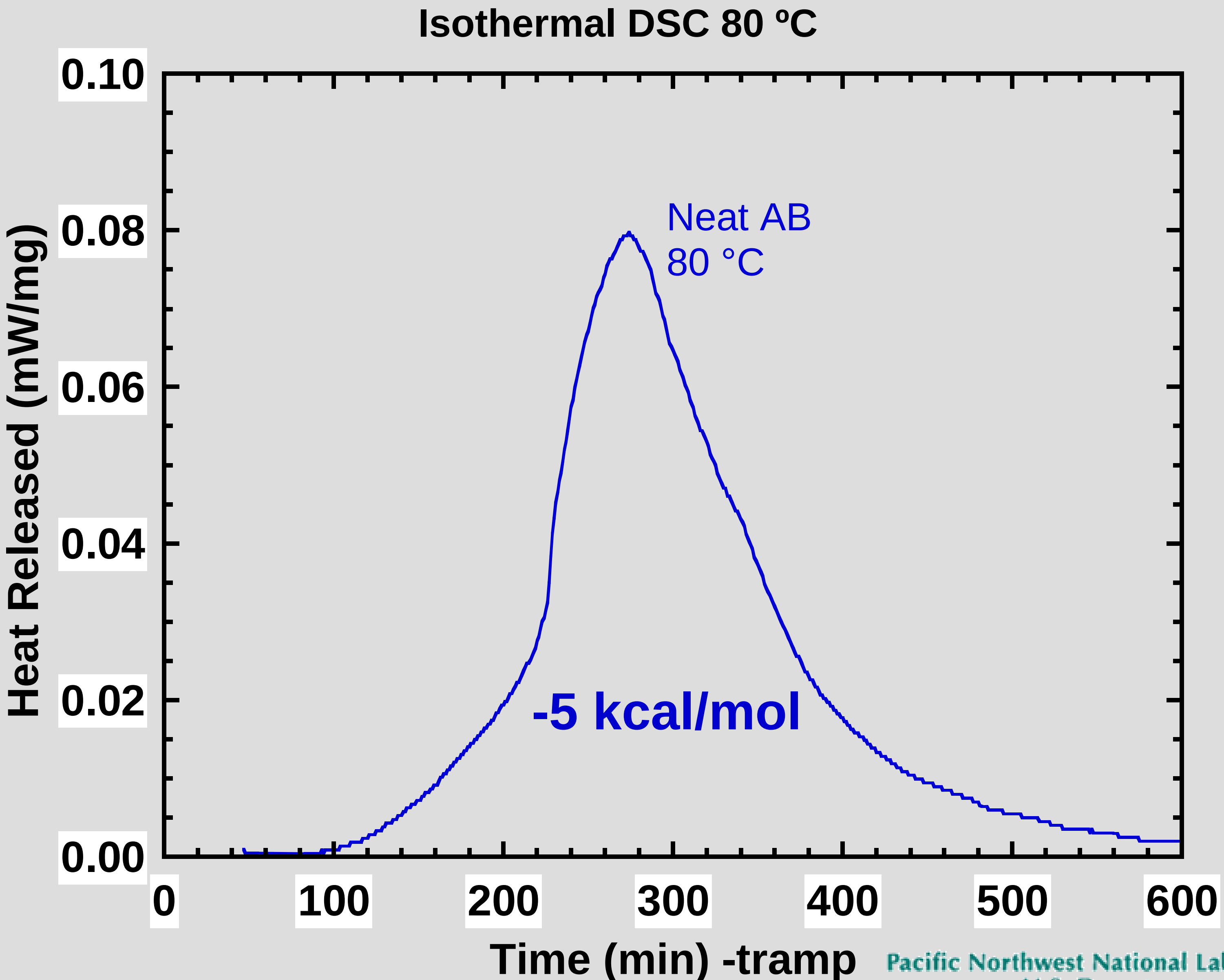
Use isothermal DSC

DSC temperature ramp 1 ºC/min

