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Improvement of Hydrogen Storage Properties of Complex Metal Hydrides Through Hydridic-Protic Interactions

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# Complex metal hydrides for H$_2$ storage

Allred-Rochow Electronegativity Ref: **Huheey, J.E. Inorganic Chemistry ; Harper & Row: New York, 1983**

Legend:
- 🟩 Ionic hydrides
- 🟪 Covalent polymeric hydrides
- 🟦 Covalent hydrides
- 🟥 Metallic hydrides

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.20																	He
LiH 0.97	BeH$_2$ 1.47											BH$_3$ 2.01	CH$_4$ 2.50	NH$_3$ 3.07	H$_2$O 3.50	HF 4.10	Ne
NaH 1.01	MgH$_2$ 1.23											AlH$_3$ 1.47	SiH$_4$ 1.74	PH$_3$ 2.06	H$_2$S 2.44	HCl 2.83	Ar
KH 0.91	CaH$_2$ 1.04	ScH$_2$ 1.20	TiH$_2$ 1.32	VH VH$_2$ 1.45	CrH (CrH$_2$) 1.56	Mn 1.60	Fe 1.64	Co 1.70	NiH$_{<1}$ 1.75	CuH 1.75	ZnH$_2$ 1.66	(GaH$_3$) 1.82	GeH$_4$ 2.02	AsH$_3$ 2.20	H$_2$Se 2.48	HBr 2.74	Kr
RbH 0.89	SrH$_2$ 0.99	YH$_2$ YH$_3$ 1.11	ZrH$_2$ 1.22	(NbH$_2$) 1.23	Mo 1.30	Tc 1.36	Ru 1.42	Rh 1.45	PdH$_{<1}$ 1.35	Ag 1.42	(CdH$_2$) 1.46	(InH$_3$) 1.49	SnH$_4$ 1.72	SbH$_3$ 1.82	H$_2$Tc 2.01	HI 2.21	Xe
CsH 0.86	BaH$_2$ 0.97	LaH$_2$ LaH$_3$ 1.08	HfH$_2$ 1.23	TaH 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	(AuH$_3$) 1.42	(HgH$_2$) 1.44	(TlH$_3$) 1.44	PbH$_4$ 1.55	BiH$_3$ 1.67	H$_2$Po 1.76	HAt 1.90	Rn

Complex hydrides:

NaAlH$_4$:	5.6 mass%
LiNH$_2$:	8.8 mass%
LiBH$_4$:	13.6 mass%
Mg(BH$_4$)$_2$:	15.0 mass%
Al(BH$_4$)$_3$:	16.8 mass%

Reversible complex metal hydrides

$$M(AH_x)_y \underset{\textbf{Abs.}}{\overset{\textbf{Des.}}{\rightleftharpoons}} MA_y + 1/2xyH_2$$

$$2NaAlH_4 \overset{TiCl}{\rightleftharpoons} 2NaH + 2Al + 3H_2$$
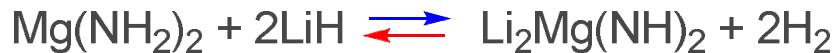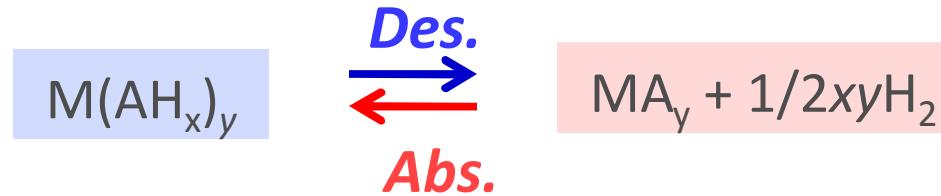
Bogdanovic *et al. J. Alloys Comp.* **1997**, *253-254*, 1
Bogdanovic, Schwickardi, *U.S. Patent* 6,106,801, **2000**

$$Mg(NH_2)_2 + 2LiH \rightleftharpoons Li_2Mg(NH)_2 + 2H_2$$

Cheng *et al. Angew. Chem. Int. Ed.* **2009**, *48*, 5828
Luo *et al. J. Alloys Comp.* **2004**, *381*, 284

$$2LiBH_4 + MgH_2 \rightleftharpoons 2LiH + MgB_2 + 4H_2$$

Pinkerton *et al. J. Phys. Chem. C* **2007**, *111*, 12881
Vajo *et al. J. Phys. Chem.* C. **2005**, *109*, 3719

$$Mg(BH_4)_2 \rightleftharpoons MgB_2 + 4H_2$$

Soloveichik *et al. Int. J. Hydrogen Energy*, **2009**, *34*, 916
Severa *et al. Chem. Commun.* **2010**, *46*, 421

high dehydrogenation temperatures

high pressure required for rehydrogenation

Problems & Challenges

contamination of H_2 gas with impurity gases

loss of capacity upon cycling

stable intermediates ($[B_{12}H_{12}]^{2-}$, $[NH]^{2-}$, etc.

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Hydridic – protic interactions

$$H-H \quad \xrightarrow{} \quad \left[H_3B-NH_2 \right]$$

B—N bond

$M(BH_4)_x(NH_3)_y$
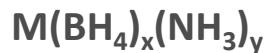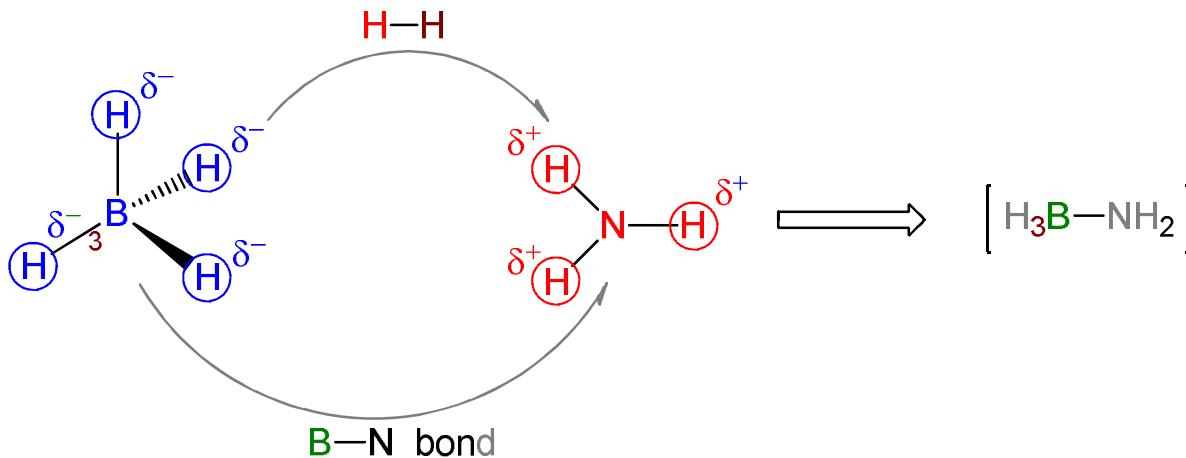
Ammonia complex of magnesium borohydride, $[Mg(BH_4)_2(NH_3)_2]$

  Soloveichik *et al.*, *Inorg. Chem. C*, **2008,** *47*, 4290.

