Amide-hydride Combinations for Hydrogen Storage

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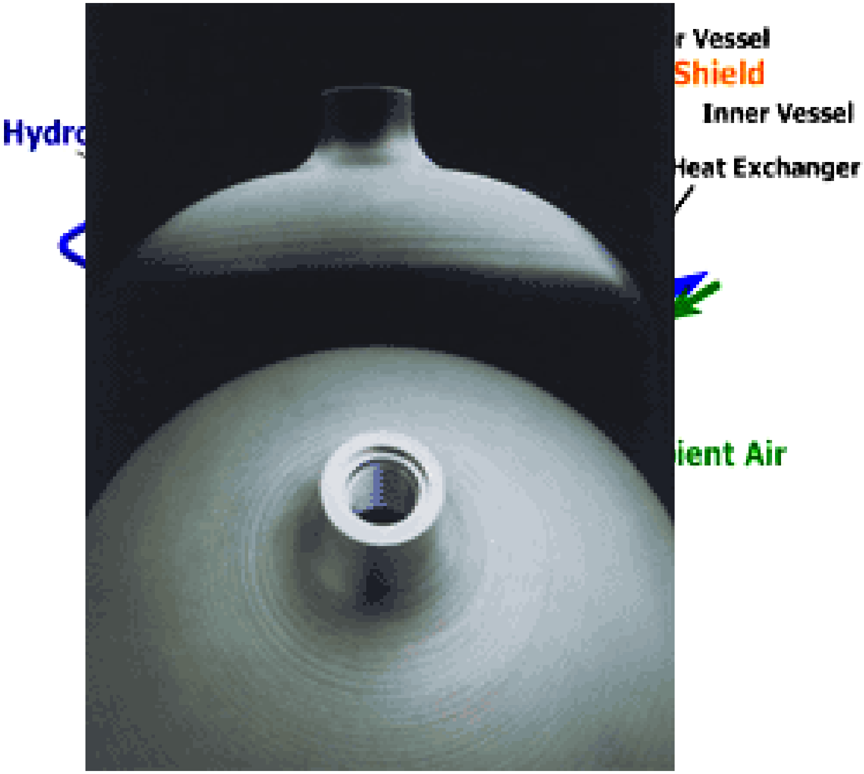
Outline

I. Introduction to Hydrogen Storage

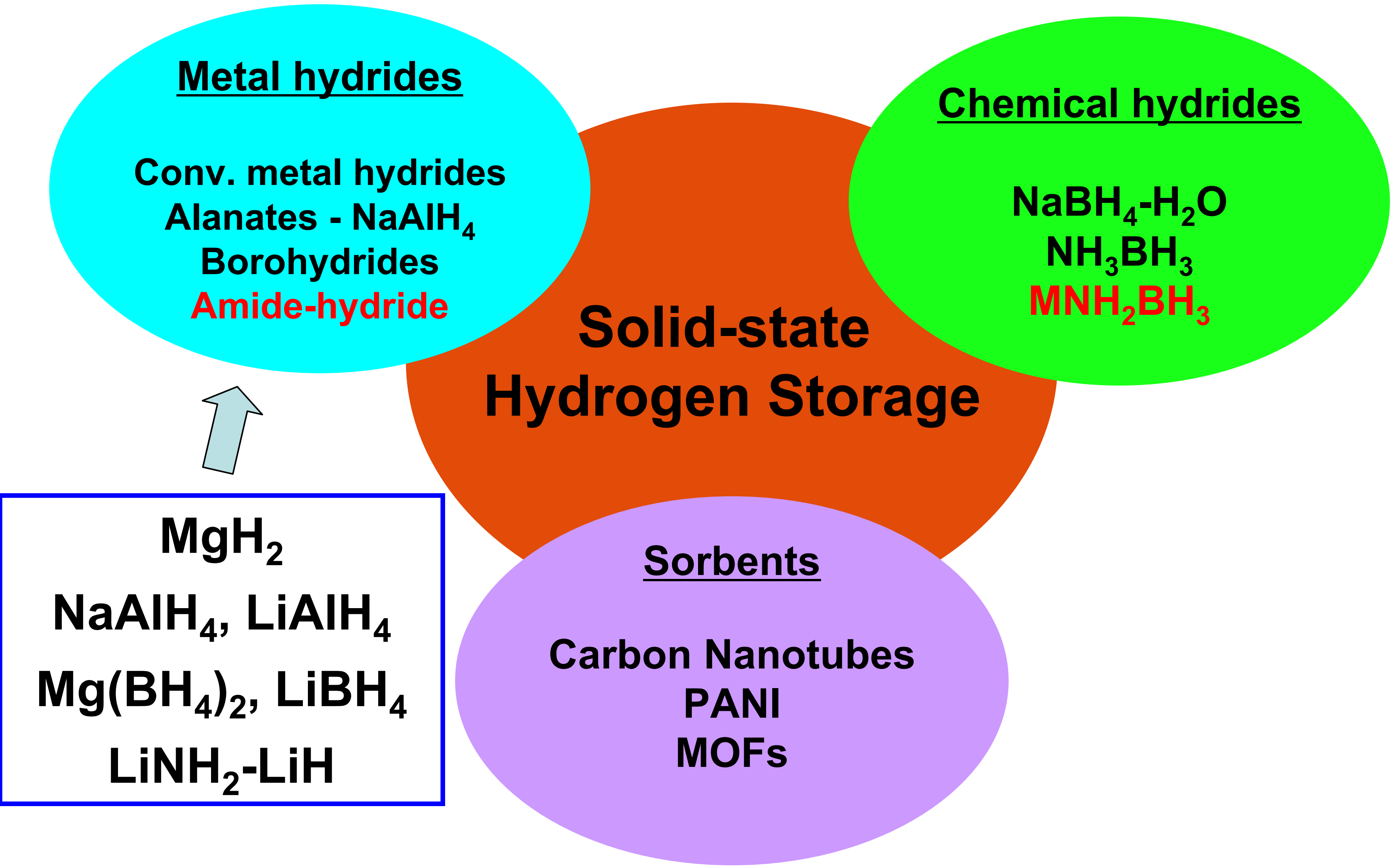
II. Hydrogen from Amide-hydride Combinations

