

Hydrogen Storage Characterization and Optimization Research Effort

Tom Autrey, Mark Bowden, Abhi Karkamkar,
Bojana Ginovska, Herman Cho, Marina
Chong, Adrian Houghton, Gary Edvenson

Pacific Northwest National Laboratory
June 8, 2016

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline and Budget

- Project Start Date: Oct 2015
- Project End Date: Sept 2018
- Total PNNL Project Budget: \$2,305,000
- Project Budget FY16: \$805,000
 - Total DOE Funds Spent as of 3/31/16: \$393,673

Partners

NREL - Tom Gennett, Phil Parilla

NIST - Craig Brown, Terry Udovic

LBNL - Jeff Long, Martin Head-Gordon

Barriers

General:

A. Cost; B. Weight and Volume; C. Efficiency; E. Refueling Time

Reversible Solid-State Material:

M. Hydrogen Capacity and Reversibility; N. Understanding of Hydrogen Physi- and Chemi- sorption; O. Evaluation Facilities.

Collaborators

HyMARC - Brandon Wood, Vitalie Stavila, Lenny Klebanoff

Hawaii – Craig Jensen

ORNL – Bob Bowman

IEA-HIA Task 32 –B Hauback, P Chen, D Chandra, T Vegge, Y Filinchuk, S Orimo

AIST – Q Xu, Y Himeda, H Kawanami

Relevance

Project Objectives:

- **Characterization:** Develop new capabilities (i.e., NMR and calorimetry) to compliment (PCT, TPD, TC) at NREL, (DRIFTS) at LBNL and (neutrons) at NIST to investigate the properties of promising new hydrogen storage materials.
- **Validation:** Test and confirm '*claims and theories*' critical to the design of new hydrogen storage materials that show promise to exceed DOE targets.

Impact:

- Rational design of new materials. The combination of the experimental capabilities will provide an opportunity to better understand the properties of gas-solid interactions in high surface area materials as well as providing insight into the kinetic and thermodynamic bottlenecks in complex hydrides.
- Access to characterization capabilities. Ready access to characterization & validation capabilities will accelerate research progress.

Approach (to characterization)

▶ Low temperature ^1H NMR

- 5-300 K, 15 – 1000 m torr
- Gas solid interactions
- Structure, dynamics, ΔH (compliments neutrons, IR & PCT)
- *Use to investigate properties favorable for binding more than one H_2 per metal site*

▶ Liquid NMR (^{11}B , ^{15}N , ^{13}C , ^1H)

- 200-400 K, 1 – 200 bar
- K_{eq} , ΔH , ΔS of H_2 uptake and release (compliments PCT and calorimetry)
- *Use to identify key intermediates and measure K_{eq} as function of temperature and pressure.*

▶ High temperature NMR (^{11}B , ^{15}N , ^{27}Al , ^{23}Mg)

- 300-500 K, 1 – 200 bar
- In-situ evolution of amorphous & crystalline structures (compliments diffraction, TPD)
- *Use to investigate key intermediates involved in rate limiting steps in reversible H_2 uptake in complex hydrides*

▶ Reaction Calorimetry

- 300-500 K, 1 – 200 bar
- Thermochemistry and kinetics (compliments PCT & DSC)
- *Use to measure rates and enthalpies of H_2 uptake and release in liquid and solid storage materials.*

Approach (to validation)

▶ Physi-sorption (Sorbent)

- $H_2 - M^+ \rightleftharpoons H_2$
- *modified structure to enable the binding energy 2 H₂'s per metal site. What are the best characterization methods to validate and understand physics and chemistry of binding 2 H₂'s per metal site in amorphous materials?*

▶ Chemi-sorption (solid)

- $Mg(BH_4)_2 \rightleftharpoons Mg(B_{10}H_{10}) + H_2$
- *What intermediate species are the bottlenecks to faster rates? What properties of additives or catalysts are required? What are the best characterization methods to identify key intermediates?*

▶ Physi-sorption (Inorganic Framework)

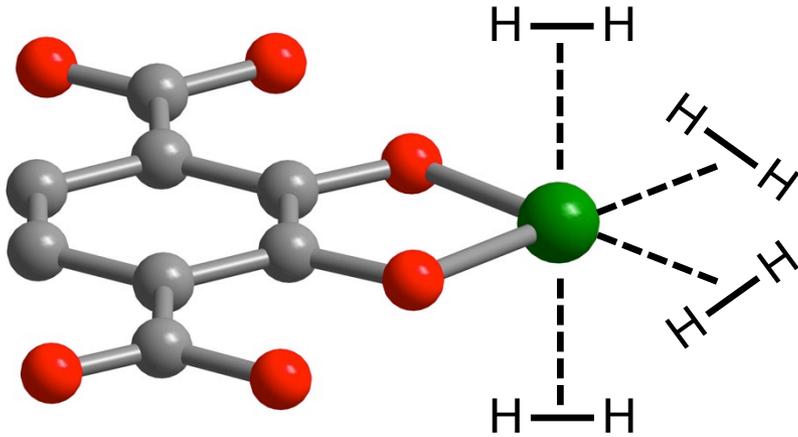
- **H₂ at near ambient temperature**
- *investigate new approaches and materials to enable H₂ uptake and release at ambient temperatures and moderate pressures.*

▶ Chemi-sorption (liquid)

- **s-triazine, T_c = 50 or 150 °C**
- *theory used to predict structures with reduce the binding enthalpy. What are the best characterization methods to validate predictions of binding enthalpies?*

Accomplishments

I. Low temperature solid state ^1H NMR spectroscopy to gain insight into physisorption of H_2 in sorbents



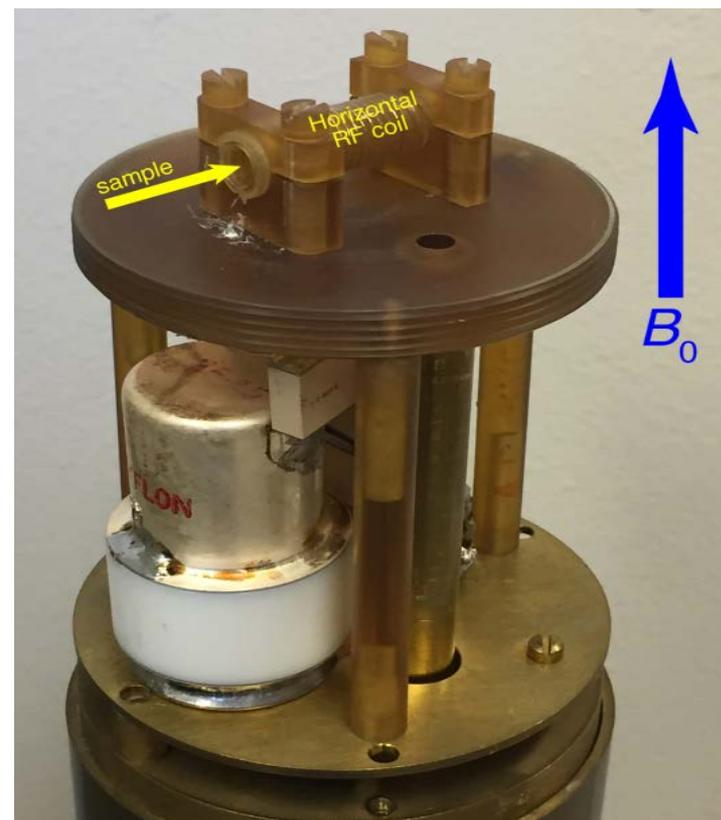
Developing new characterization methods that compliment neutron and IR studies to test the theory that 2 or more H_2 's can be bonded to a single metal site.

NMR probe modifications



Herman Cho

- **Horizontal probe arrangement**
 - A horizontal probe arrangement will provide ca. 5X enhanced sensitivity compared to the vertical probe arrangement at the same magnetic field.
- **7.05 T magnet (300 MHz ^1H)**
 - a 50% higher magnet field for greater sensitivity (and a bonus for available instrument time with the proximity of 4 different 300 MHz magnets at PNNL).
- **Liquid helium cryostat (5 – 300 K)**
 - Lower temperature will simplify the pressure requirements to observe and quantify hydrogen binding to open metal sites in MOFs.
 - In addition the liq He NMR provides a direct comparison with the liq He IR capabilities being developed at LBNL.