$M_x(BH_4)_y(NH_2)_z$
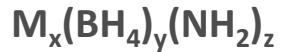
$Li_2(BH_4)(NH_2)$ => synthesized from $LiBH_4$ and $LiNH_2$ (1:1)

  Chater *et al.*, *Chem. Commun.* **2007,** 4770.

$Li_4(BH_4)(NH_2)_3$ => synthesized from $LiBH_4$ and $LiNH_2$ at 180 ºC (bcc, a=10.66 Å)

  David, Anderson *et al.*, *Chem. Commun.* **2006,** 2439.

$Li_4(BH_4)(NH_2)_3$ displays partial reversibility in the presence of MgH_2

  Yang *et al.*, *Angew. Chem. Int. Ed.*, **2008,** *47*, 882.

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Modeling complex equilibria

with Mark Allendorf and Prof. Sholl's group (Georgia Tech)

DFT (enthalpy, entropy, heat capacity) and FactSage (thermochemical calculations)

Phase equilibrium calculations can provide valuable insight into complex hydride decomposition chemistry

- Gas phase
  - Fuel-cell poisons (e.g. NH_3)
  - Storage capacity, reversibility
  - Safety (e.g., H_2O or O_2 reactions)
  - System design and operating conditions
- Condensed phase
  - Multiple stable products
  - Parasitic reactions
  - Effects of T, P, reaction stoichiometry
- Products of equilibrium modeling
  - Identify most stable products
  - Predict harmful gas-phase species
  - Kinetic vs. thermodynamic products

Gas phase H_2 NH_3 B_2H_6

Solid phase
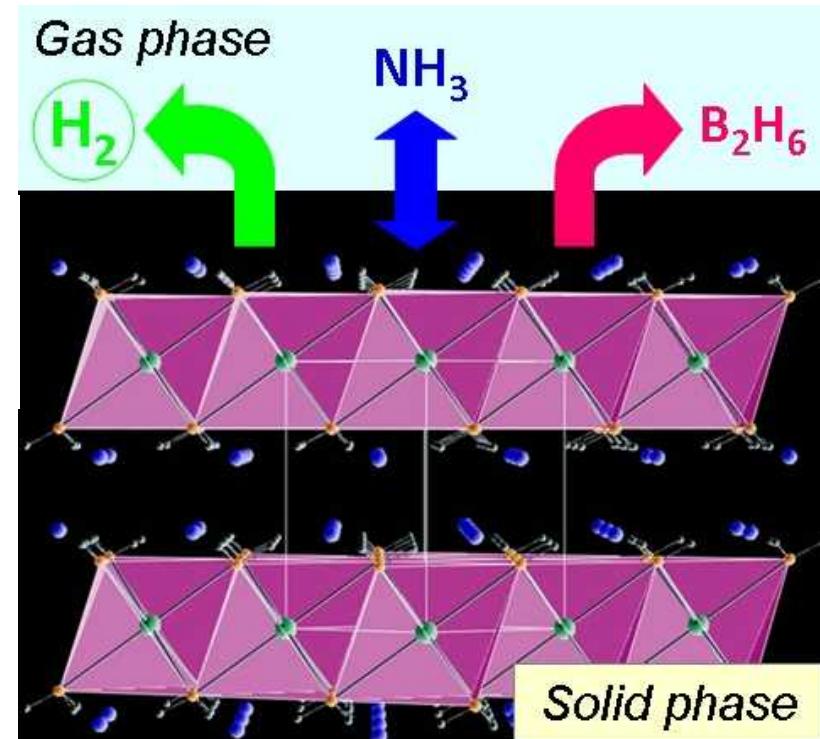
Gibbs energy minimization

$$G = \sum_{\substack{ideal \\ gas}} n_i (g_i^o + RT \ln P_i)$$

$$+ \sum_{\substack{pure \\ condensed \\ phases}} n_i g_i^o$$

$$+ \sum_{solution-1} n_i (g_i^o + RT \ln X_i + RT \ln \gamma_i)$$

$$+ \sum_{solution-2} n_i (g_i^o + RT \ln X_i + RT \ln \gamma_i)$$

$$+ \quad \cdots$$

$$+ \quad \cdots$$

Where,

n_i :   moles

P_i :   gas partial pressure

X_i :   mole fraction

γ_i :   activity coefficient

g_i^o :   standard molar Gibbs energy

We determine the combination of n_i, P_i and X_i that minimizes the total Gibbs energy G of the system.

In this investigation the equilibrium products are an ideal gas and pure solid compounds