III. Nano-Materials and Catalysts

Liquid Hydrogen

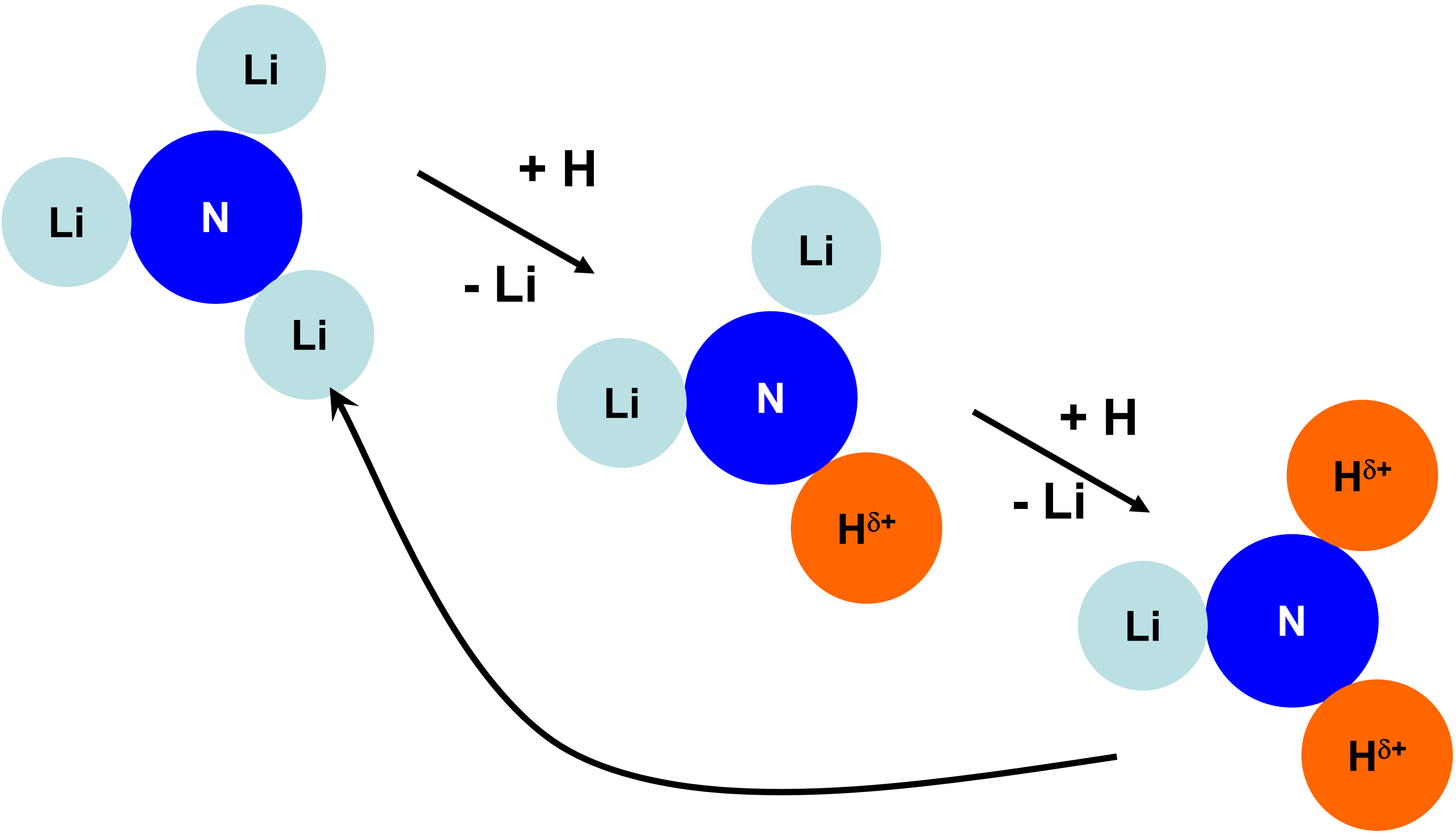


Compressed H_2


Metal hydrides
Conv. metal hydrides
Alanates - $NaAlH_4$
Borohydrides
Amide-hydride
Chemical hydrides
$NaBH_4$-H_2O
NH_3BH_3
MNH_2BH_3
Solid-state Hydrogen Storage