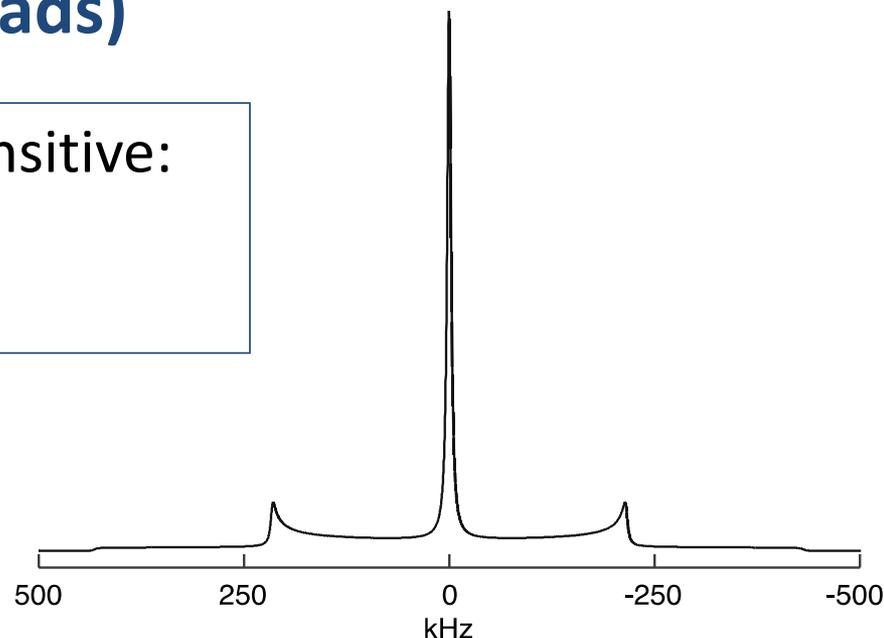
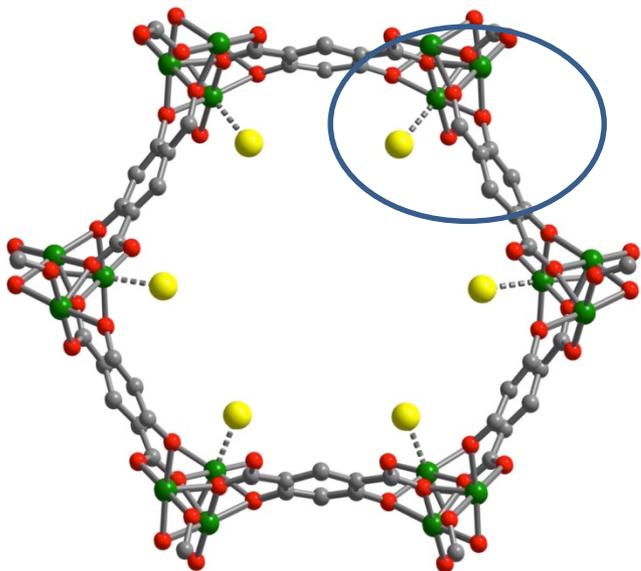
*NMR Methods for Characterizing the Pore Structures and Hydrogen Storage Properties of Microporous Carbons. Anderson, McNicholas, Kleinhammes, Wang, Liu, Wu. J. AM. CHEM. SOC. 2010, 132, 8618

**Using lower temperature range
reduces required pressure needs**

Predicting ^1H NMR signal for H_2 bond to metal center



- Mg_2 m-(dobdc). ^1H NMR very sensitive:
 - 10 mg MOF ca. 50 μmol M^+
 - H_2 gas STP ca. 40 $\mu\text{mol}/\text{ml}$

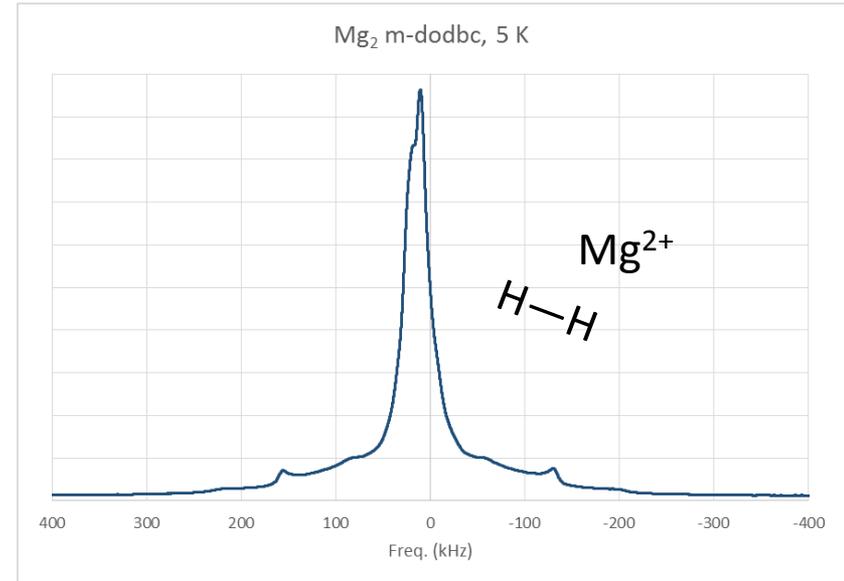
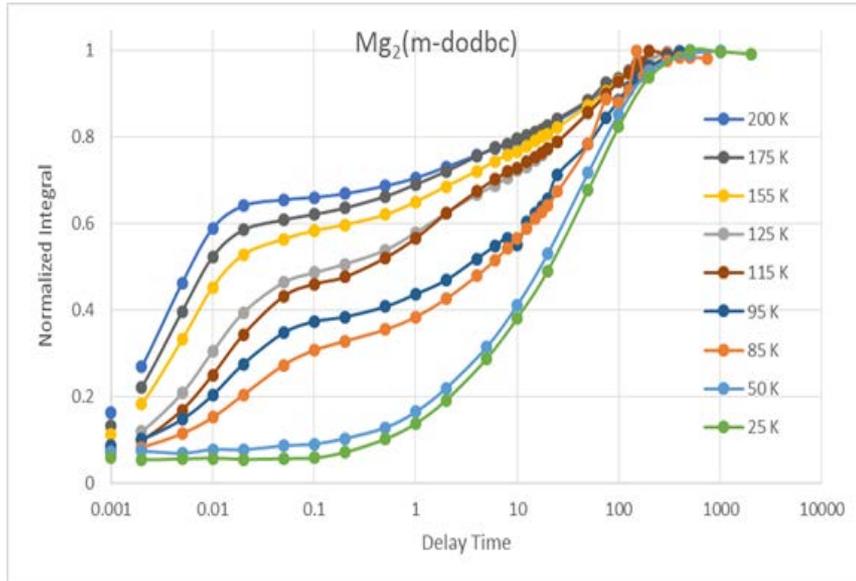


Calculated solid state NMR Pake pattern for static H_2 bond to $\text{Mg}_2(\text{dobdc})$.
Narrow peak is Aryl-H and broad peak ca. 470 KHz is H_2 -M interaction.