📖   Bale *et al.*, *Calphad*, **2009**, *33*, 295

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- Compute missing thermodynamics
  - DFT: Ground-state energies (0 K)
  - PHONON: finite-temperature thermodynamics (C_p°, S°, ΔH°)
- FactSage package (commercial software)
  - Compute equlibrium at constant T,P
  - Include all relevant gas-, liquid-, and solid-phase species
- Metal hydrides and decomposition products
  - Li-B-C-Mg crystalline phases
  - $\Delta H_f^\circ (298)$, $\Delta S^\circ (298)$, $C_p(T)$
    - DFT + phonon calculation
- Thermodynamic data sources:
  - Gas phase:
    - *JANAF Tables*
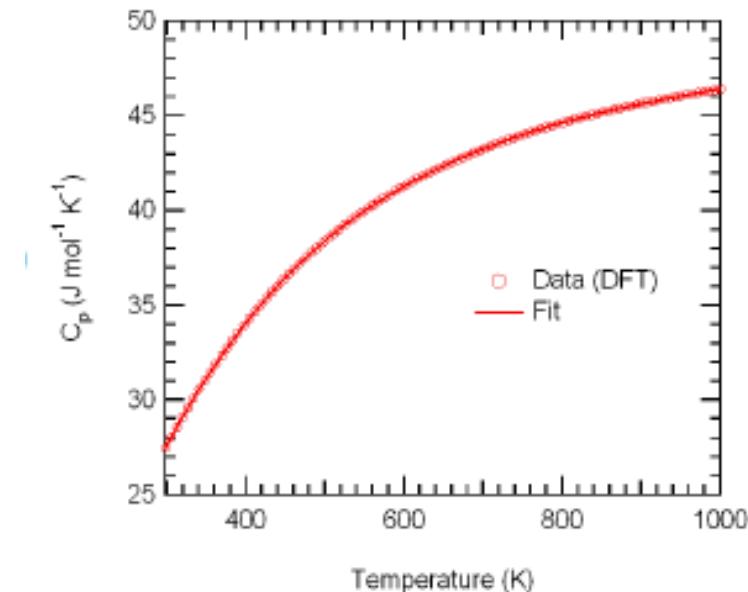
$$C_p = a + bT + cT^2 + dT^3$$

Polynomial fit to C_p for MgH_2. Data from DFT and phonon calculation

Modeling the LiNH$_2$ – LiH system

LiNH$_2$ + LiH: equilibrium shifts away from N$_2$ and NH$_3$

Nominal reactions

LiNH$_2 \leftrightarrow$ 0.5Li$_2$NH + 0.25N$_2$ + 0.75H$_2$

2LiNH$_2 \leftrightarrow$ Li$_2$NH + 0.5N$_2$ + 1.5H$_2$

2LiNH$_2 \leftrightarrow$ Li$_2$NH + NH$_3$

LiNH$_2$ + LiH $\leftrightarrow$ Li$_2$NH + H$_2$
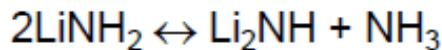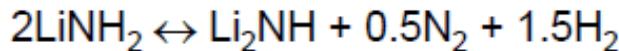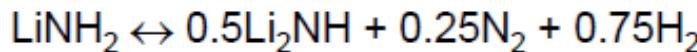
Predicted composition

- Consistent with experiment
- T$_{decomp}$ decrease ~ 40 K
- N$_2$ converted to Li$_2$NH, enhancing H$_2$ yield
- NH$_3$:
  - NH$_3$: H$_2$ ~ 10^{-3} (agrees Hino et al. FTIR data *J.Alloys Cmpd.* 2007)
  - Decreased ~ 4X vs. LiNH$_2$ alone

📖 K.C. Kim, M.D. Allendorf, V. Stavila, D.S. Sholl. *Phys. Chem. Chem. Phys.* DOI: 10.1039/c001657h

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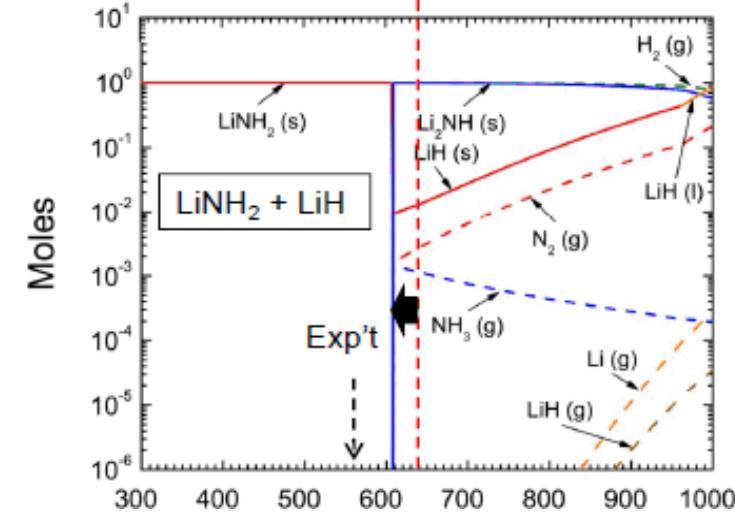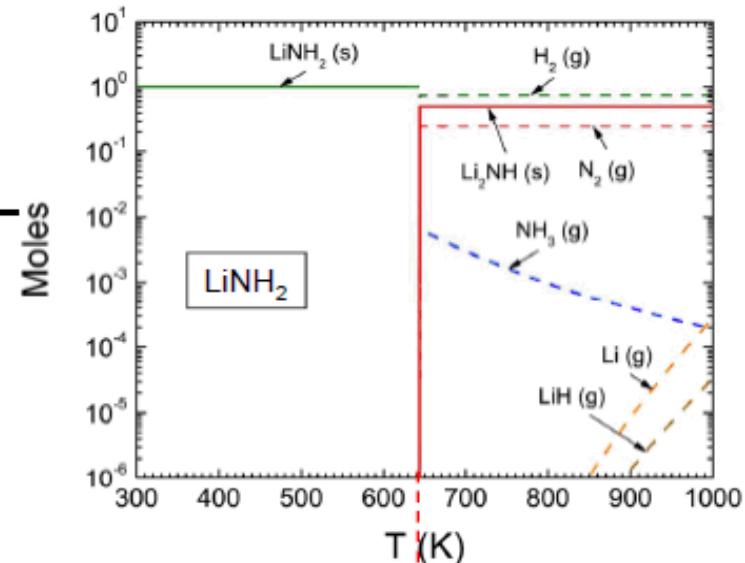
Hydrogen storage in $2LiNH_2 - MgH_2$
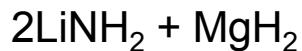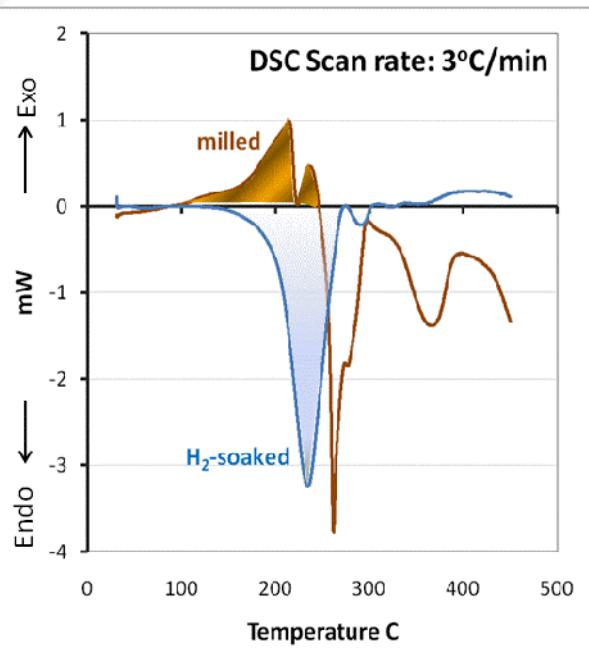
$2LiNH_2 + MgH_2$