Sorbents
Carbon Nanotubes
PANI
MOFs
MgH_2
$NaAlH_4$, $LiAlH_4$
$Mg(BH_4)_2$, $LiBH_4$
$LiNH_2$-LiH

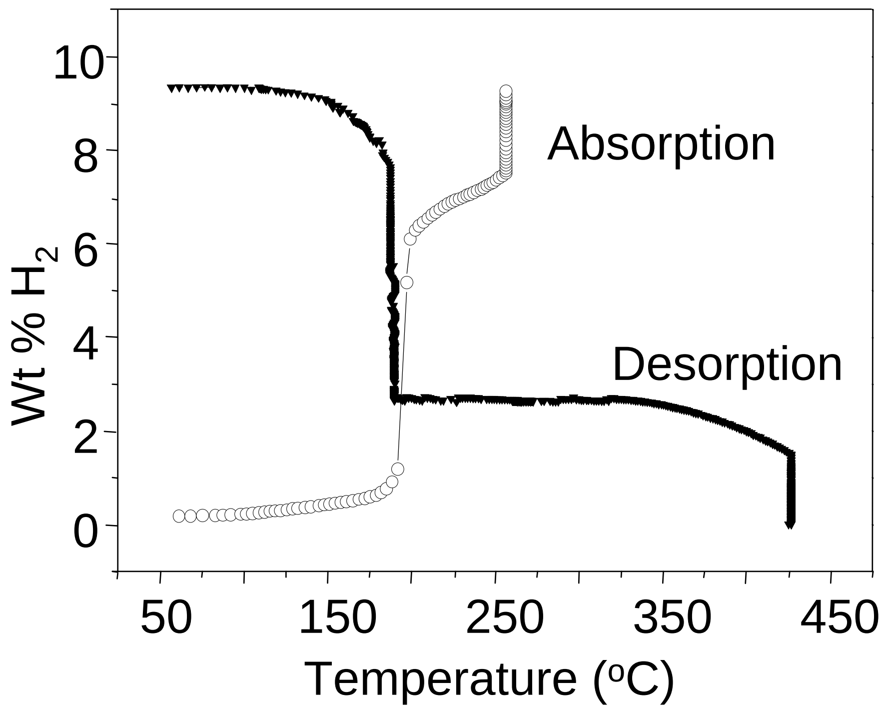
II. Hydrogen from Amide-Hydride Combinations

$Li_3N + 2H_2 \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow LiNH_2 + 2LiH$