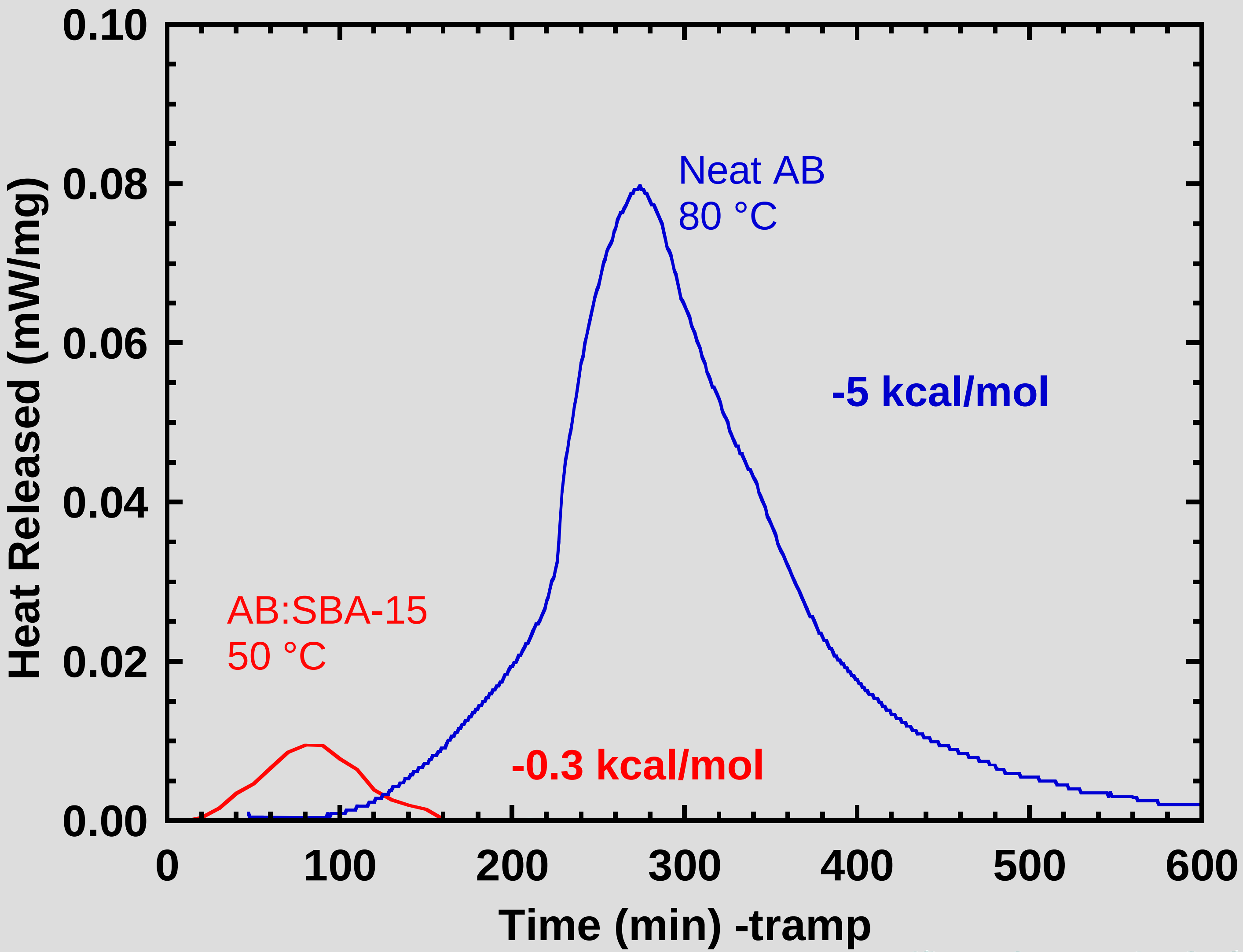
Thermochemistry Comparison

ΔH_{rxn} for loss of H_2 from AB (neat vs. scaffold)