Effect of H_2 soaking on desorption
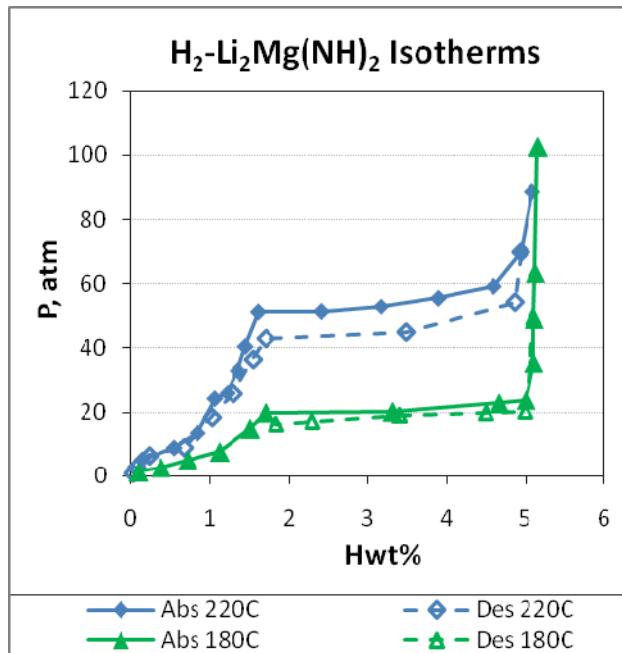
KH dramatically aids absorption kinetics
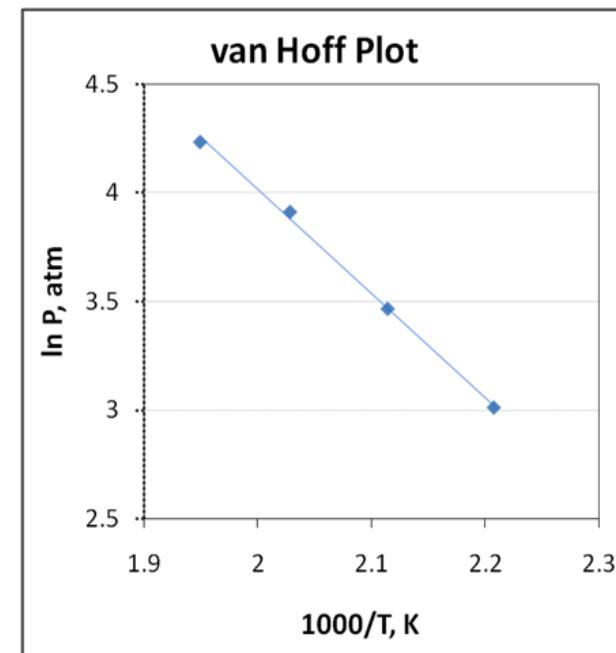

$$\frac{\Delta H_o}{RT} - \frac{\Delta S_o}{R} = \ln P_{eq}^{H_2}$$

ΔH_{des} = 42 kJ/mol-H_2

- $2LiNH_2$-MgH_2 represents a promising near-term H_2 storage material
- Catalytic amounts of KH and KNH_2 aid absorption kinetics

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Borohydride – ammonia adducts

Motivation: The presence of both 'hydridic' and 'protic' hydrogen atoms

$$M^1(BH_4)_x + M^2(BH_4)_y + zNH_3 \longrightarrow M^1M^2(BH_4)_{x+y}(NH_2)_z$$

$$Ca(BH_4)_2 \xrightarrow[\text{THF}]{+NH_3,\ -20\ ^\circ C} Ca(BH_4)_2 \cdot xNH_3$$

$$M(BH_4)_y + Ca(BH_4)_2 \xrightarrow[\text{THF}]{+NH_3,\ -20\ ^\circ C} MCa(BH_4)_{2+y}\ xNH_3\ \ (M=Li, Mg)$$

$$Ti(BH_4)_3 \xrightarrow{+NH_3,\ -33\ ^\circ C} Ti(BH_4)_3 \cdot xNH_3$$

XRD

Ca(BH$_4$)$_2$-NH$_3$
MgCa(BH$_4$)$_4$-NH$_3$
LiCa(BH$_4$)$_3$-NH$_3$
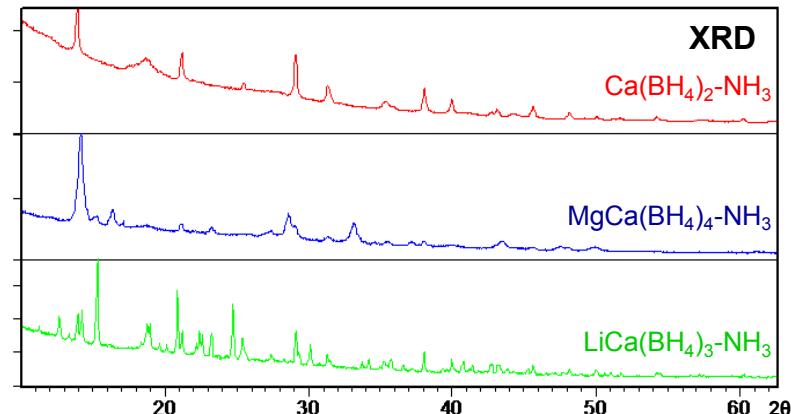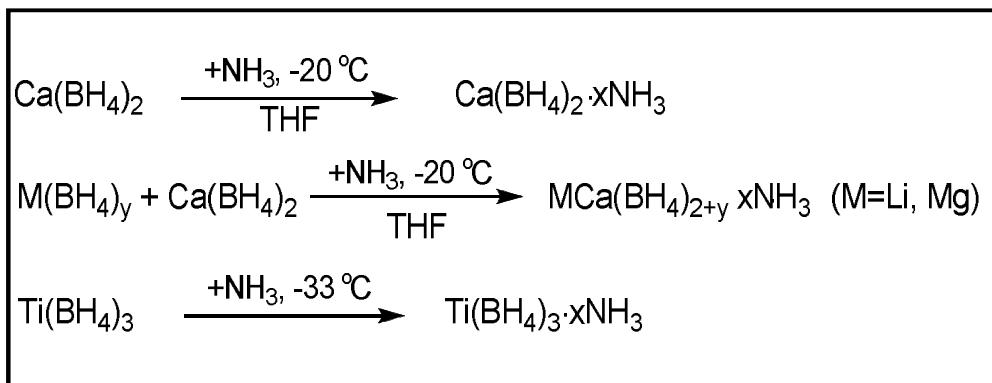
➢ The BH$_4$-NH$_3$ compounds display increased air- and moisture stability compared to the initial borohydrides