*Kapelewski, Geier, Hudson, Stück, Mason, Nelson, Xiao, Hulvey, Gilmour, FitzGerald, Head-Gordon, Brown, Long. J. Am. Chem. Soc. 2014, 136, 12119

Progress: ^1H spectra of $\text{Mg}_2\text{-m-dobdc}$ dosed with 0.5 H_2

Andy Lipton, Adrian Houghton, Mark Bowden, Jerry Birnbaum, Greg Coffey

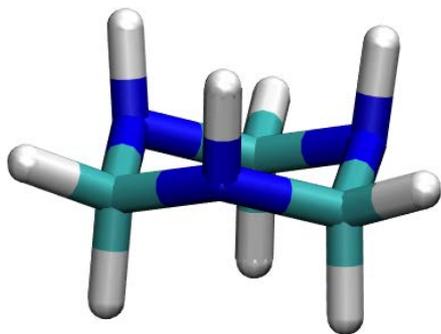


► T_1 measurements consistent with three different H_2 environments over temperature range from 25 – 225 K

► Pake pattern provides insight into structure and dynamics of $\text{H}_2\text{-Mg}^{2+}$ interaction. *Not static even at 5 K*

Accomplishments

II. Experimental approaches to determine thermodynamic properties of liquid carriers



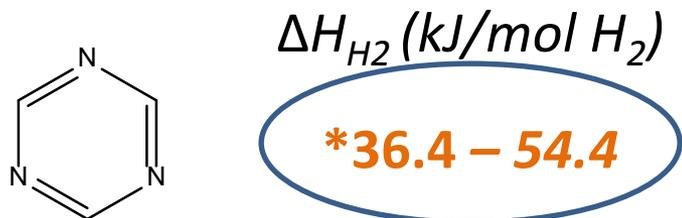
Progress on using NMR spectroscopy and reaction calorimetry to benchmark calculated enthalpies of H_2 uptake and release in liquid carriers.

Why is there discrepancy in ΔH_{H_2} for triazine?

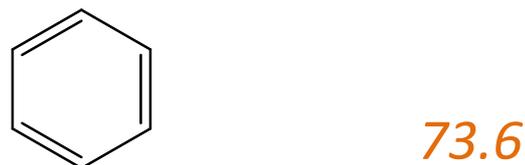
Approaches to liquid carriers and benchmarking theory



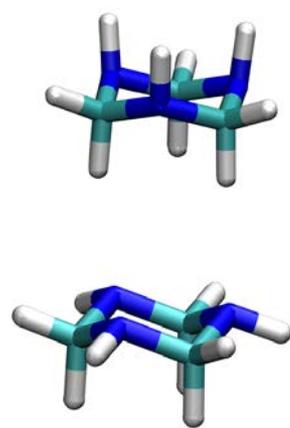
Bojana
Ginovska



*Air Products final report and Clot, Eisenstein, Crabtree, CHEM. Comm. 2231, 2007 B3PW91/aug-cc-pVDZ



- Range of 36 to 54 kJ/mol too large to be useful.
- What is required level of theory to get accurate predictions of enthalpy?



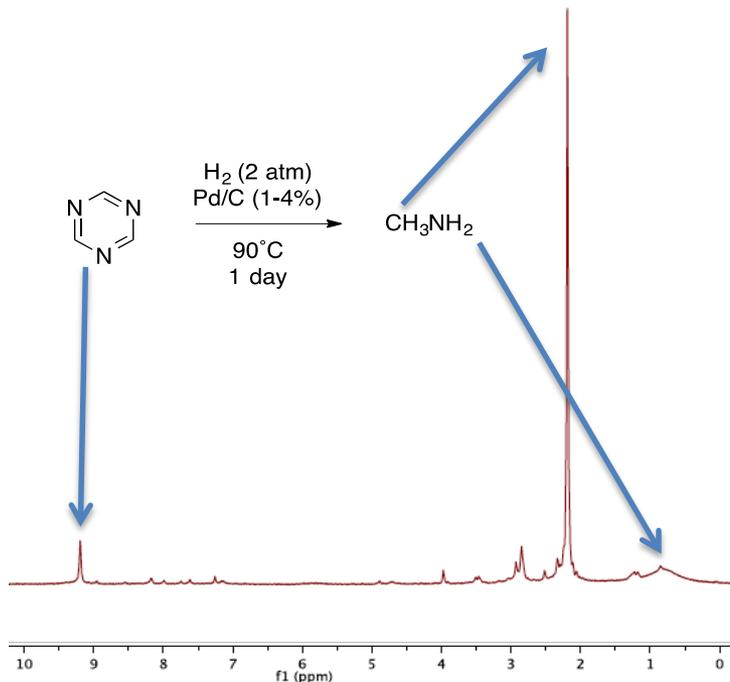
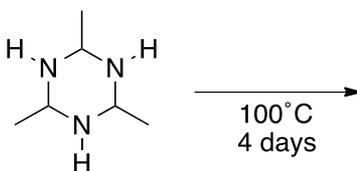
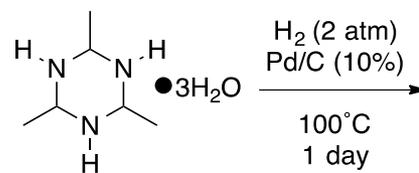
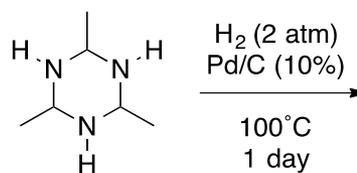
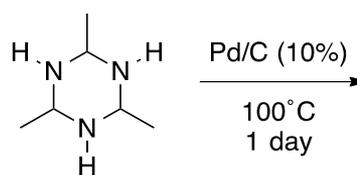
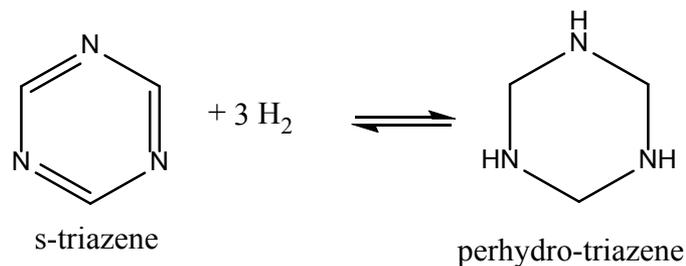
- Bojana screened 4 isomers of triazine at B3LYP+D2/dzvp2, range from most stable is 43-57 kJ/mol H_2
- Adrian screening for catalysts to use in reaction calorimeter to measure heat to obtain experimental ΔH_{H_2} to benchmark theory

Catalyst screening for triazine hydrogenation.

Use NMR to screen for optimum reaction conditions (catalysts, temperature, reaction time) for calorimetry experiments



Adrian Houghton

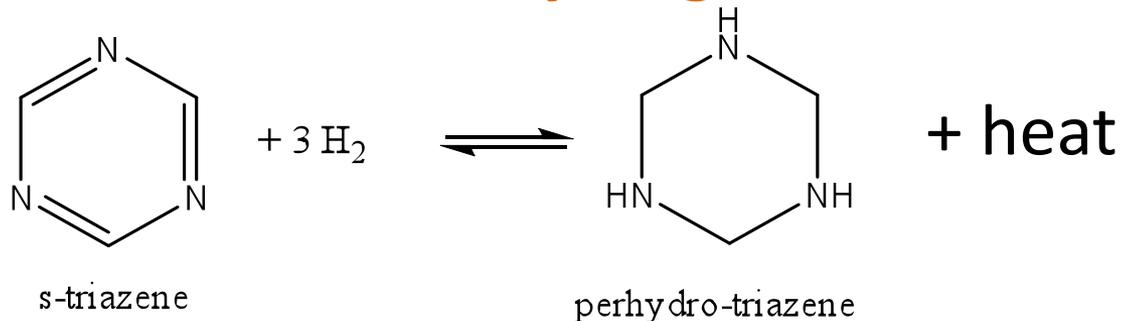


Triazine too easy to hydrogenate!