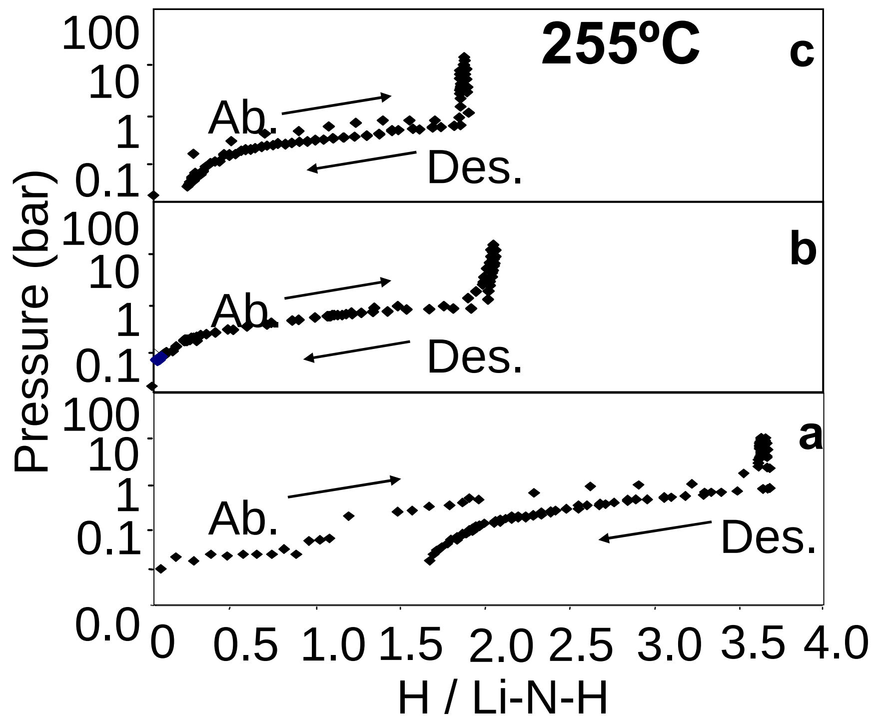


$LiNH_2 + 2LiH \leftrightarrow Li_2NH + LiH + H_2 \leftrightarrow Li_3N + 2H_2$ **10.5wt%**