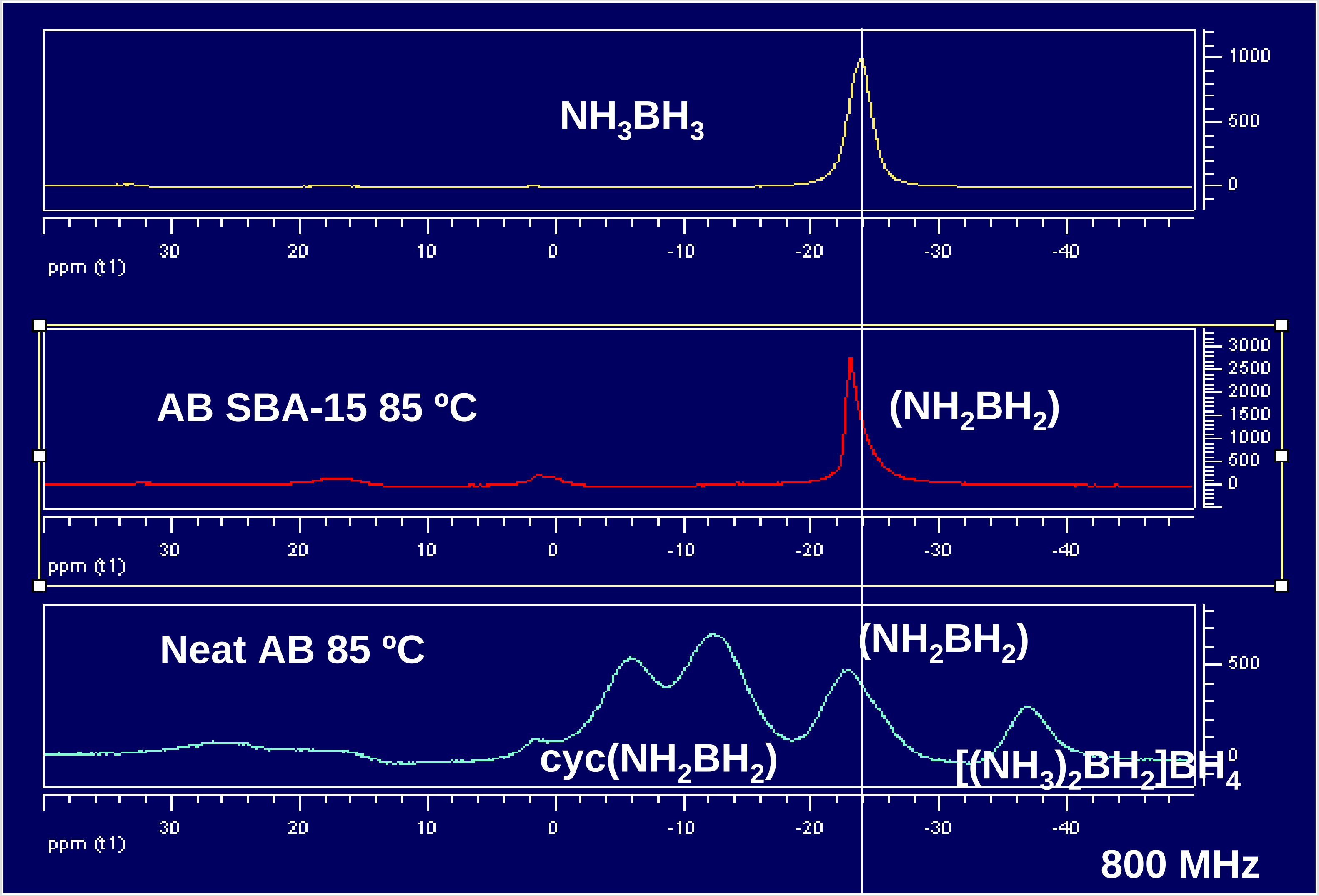
Thermochemistry H_2 release



Thermochemical Comparison



Change in Thermochemistry



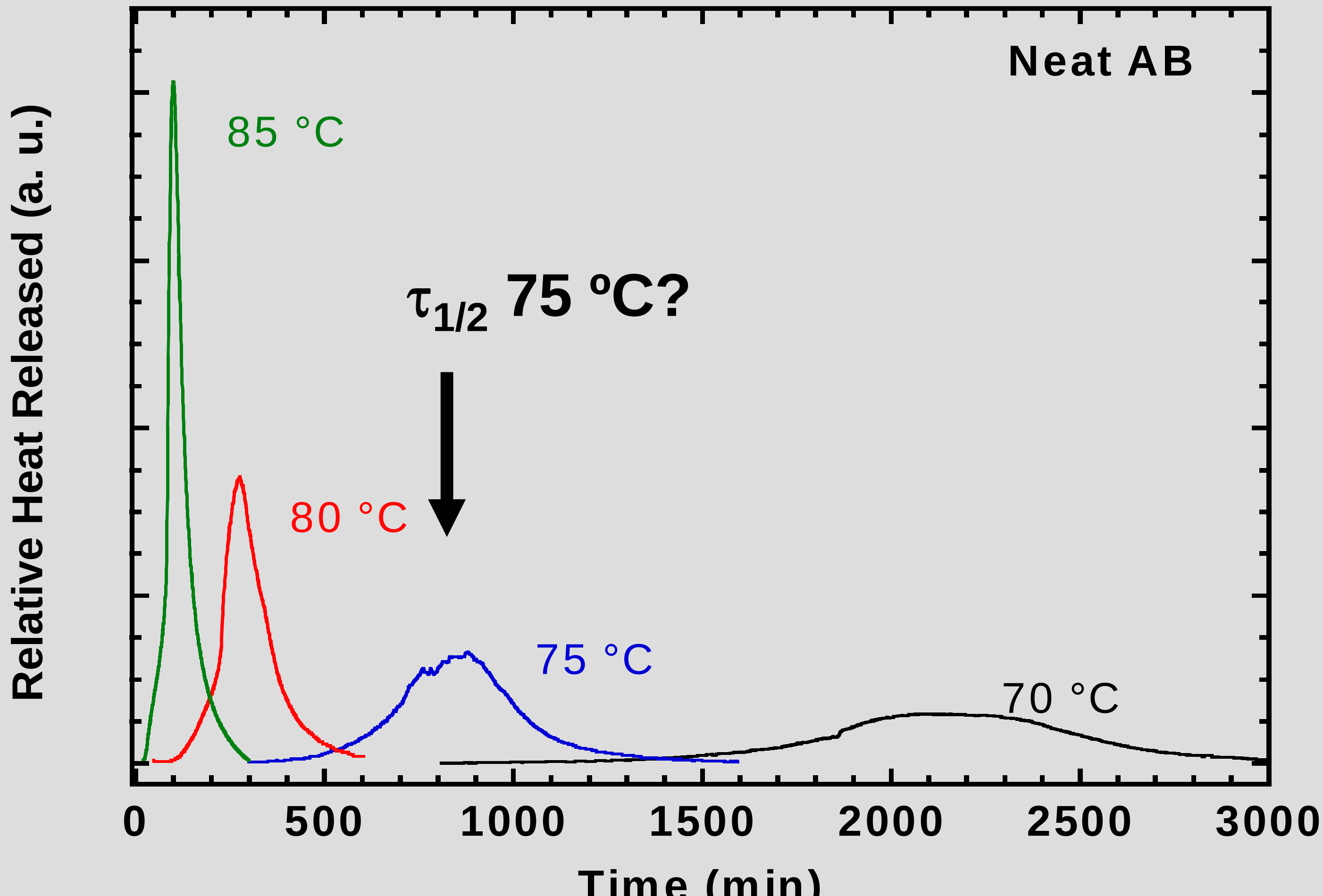