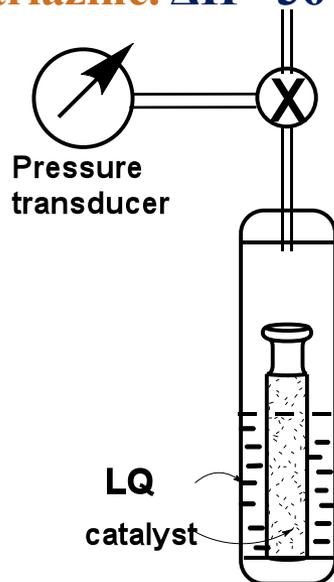
Reaction calorimetry: direct measure of heat of triazine hydrogenation



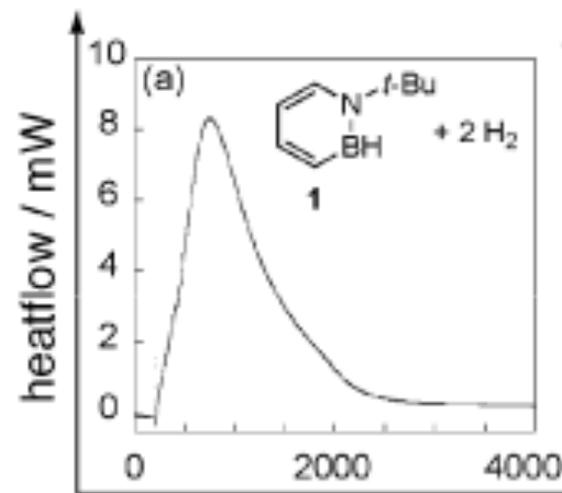
Abhi Karkamkar



First experiments. Measurement of enthalpy of H₂ uptake by triazine. $\Delta H = 36$ or 54 kJ/mol H₂?



Campbell,
Abbey, Neiner,
Grant, Dixon, Liu
**J. AM. CHEM.
SOC. 2010, 132,
18048**



Heat of hydrogenation of CBN

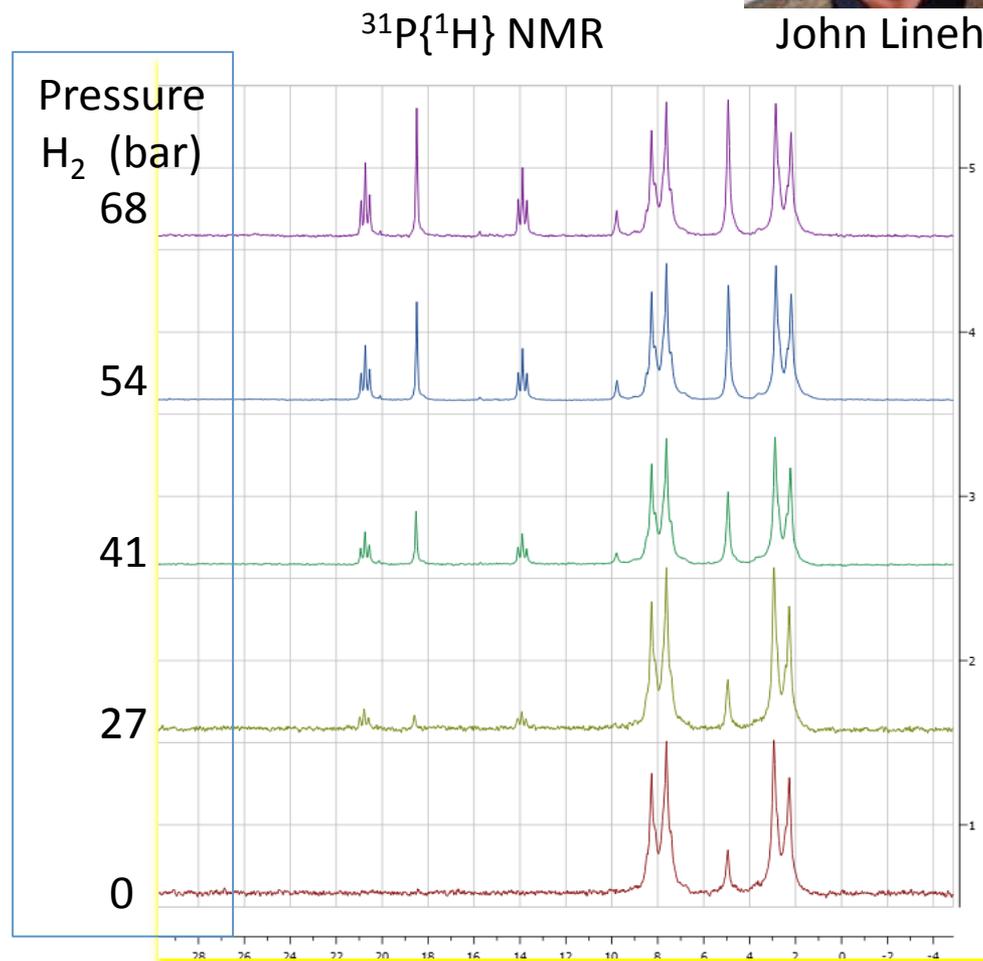
Using variable P, T liquid NMR to measure K_{eq} in liquid carriers (compare to calorimetry)



John Linehan

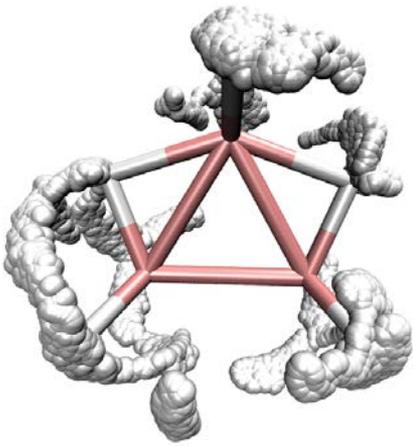


- ▶ Machined in-house, bottom is virgin PEEK, Top is carbon-filled PEEK
- ▶ pressure tested to 1,000 bar
- ▶ temperature range : 170 to 370 K



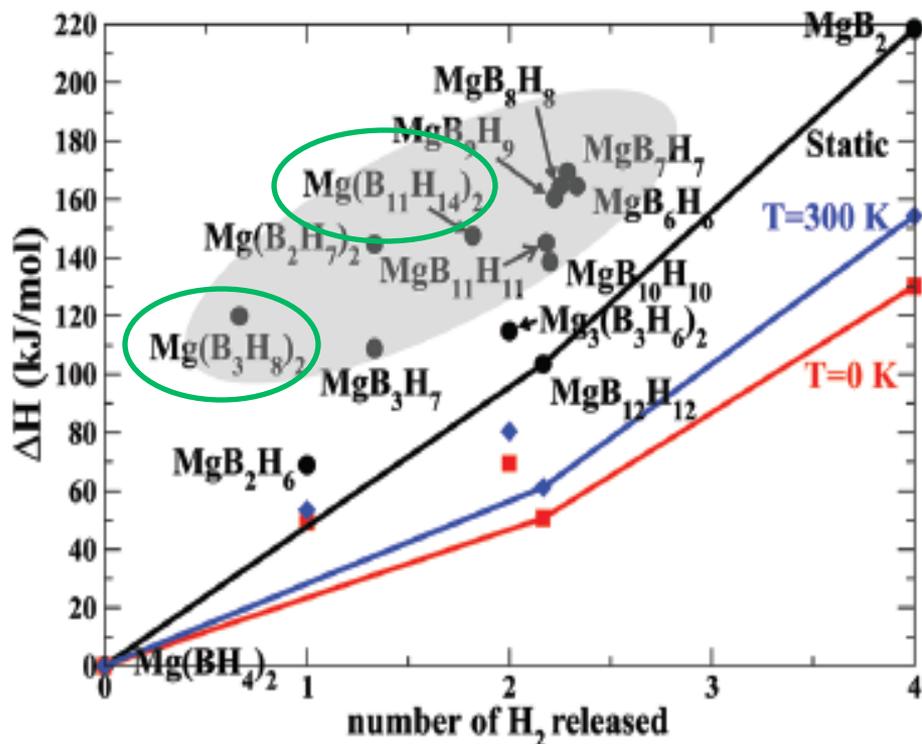
Accomplishments

III. Using solid state MAS in-situ NMR spectroscopy to gain insight into reaction pathways leading to reversible H_2 in solid complex hydrides.



Validation of the claim that $Mg(BH_4)_2$ can be regenerated from $Mg(B_{10}H_{10})$ and progress on developing in-situ characterization methods to study the evolution of borane clusters in presence and absence of additives.