➢ *Ca(BH$_4$)$_2$•NH$_3$, MgCa(BH$_4$)$_4$•NH$_3$* and *LiCa(BH$_4$)$_3$•NH$_3$* adducts release significant amounts of NH$_3$ upon heating, confirmed by gas phase analysis

➢ New systems based on transition metals (*e.g.* Ti(III) and Mn(II)) are currently under investigation

% weight loss   TGA

Ca(BH$_4$)$_2$-NH$_3$
MgCa(BH$_4$)$_4$-NH$_3$
LiCa(BH$_4$)$_3$-NH$_3$

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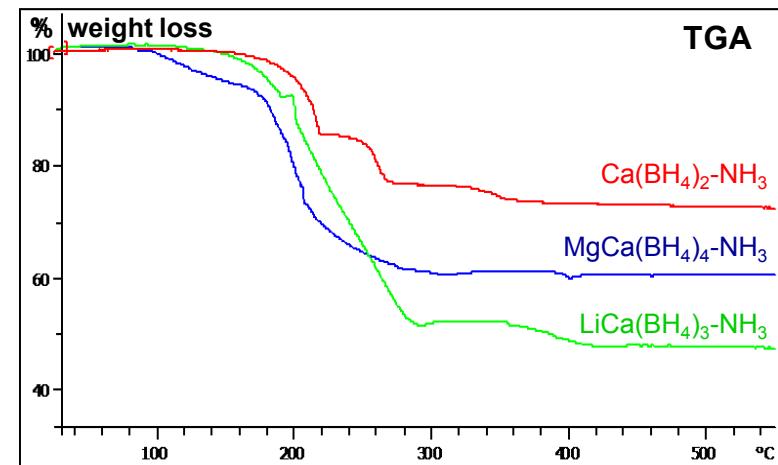
Mg(BH$_4$)$_2$ – LiNH$_2$ and LiBH$_4$ – Mg(NH$_2$)$_2$
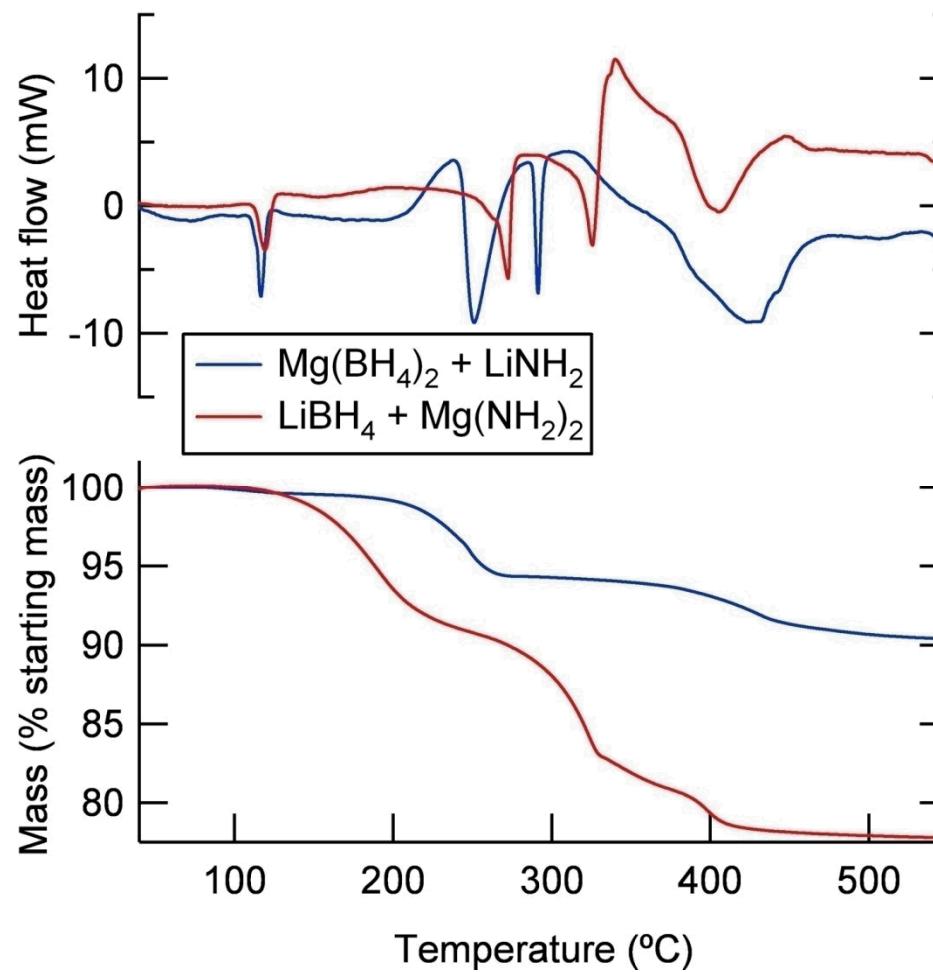
> ➤ The major product of thermal decomposition of Mg(BH$_4$)$_2$-LiNH$_2$ is H$_2$; both NH$_3$ and H$_2$ are released from Mg(BH$_4$)$_2$-LiNH$_2$