TG

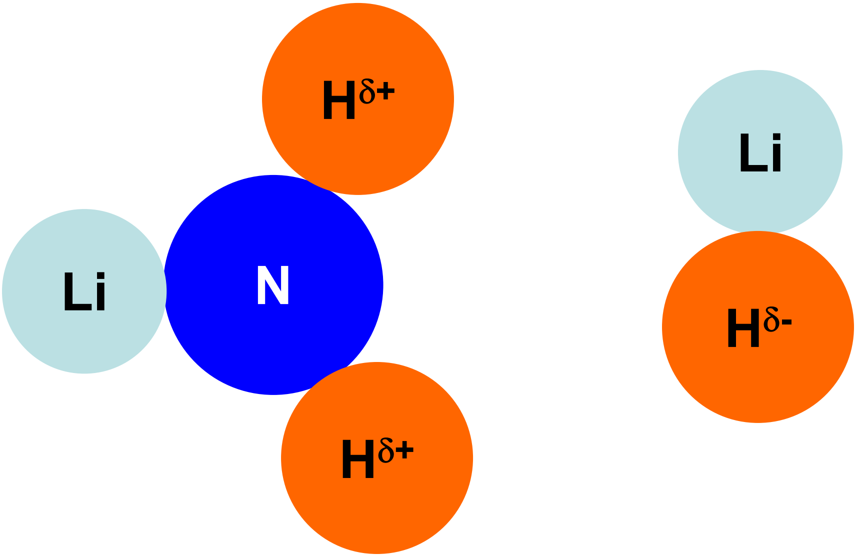


PCT



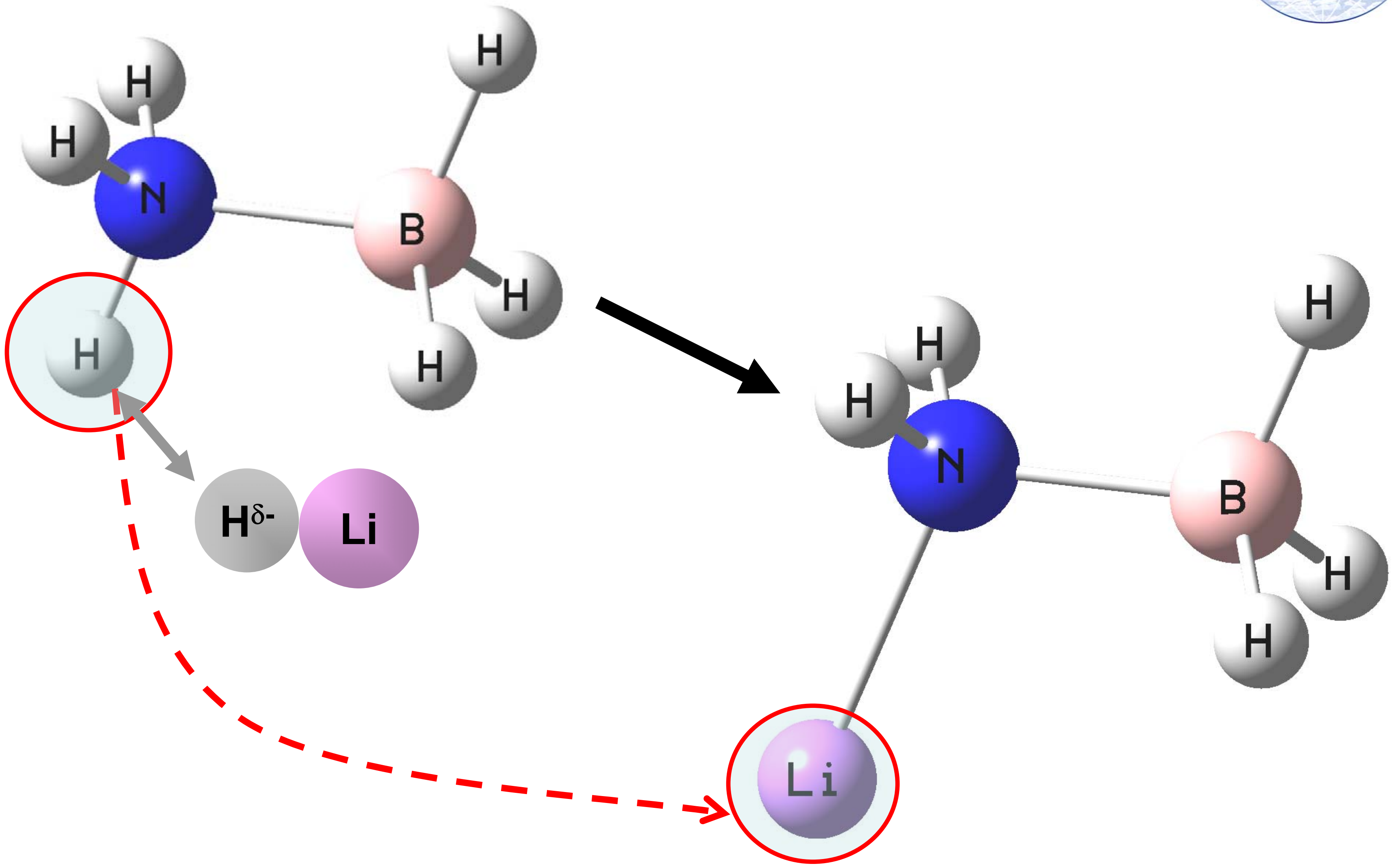
-- *Nature* 420 (2002) 302

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2$$

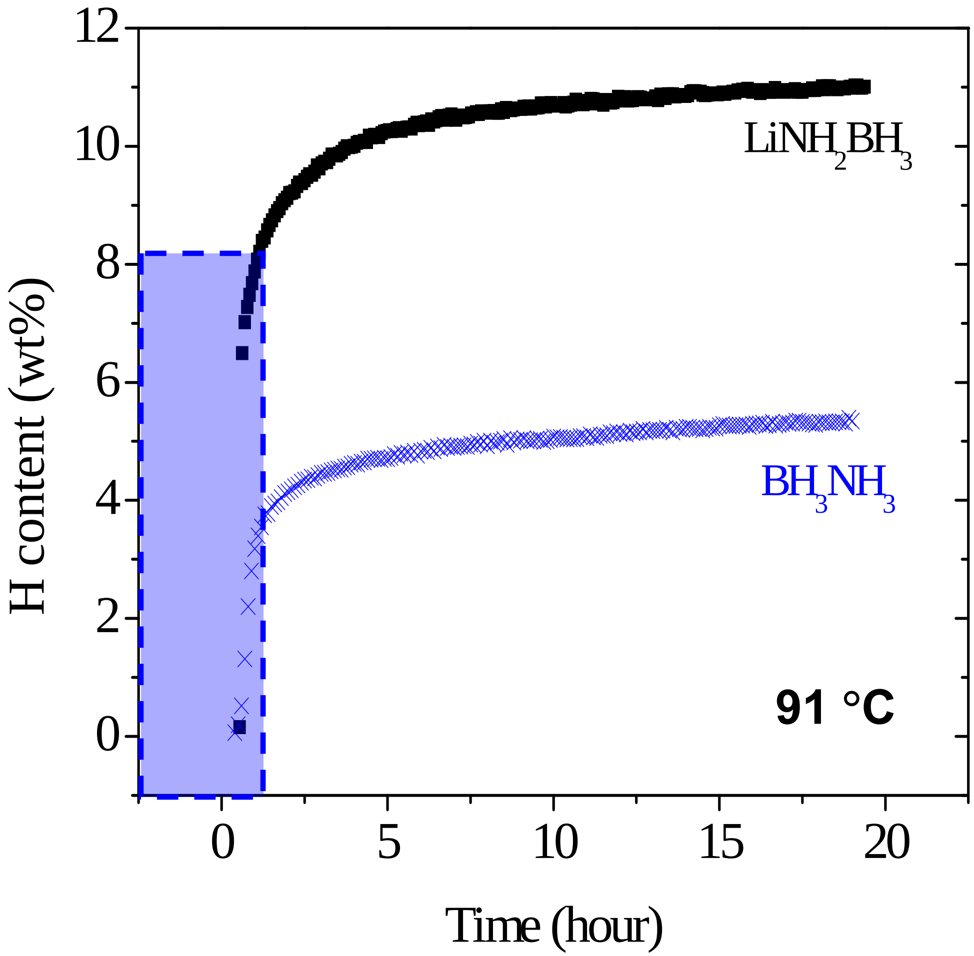


$$H^+ + H^- \rightarrow H_2 \qquad \Delta H = -17.37\ eV$$

$$LiH + NH_3BH_3 \rightarrow LiNH_2BH_3 + 2H_2$$



$LiNH_2BH_3 \rightarrow [LiNBH] + 2\ H_2$ 10.9 wt%