Requires change in products

Kinetic Comparison

E_a for loss of H_2 from AB (neat vs. scaffold)

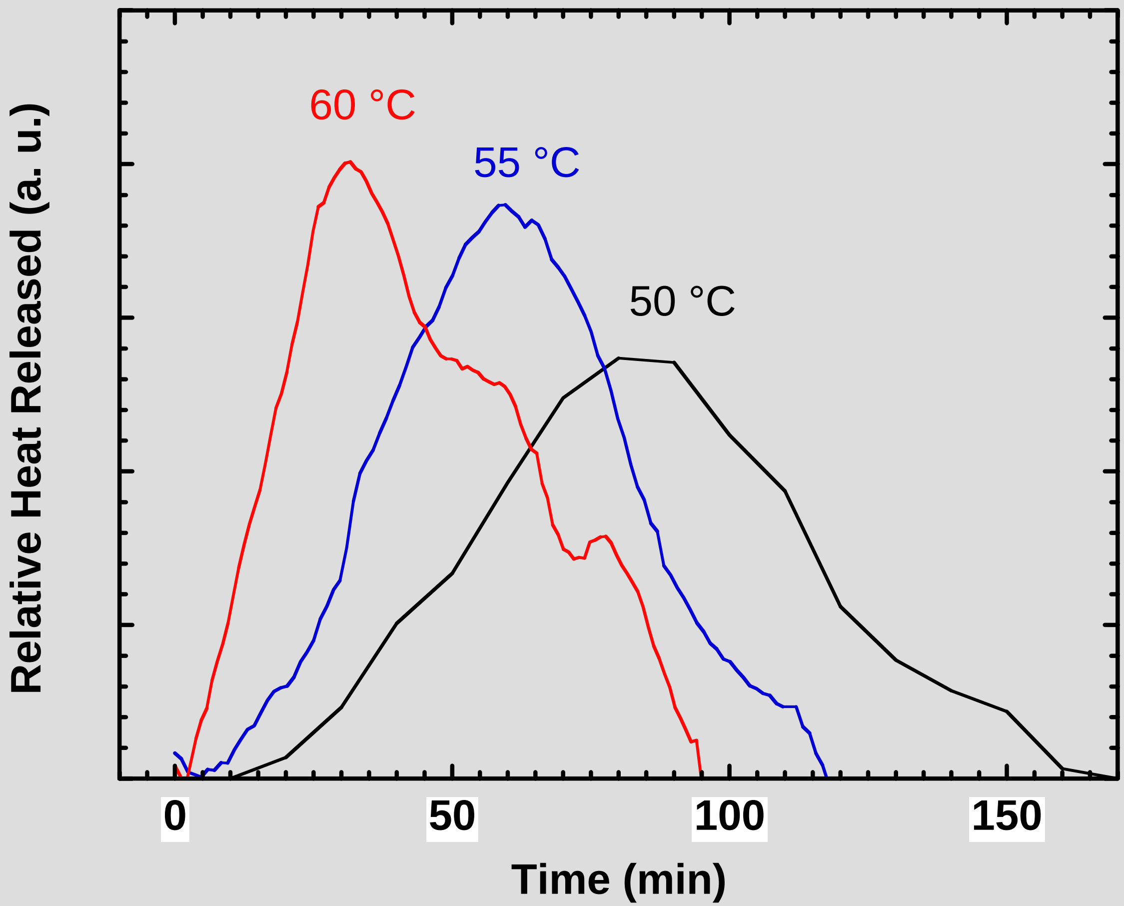
Temperature dependence of H_2 loss from AB