Why is in-situ MAS NMR important? *Can it help us to understand the discrepancy between experiment & theory?*

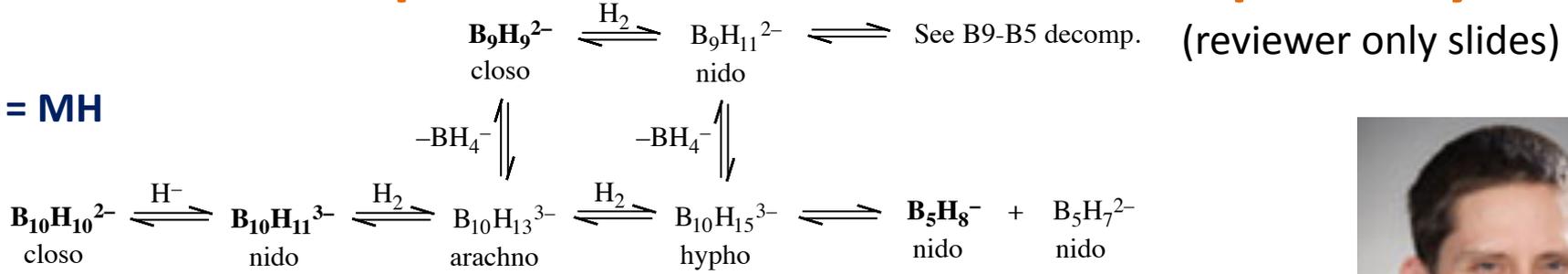


- Validated that $\text{Mg}(\text{BH}_4)_2$ can be regenerated from $\text{Mg}(\text{B}_{10}\text{H}_{10})$
- Can we understand the discrepancy between experiment and theory (for B_3H_8 & $\text{B}_{11}\text{H}_{14}$)?
- Develop rational reaction pathway based on chemistry (BH condensation and Wades rules)

Figure from J. Phys. Chem. C 2012, 116, 10522

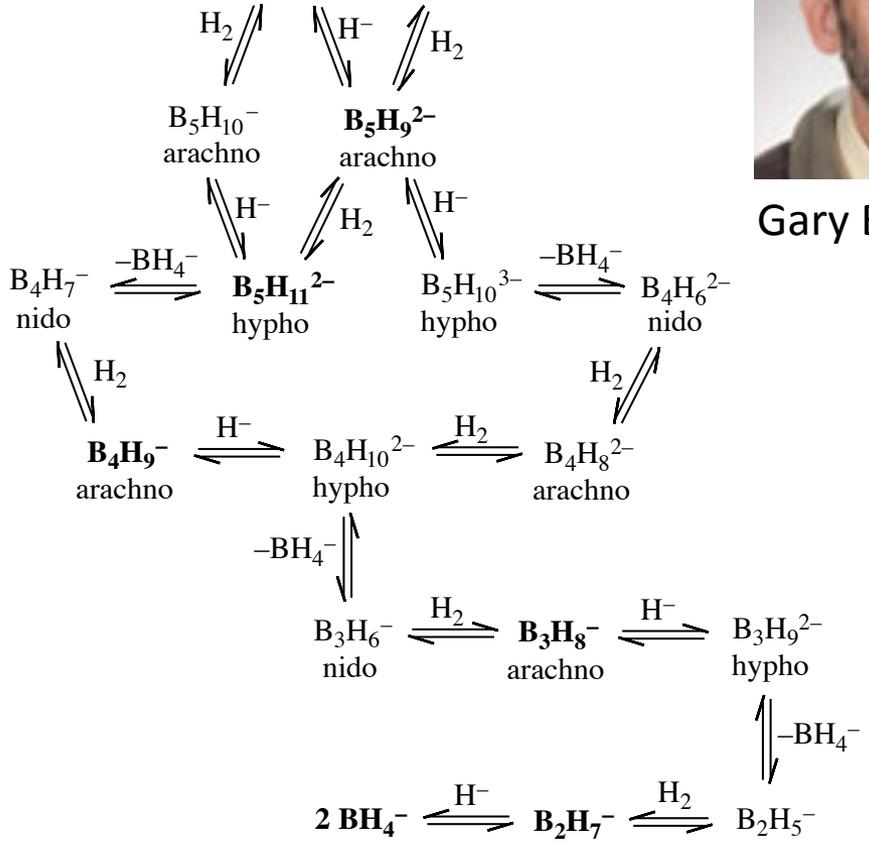
'Wades rules' to predict structures in reaction pathways

$H^- = MH$



Progress: provided 1st rational pathway for regeneration of $Mg(BH_4)_2$ from $Mg(B_{10}H_{10})$

- *Wades rules* (polyhedral skeletal electron pair theory) sets limits to 'infinite' number of borane clusters.
- Can suggest catalysts and additives to enhance kinetics



Gary Edverson

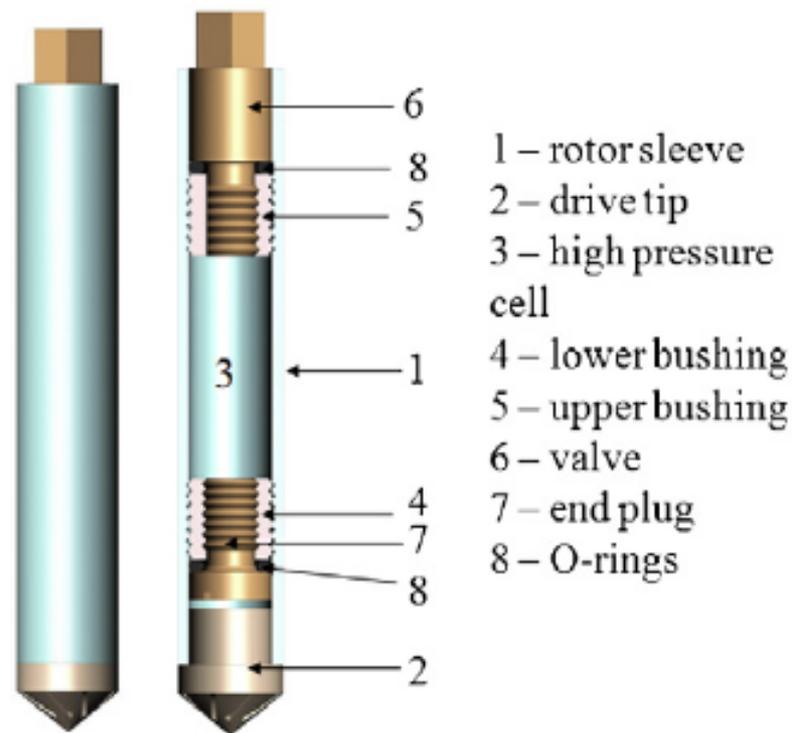
Unique in-situ MAS Variable P, T



Pacific Northwest
NATIONAL LABORATORY

The **HP MAS NMR*** capability developed in EMSL at PNNL enables the following capabilities

- High-pressure (up to 200 bar) NMR analysis of solids, liquids, gasses (e.g., CO₂, CH₄, H₂, He, N₂).
- Temperature range ambient to 200 °C.
- Uses the full internal diameter of the sample cell for increased volume and sensitivity
- Sealing mechanism outside the RF coil of a probe so interference from background signals is eliminated.
- Sample cell can be reused, i.e., reopened, and resealed under pressure.
- Typically analysis used for ¹³C NMR spectroscopy but also ²³Na, ²⁵Mg, ¹⁵N, ¹¹B and ⁴³Ca –enriched samples.
- Uses standard commercial solid-state NMR probes in 7.5 mm and 6 mm OD rotors.