Ca(BH$_4$)$_2$ – LiNH$_2$ and Ca(BH$_4$)$_2$ – NaNH$_2$
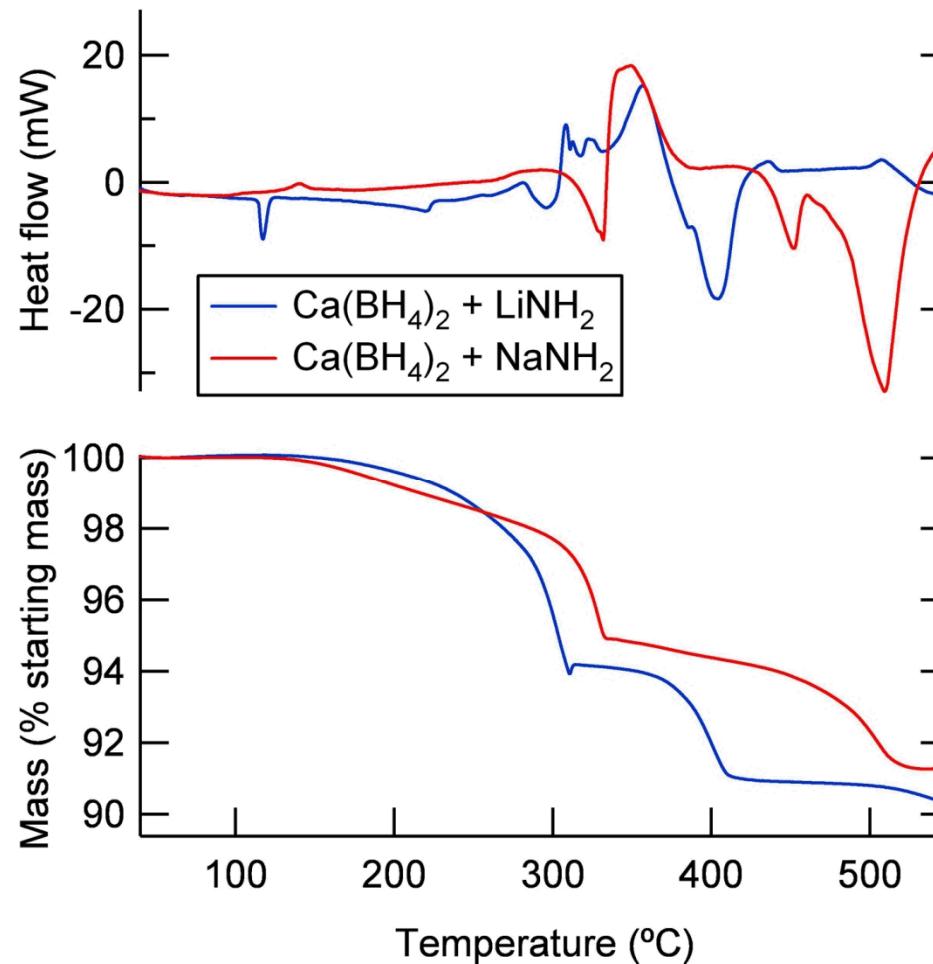
> ➤ Cryo-milling of Ca(BH$_4$)$_2$ with LiNH$_2$ and NaNH$_2$ results in a decrease in H$_2$ desorption by 40 to 100 ^{o}C compared to pure Ca(BH$_4$)$_2$.

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STMBMS: Simultaneous Thermogravimetric Modulated – Beam Mass-Spectrometry

with Rich Behrens and Aaron Highley

Instrument details:

➢ Knudsen effusion cell installed within a furnace and a microbalance

➢ Simultaneous modulated molecular beam mass spectrometer provides time-dependent species info

➢ High accuracy FTMS for species identification

Data:

➢ Species

➢ Number density

➢ Rate of evolution

➢ Partial pressure

➢ Temperature

Data is correlated to determine reaction kinetics

📖 R. Behrens, Jr., *J. Rev. Sci. Instr.,* **1987**, *58*, 451.