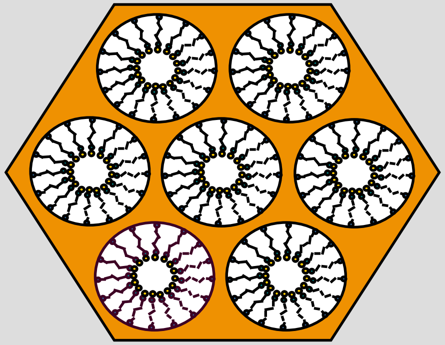
$$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$$



Isothermal DSC (kinetics)

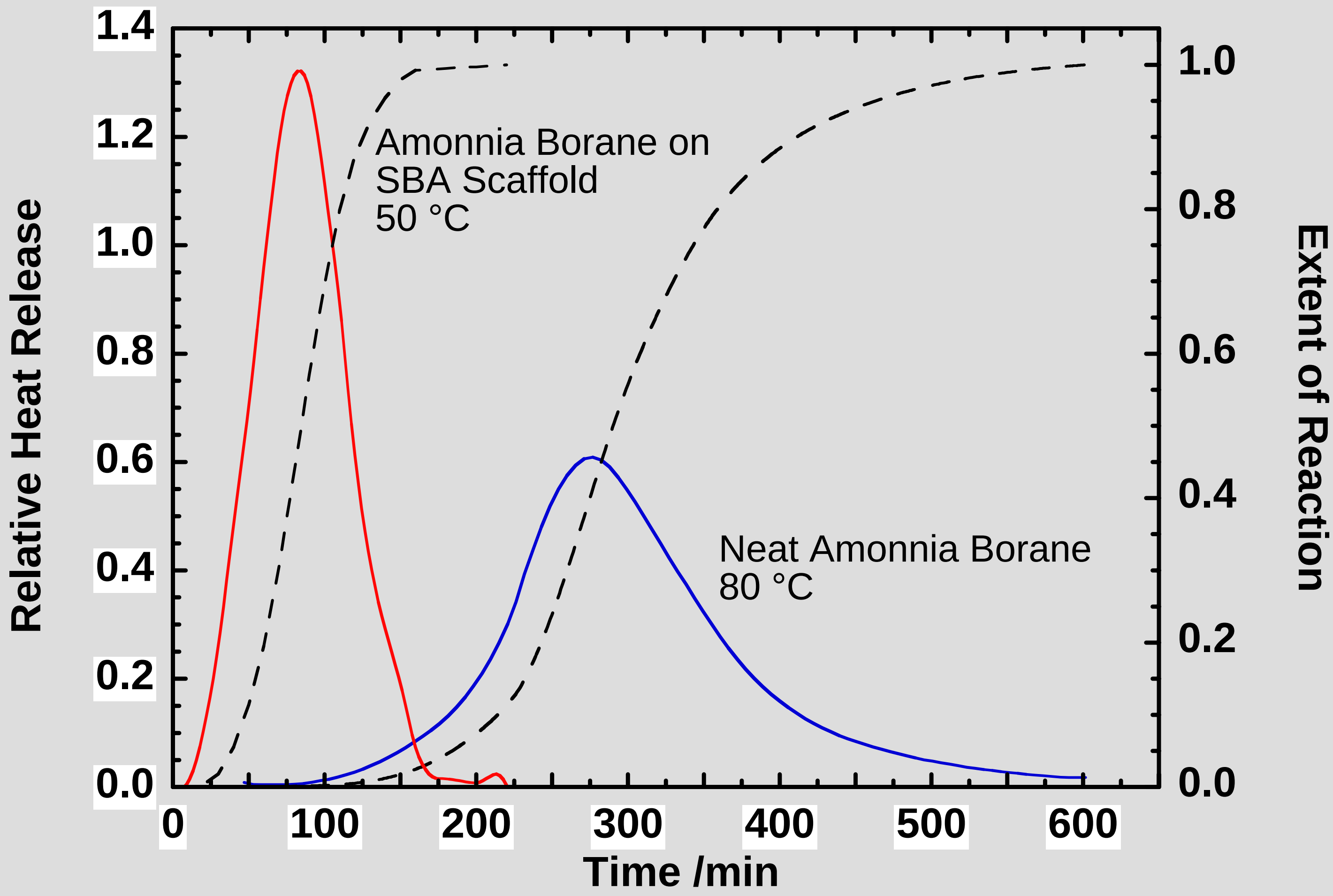
Temperature dependence of H_2 lose from AB/SBA15
$NH_3BH_3(s) \rightarrow (NH_2BH_2)(s) + H_2$