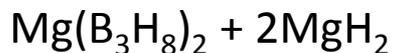
*Hoyt, Turcu, Sears, Rosso, Burton, Felmy, Hu. 2011. Journal of Magnetic Resonance, 2011, 212, 378

Progress on Approach to In-situ MAS Variable P, T



Marina Chong

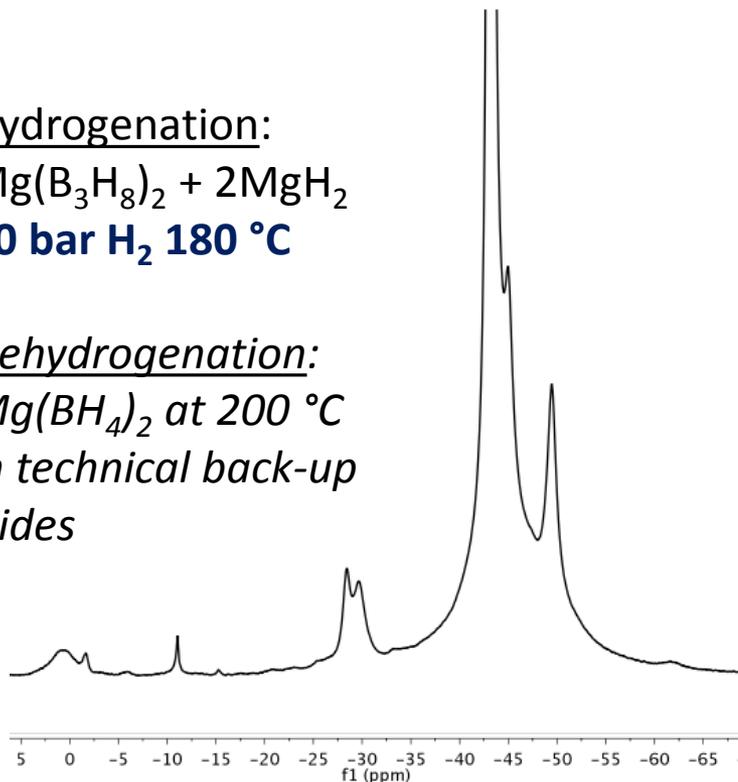
Hydrogenation:



50 bar H₂ 180 °C

Dehydrogenation:

*Mg(BH₄)₂ at 200 °C
in technical back-up
slides*



Sarah Burton and David Hoyt

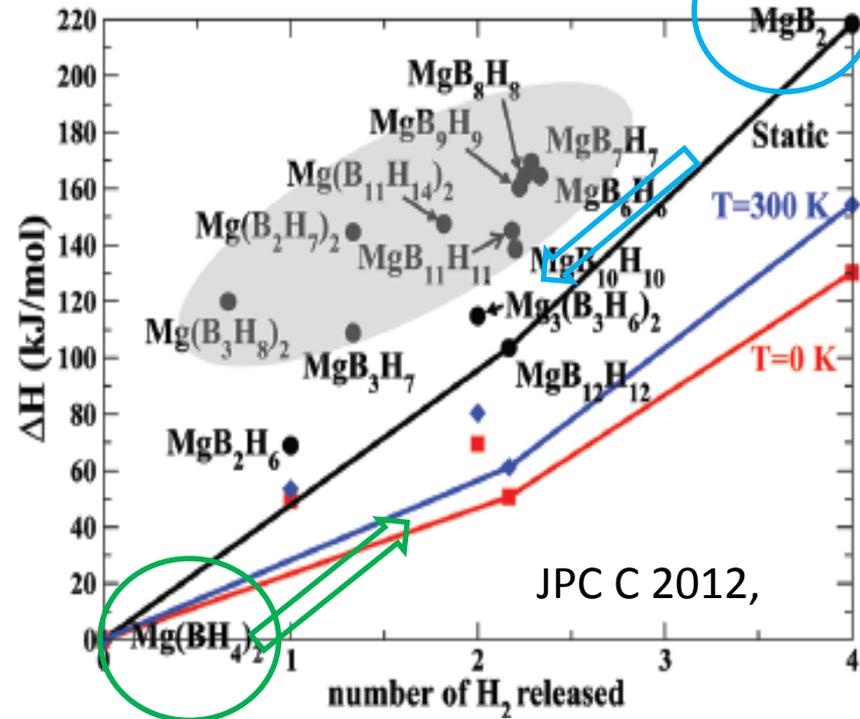
- $\text{Mg}(\text{BH}_4)_2 \rightleftharpoons \text{Mg}(\text{B}_{10}\text{H}_{10})_2 + \text{H}_2$
- U Hawaii (C Jensen) *in-situ* ¹¹B NMR to elucidate reversible reaction pathways of magnesium borohydride in presence of additive.
- Prepare *authentic clusters*, i.e., B₃H₈, B₉H₁₄, B₁₀H₁₀, B₁₁H₁₄, B₁₂H₁₂ for NMR, neutron and X-ray spectroscopy

Collaborations with HyMARC

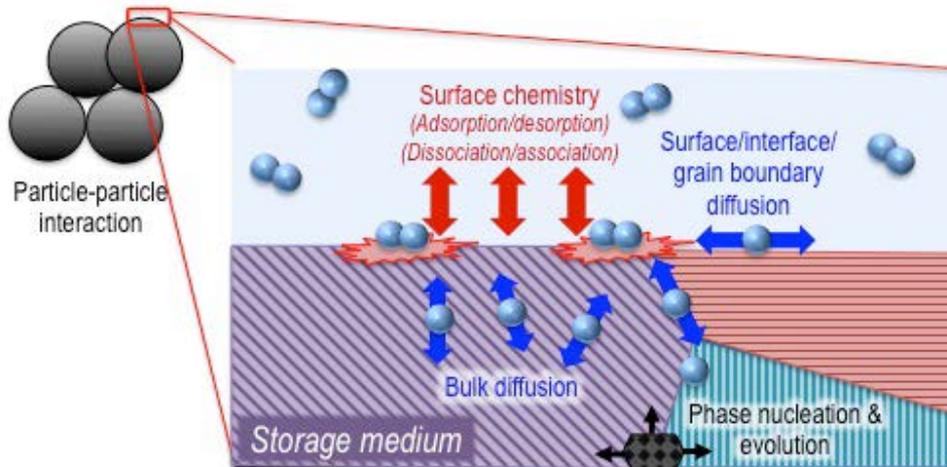
Connecting chemistry with the physio-chemistry phenomena to increase efficiency of reversibility

HyMARC- phase boundaries, surface chemistry, microstructure

PNNL/Hawaii - chemistry *within* a phase and additives to minimize phase separation



HyMARC physio-chemical processes



¹¹B NMR – what are common intermediates? (reviewer only slides) 20

Key accomplishments & future work

(I) Measure the first ^1H NMR spectra of H_2 physi-sorbed to $\text{Mg}_2\text{-m-dobdc}$ MOF

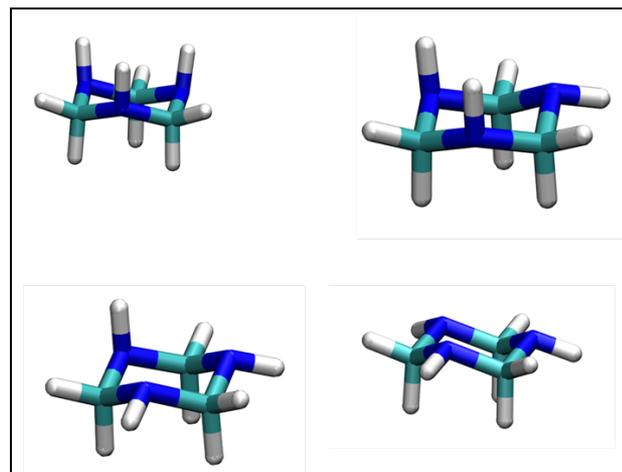
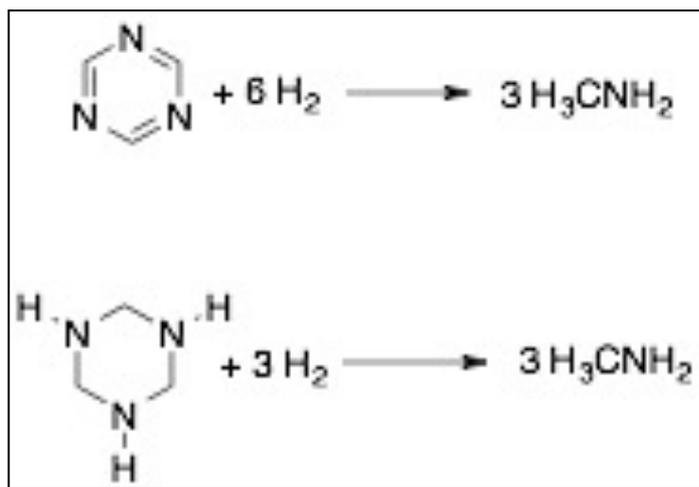
- *calc binding energy of H_2 from T_1 data*
- *Develop dynamics models to fit experimental NMR data. NIST neutron (QENS and INS) and LBNL FTIR will compliment the NMR experiments*
- *Calculate and look for the ^1H NMR spectra for 2 H_2 's per metal site.*
- *Test new dosing 'coffey' cell*