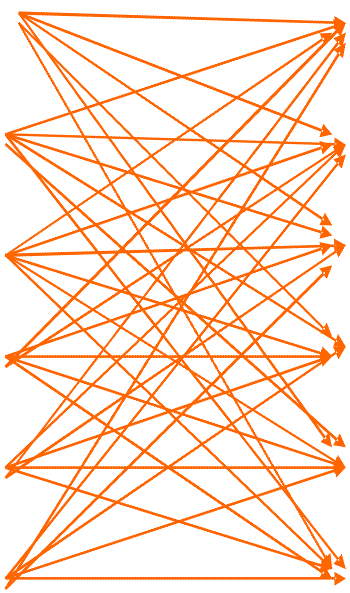


- ~ 90 °C
- 2 equiv. H_2 desorption
- > 10 wt% in 17 hrs.
- ~ 8 wt% in 1st hour
- The rest of H_2 takes long time to desorb

-- *Nature Mater* 7 (2008) 138

Amide-hydride Combinations

Amides	Hydrides
$LiNH_2$	LiH
$NaNH_2$	NaH
$Mg(NH_2)_2$	MgH_2
$Ca(NH_2)_2$	CaH_2
$NaCa(NH_2)_3$	$LiAlH_4$
$Li_3Na(NH_2)_4$	$NaAlH_4$