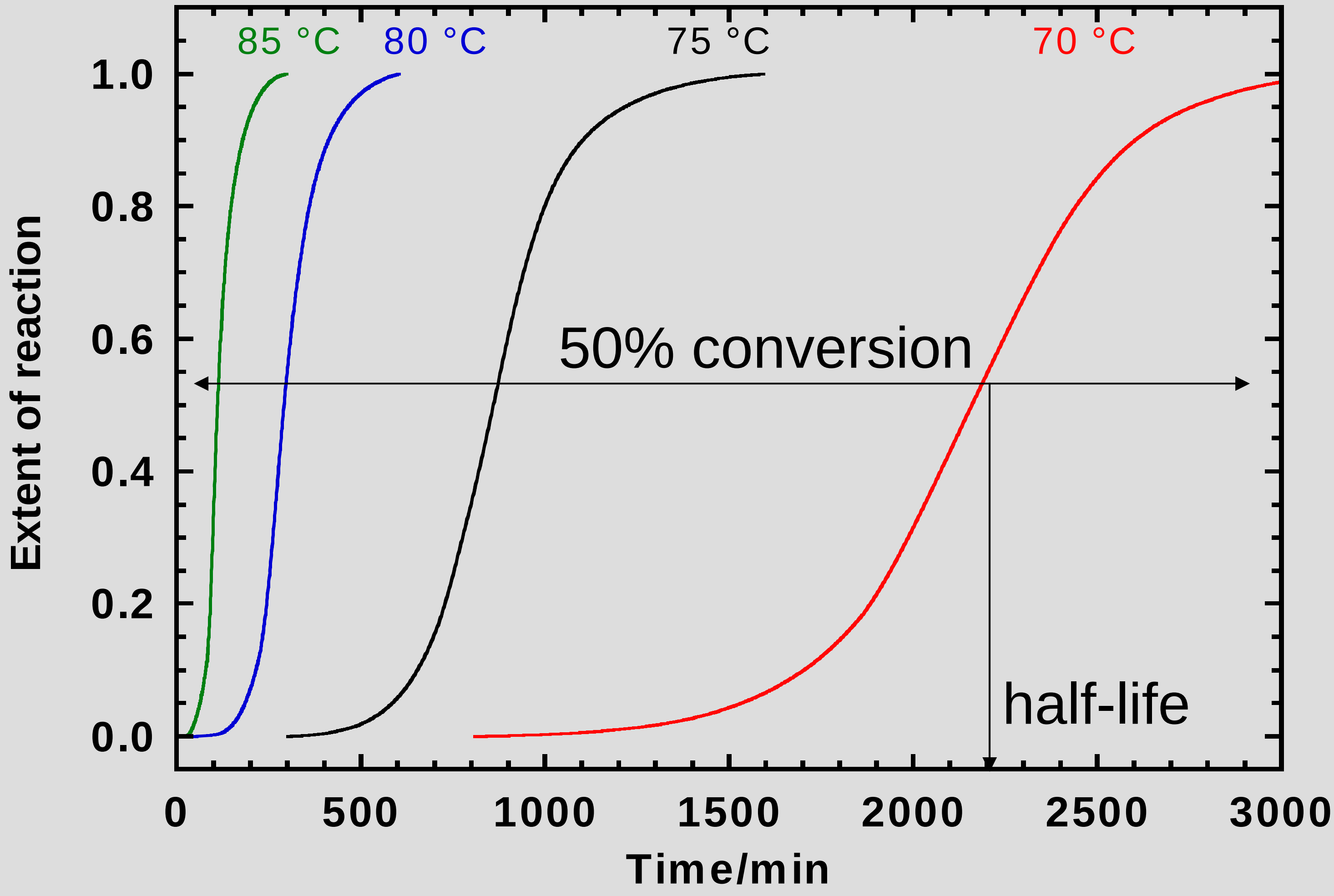


Ammonia borane in SBA-15

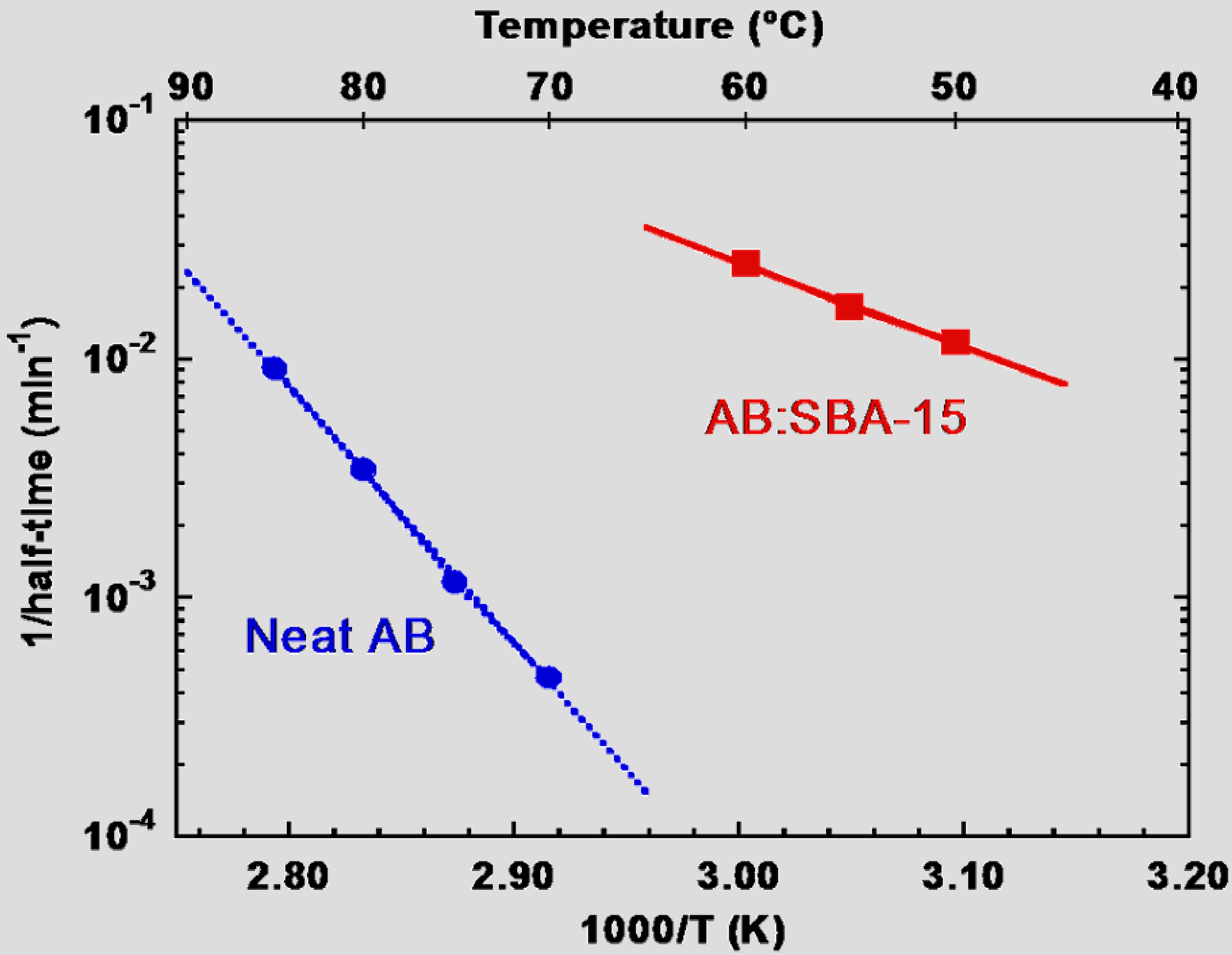
Kinetic Comparison



Rates as function of temperature

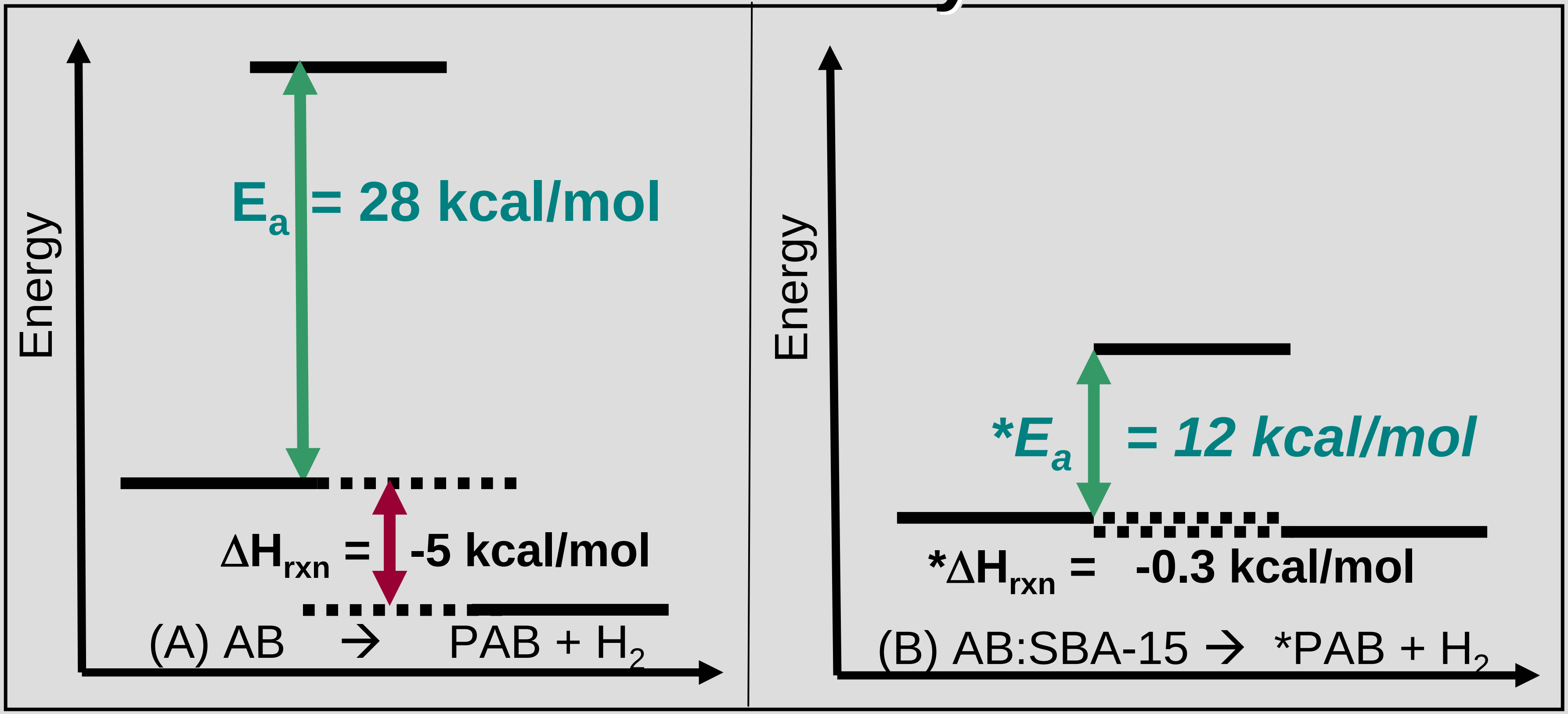


Arrhenius treatment of H_2 formation



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

Summary



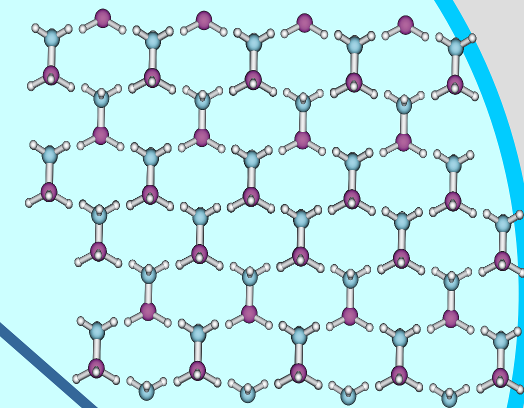
- Selectivity of H_2 release from AB
  - No borazine seen in volatile products or left behind in scaffold.
  - No cyclized products observed in NMR and DSC data show process is less exothermic
- Reactivity for H_2 release from AB
  - 1-2 orders of magnitude faster!

Research Needs

•Mechanism of H_2 formation from AB inter or intramolecular?

In neat AB are the dihydrogen bonded hydrogen atoms ‘preset’ for molecular hydrogen formation?

A barrier for nucleation and a barrier for growth.
What is nucleation site/event?



65 Å

•Why is the rate of H_2 release from AB faster in a mesoporous scaffold?

Chemical (catalytic surface interaction)
Physical (nano-phase crystal defects)

Change in products yields change in thermodynamics, what is mechanism for linear polymer growth, (B ---- OSi)?

•How general is the ‘mechanism’? Will this work help our understanding of H_2 formation from materials containing both hydridic and protic hydrogen?

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- V Viswanathan Fuel Cells
- G Whyatt Systems Eng
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