Key accomplishments & future work

(ii) Provided an explanation for the discrepancy between calculated enthalpies of hydrogenation of triazine

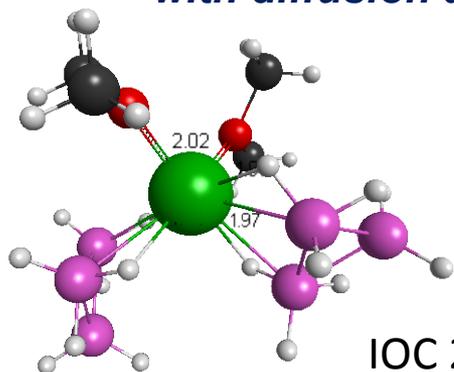
- *Measure enthalpy of hydrogenation from difference measurement. Triazine not sufficiently stable, future NMR & calorimetry experiments will focus on diazines*
- *Compare rates of heterogeneous and homogeneous catalysts for reduction of diazine in reaction calorimetry*
 - *Heterogeneous catalysts from Teng He and Ping Chen (DICP) and Qiang Xu (AIST)*
 - *Homogeneous catalysts from Nate Szymczak (U Michigan) and Craig Jensen (U Hawaii)*
- *Not only get heats of reaction but also excellent approach to compare rates and efficiencies of various catalysts*



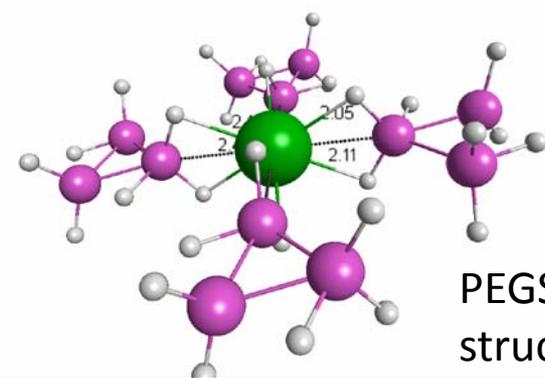
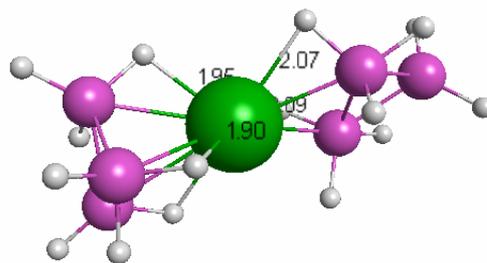
Key accomplishments & future work

(III) Developed a rational reversible reaction pathway that connects $\text{Mg}(\text{BH}_4)_2$ with $\text{Mg}(\text{B}_{10}\text{H}_{10})$.

- calculate the relative energies and NMR chemical shifts of key intermediates
 - Provide a database for closo, nido and archno intermediates
- use in-situ MAS NMR and XRD to follow the evolution of $\text{Mg}(\text{BH}_4)_2$ & $\text{Mg}(\text{B}_{10}\text{H}_{10})$
 - XRD will provide insight into crystalline phases and NMR amorphous phases
- TPD mass spec with NREL to identify volatile species
- identify discrepancy between calculated and observed B_3H_8 intermediate.
 - Theory is not 'wrong' so – understanding this will provide key insight to enable lower temperature reaction pathways
- Work with HyMARC to develop 'global' model to incorporate 'chemical kinetics' with diffusion and phase transformation kinetics



IOC 2007, 46, 9060.



PEGS
structure

What does success look like?

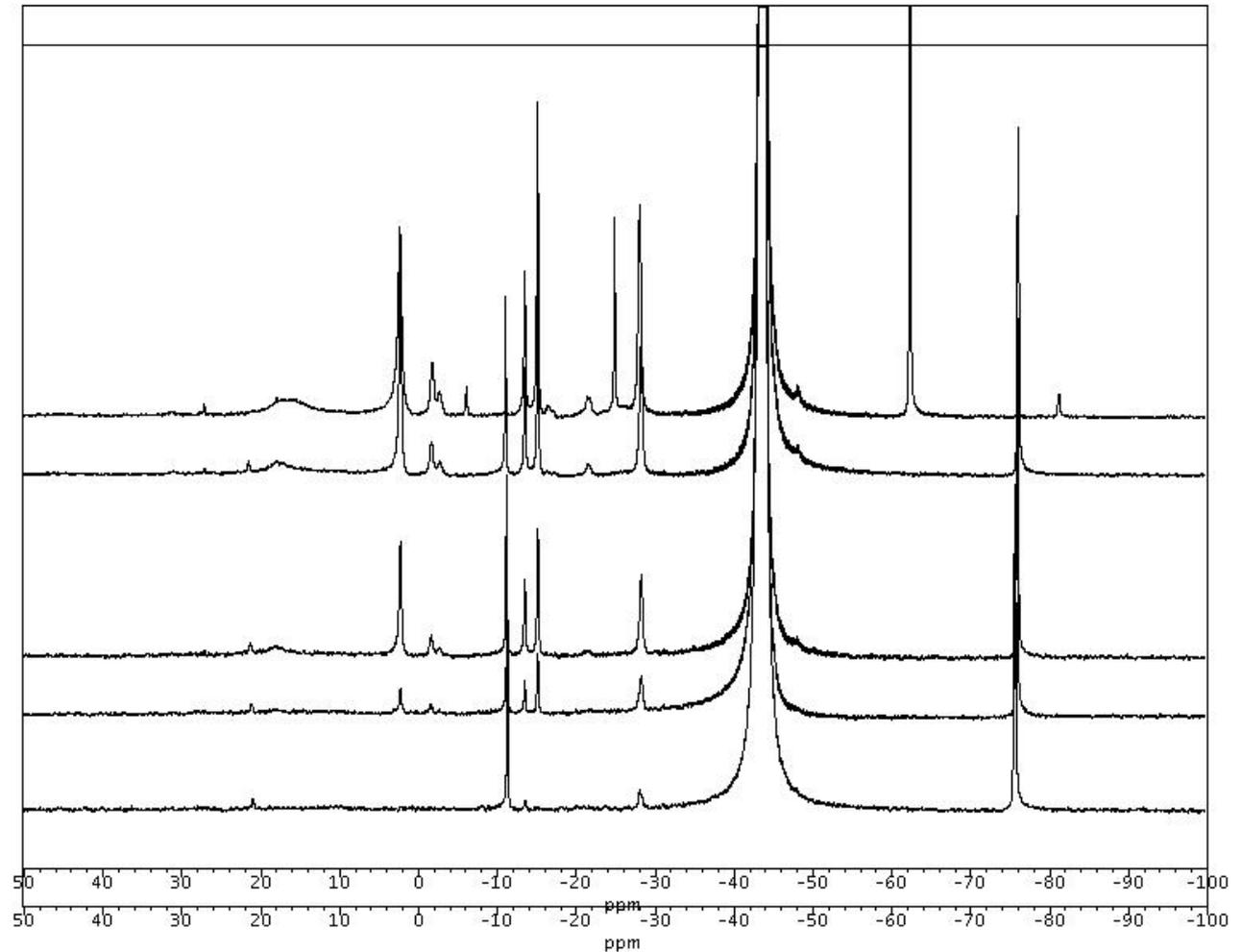
► In one year...