H_2

III. Nanosized Materials and Catalysts

3.1 Nano-Materials

$$Mg(NH_2)_2 + 2LiH \leftrightarrow Li_2Mg(NH)_2 + 2H_2 \quad 5.5\ wt.\%$$

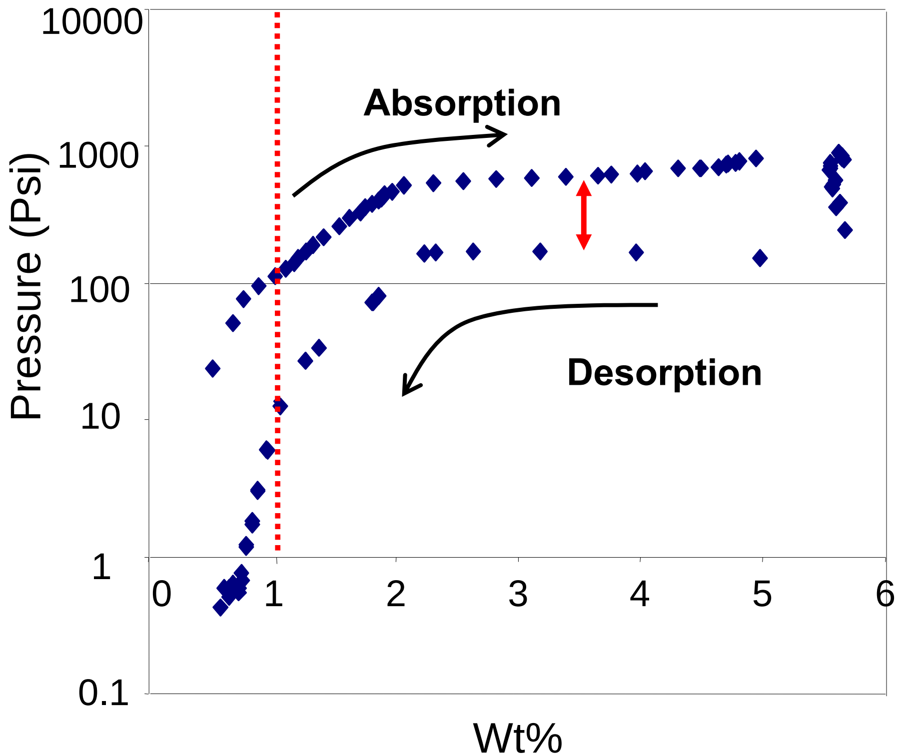
Ref:

- *Chen P et al. Oral presentation at MRS Fall Meeting 2003 (Boston).*
- *Xiong ZT, Wu GT, Hu JJ, Chen P et al. Adv Mater 2004; 16:1522.*
- *Luo WF. J Alloy Compd 2004; 381:284.*
- *Leng HY, Ichikawa T, Hino S, et al. J Phys Chem B 2004; 108:8763.*
- *Nakamori Y, Orimo S. J Alloy Compd 2004; 370:271.*
- *Xiong ZT, Hu JJ, Wu GT, et al. J Alloy Compd 2005; 398:235.*

etc.