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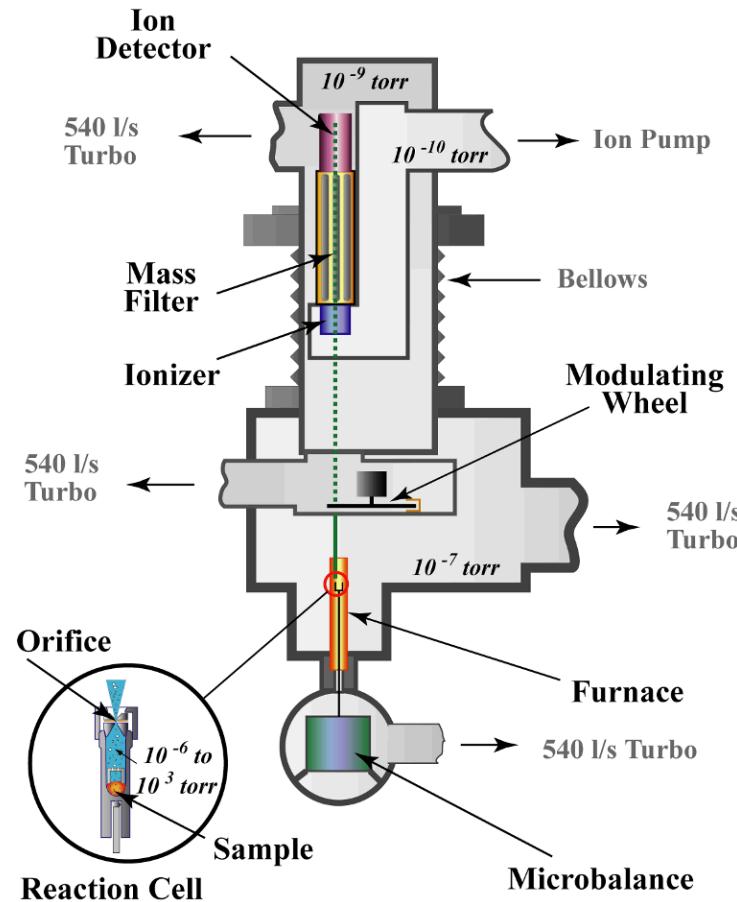
Ca(BH$_4$)$_2$–LiNH$_2$ and Ca(BH$_4$)$_2$– NaNH$_2$
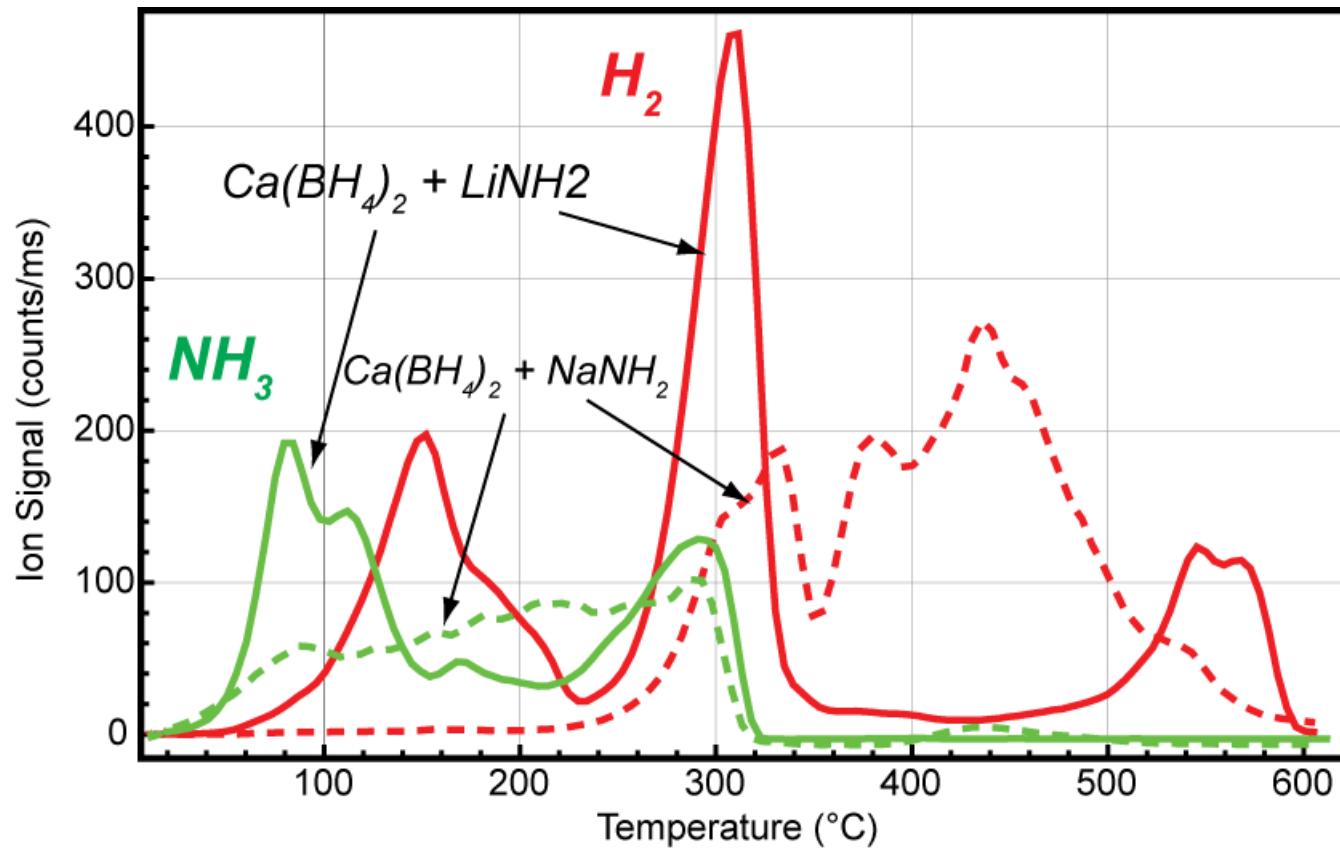
> ➢ NH$_3$ release from Ca(BH$_4$)$_2$-LiNH$_2$ and Ca(BH$_4$)$_2$-NaNH$_2$ materials occurs at temperatures <320 ºC. Most of the H$_2$ is released from Ca(BH$_4$)$_2$-LiNH$_2$ by 340 ºC.

Mg(BH$_4$)$_2$ – LiNH$_2$ and LiBH$_4$ – Mg(NH$_2$)$_2$
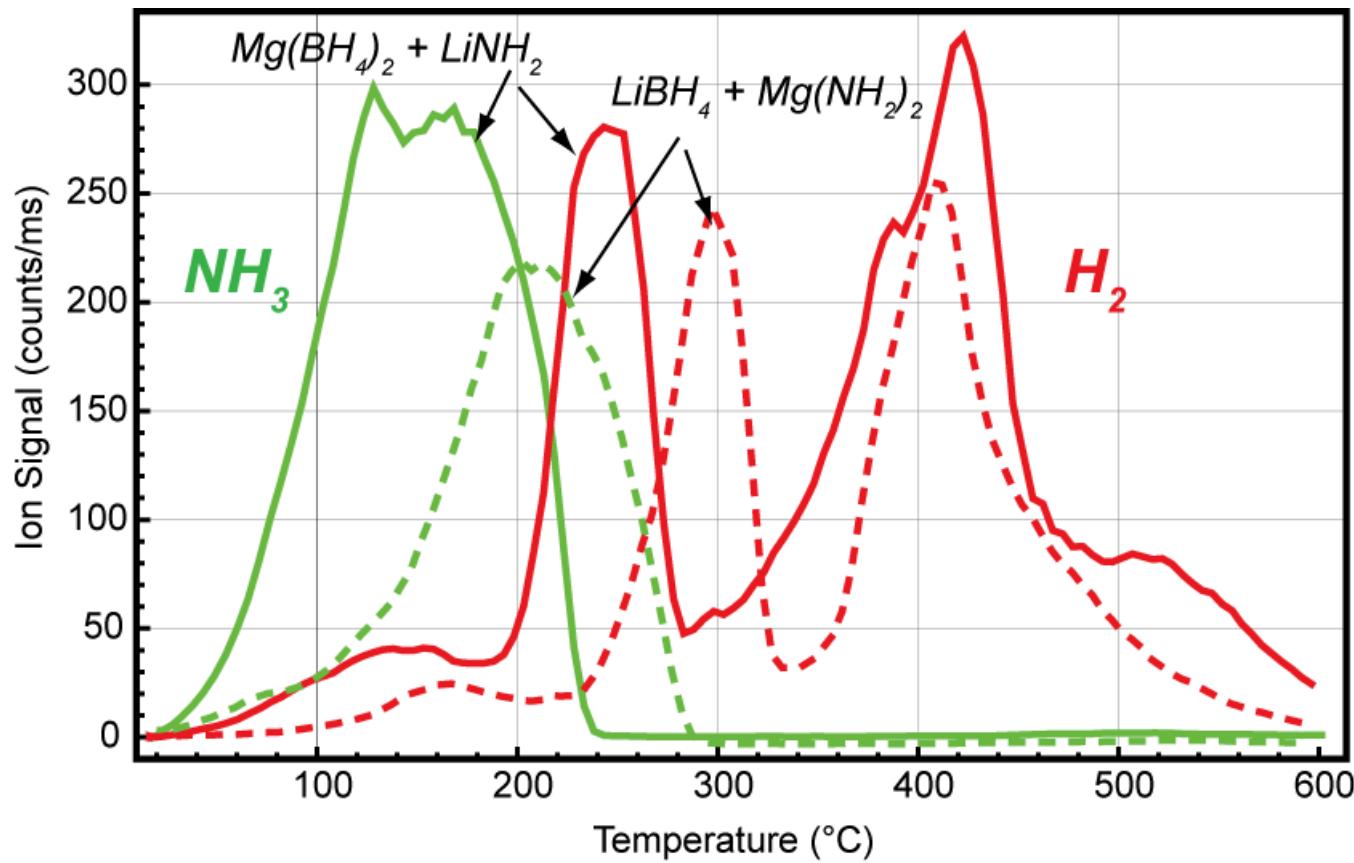
> NH$_3$ release from Mg(BH$_4$)$_2$-LiNH$_2$ and LiBH$_4$-Mg(NH$_2$)$_2$ is virtually completed by 240-280 °C. H$_2$ desorbs in several steps in a wide temperature range.