- NMR methods to **validate** 2 H₂'s / metal site in an amorphous material
- **Validation** of key additives to increased rate of H₂ uptake and release in “BH₄/B₁₀H₁₀” cycle.
- Publishing reaction scheme to **characterize** reaction connecting BH₄ with B₁₀H₁₀ providing structures and energetics to benchmarked with experiment.
- Publishing **characterization** studies from combined MAS NMR (Hawaii), X-ray diffraction (Hauback) and K-edge x-ray absorption study following evolution of boron clusters in Mg(BH₄)₂ decomposition.
- Testing connectivity of chemical kinetic model (Bojana Ginovska) and physical modeling (Brandon Wood) to **characterize** reactivity of Mg(BH₄)₂.
- Assisting new FOA project with in-situ NMR measurements to **characterize and validate** proposed reaction pathways (e.g., ¹⁵N, ⁷Li, ¹¹B).
- Published **characterization** methods using reaction calorimetry to screen catalysts for H₂ uptake by liquid carriers and measure enthalpies to **validate** theory and measure of enthalpy of hydrogenation of triazine and diazine.

Technical back-up slides

In-situ solid state MAS ^{11}B NMR

- ▶ Dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ at 200 C



Borane cluster information library

Anion	Class	Crystal structures
B12H12(2-)	closo-12	Single crystal structure of Li2B12H12: See .cif data from Inorganic Crystallographic Database. Calculations for Li2B12H12: Ohba, N.; Miwa, K.; Aoki, M.; Noritake, T.; Towata, S.; Nakamori, Y.; Orimo, S.; Züttel, A. Phys. Rev. B 2006, 74, 075110. K2B12H12:Tiritiris, I.; Schleid, T. Zeitschrift fuer Anorganische und Allgemeine Chemie (2003), 629(7-8), 1390-1402.
		M2B12H12 single crystal structures: Tiritiris, I.; Schleid, T.; Mueller, K. Appl. Magn. Reson. (2007) 32, 459-481 DOI 10.1007/s00723-007-0037-9
B12H13(3-)	nido-12	Single crystal structure of (CH3)2C2B10H11(-): Getman, Knobler, Hawthorne Inorg. Chem. 1990, 29, 158-160. DOI: 10.1021/ic00327a004
B12H15(3-)	arachno-12	Calculated structure of 12-vertex arachno structure: Wrackmeyer, B.; Schanz, H-J.; Hofmann, M.; Schleyer, P.v.R. Angew. Chem., Int. Ed. (1998), 37(9), 1245-1247. Single crystal structure of arachno-7-CH3-7,12-CNB10H13-: See Sneddon, et.al. J. Am. Chem. Soc. 1996, 118, 6407-6421. DOI: 10.1021/ja960787m
B12H17(3-)	hypho-12	
B11H11(2-)	closo-11	Volkov, O.; Dirk, W.; Englert, U.; Paetzold, P. Z. Anorg. Allg. Chem. 1999, 625, 1193-1201.
B11H13(2-)	nido-11	Isoelectronic phosphaborane structure: B10H12PCH3 CAS#: 57108-87-9 Shore, et.al. Inorg. Chem. 1989, 28, 3616-3618
B11H14(3-)	arachno-11	
B11H16(3-)	hypho-11	C3B8 hypho structure: Londesborough M. G S; Janousek Z.; Stibr B.; Hnyk D.; Plesek J.; Cisarova I. Dalton Transactions (2007), (12), 1221-8. DOI: 10.1039/b618082e. Single crystal structure of hypho-12-Bn-12,13-CNB9H15: See Sneddon, et.al. J. Am. Chem. Soc. 1996, 118, 6407-6421. DOI: 10.1021/ja960787m
B10H10(2-)	closo-10	Single crystal structure of K2B10H10: See .cif data from Inorganic Crystallographic Database.
B10H11(3-) or B10H12(2-)	nido-10	Calculated structure of B10H12(2-): Hoffman, M.; Schleyer, P. v.R. Inorg. Chem. 1998, 37, 5557-5565.
B10H13(3-) or B10H14(2-)	arachno-10	Crystal structure of B10H10-2MeCN: van der Maas Reddy, J.; Lipscomb, W. N. J. Am. Chem. Soc. 1959, 81, 754.
B10H15(3-)	hypho-10	Calculated structures for B10H12L2(2-): Hoffman, M.; Schleyer, P. v.R. Inorg. Chem. 1998, 37, 5557-5565.
B9H9(2-)	closo-9	Guggenberger, L. J. Inorg. Chem. 1968, 7, 2260-2264.
B9H11(2-)	nido-9	Crystal structure of B9H12(-): Morris, et.al. J. Chem. Soc. Dalton Trans. 1985, 1645-1654.
B9H13(2-)	arachno-9	Crystal structure of B9H13(2-): Getman, T. D.; Krause, J. A.; Niedenzu, P. M.; Shore, S. G. Inorg. Chem. 1989, 28, 1507-1510.
B9H14(3-)	hypho-9	1-CH2-2,5-S2B6H8 crystal structure: Kang and Sneddon, J.Am.Chem.Soc.,1989, 111, 3281-3289.
B8H8(2-)	closo-8	Guggenberger, L. J. Inorg. Chem. 1969, 8, 2771-2774.
B8H10(2-)	nido-8	crystal structure of B8H12 neutral "nido" but with "arachno-like" structure: Enrione, R. E.; Boer, F. P.; Lipscomb, W. N. Inorg. Chem. 1964, 3, 1659-1666

PNNL Core Capability Milestones

	End Date	Type	
Purchase components to fabricate variable pressure NMR probe	12/31/2015	Regular	complete
Perform testing on the variable temperature capability of new low temperature NMR probe 100 and 300 K at 1 bar.	3/31/2016	Regular	complete
Perform testing on the variable pressure capability of new low temperature NMR between 1-10 bar at 273 K.	6/30/2016	Regular	50%
Measure ^1H NMR of physisorbed H_2 at temperatures between 100 and 300 K at 1 & 5 bar H_2 to show that experimental heat of adsorption is within 10% of reported value.	9/30/2016	SMART	25%
Use DFT and hybrid DFT/molecular mechanics MD simulations to predict enthalpy and free energy of H_2 uptake and release in complex hydride materials.	12/31/2017	Regular	10%
Measure vapor pressure of liquid perhydrotriazine carrier as function of temperature from 300 – 450 K.	3/31/2017	Regular	
Measure ^1H NMR of sorption standard at 100 bar and 100 K. Assign the sorption and free hydrogen peaks and show that experimental heat of adsorption is within 10% of reported value.	6/30/2017	SMART	
Provide analysis and characterization of 2 samples assigned by DOE (NMR , TEM or Calorimetric)	9/30/2017	Regular	

Group Materials Milestones

Year/Qtr	Materials Discovery Milestone Name/Description	Type
FY16/Q1	I. Computational chemists will initiate investigation of the most promising structures for porous aromatic frameworks (PAFs) or block copolymer, (BCP) using first-principles electronic structure calculations with range separation and dispersion corrections.	Regular
FY16/Q2	II. Synthesize a porous aromatic framework material with metal-chelating sites and a Langmuir surface area of at least 1000 m ² /g.	Regular
FY16/Q3	III. Synthesize and characterize a carbon based sorbent with catechol functionalized pore domains that contain unsaturated metal centers attached to the materials matrix.	Regular
FY16/Q4	IV. Go/No-Go: Demonstrate the ability to bind two H ₂ molecules to one metal center in a metal-organic framework, porous aromatic framework or carbon-based material.	SMART GNG1
FY17/Q1	V. Demonstrate computational accuracy by showing that the calculated capacity for a MOF, PAF, or carbon-based material with multiple H ₂ molecules bound per metal is within 15% of the experimental capacity.	Regular
FY17/Q2	VI. Demonstrate H ₂ addition to solid-state triazine at temperatures < 100 C and pressure < 50 bar.	Regular
FY17/Q3	VII. Synthesize a framework, aerogel or polymeric material exhibiting a total H ₂ storage capacity of at least 30 g/L at temperatures above 100 K and < 150 bar.	SMART
FY17/Q4	VIII. Go/No-Go: Triazine-based hydrogen carriers: Solid phase organic carrier: if > 50g H ₂ /L uptake is observed in solid phase triazine at T < 100 C and P < 100 bar, then go. If <50 g H ₂ /L then no-go on solid phase organic carriers: Liquid phase organic carriers: if blend of perhydrotriazines are liquid at room temperature and remain liquid after H ₂ release then go. If carriers or spent fuel are solid then no go on liquid carriers.	GNG2