H-D formation in $[BH_4]^-$ / ND_3 samples

Decomposition of $Ca(BH_4)_2$ & $Mg(BH_4)_2$ & ND_3
H_2, HD and D_2 evolution
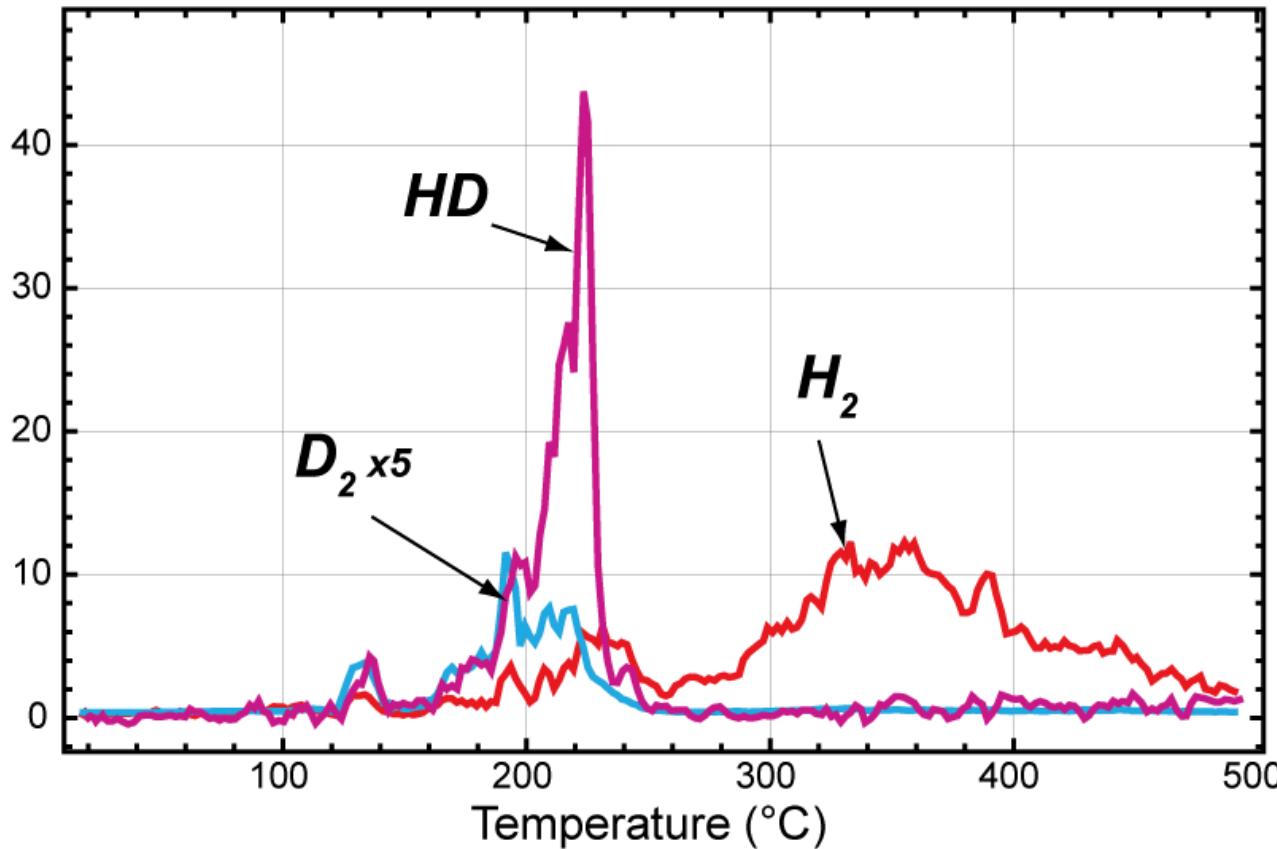
> ➤ STMBMS indicates the major product of $MgCa(BH_4)_2(NH_3)_2$ decomposition is the hydrogen – deuterium species, *i.e.* the preferred product formed through hydridic – protic interactions .

Conclusions

⇒ **Hydridic – protic interactions can be used to decrease the hydrogen desorption temperature of complex metal hydrides**

⇒ **Equilibrium modeling using DFT/FactSage calculations provide useful insights in elucidating thermodynamically favored processes near equilibrium. They also suggest kinetic limitations often govern the decomposition process.**

⇒ **Simultaneous Thermogravimetric Modulated-Beam Mass-Spectrometry reveal that hydridic-protic interactions govern the decomposition process in borohydride-amine materials.**

⇒ **The decomposition temperatures of metal borohydrides can be significantly reduced in the presence of amines and amides.**

Acknowledgements

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