Pressure-Composition-Temperature

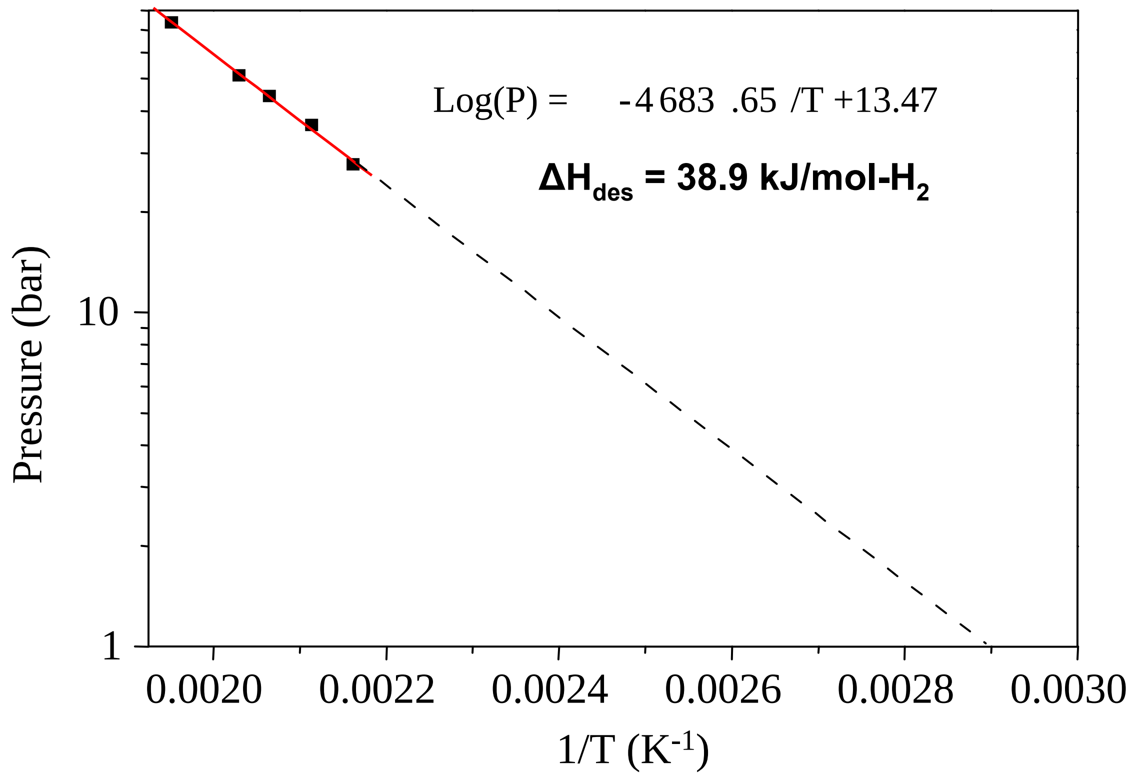
P-C-T at 180ºC



- Relatively high desorption plateau pressure, i. e., at 180ºC, the plateau pressure is above 20 bars.
- Certain hysteresis exists.
- Multi-step reaction with different thermodynamics.
- Slow when approaching equilibrium.

– Adv Mater 16 (2004) 1522.

Thermodynamics

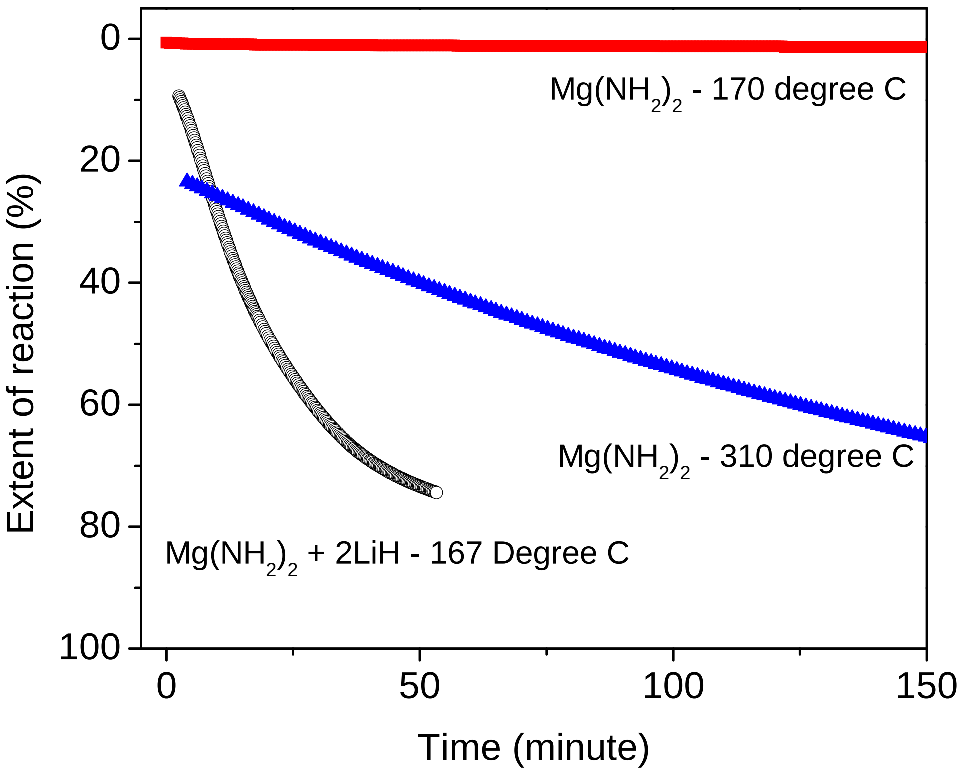


Hydrogen desorption equilibrium pressure at 80ºC is ~ 1.0 bar, close to the PEM fuel Cell operation temperature. However, there is a sever kinetic problem.

-- J Alloy Comp 398 (2005) 235.

Kinetics

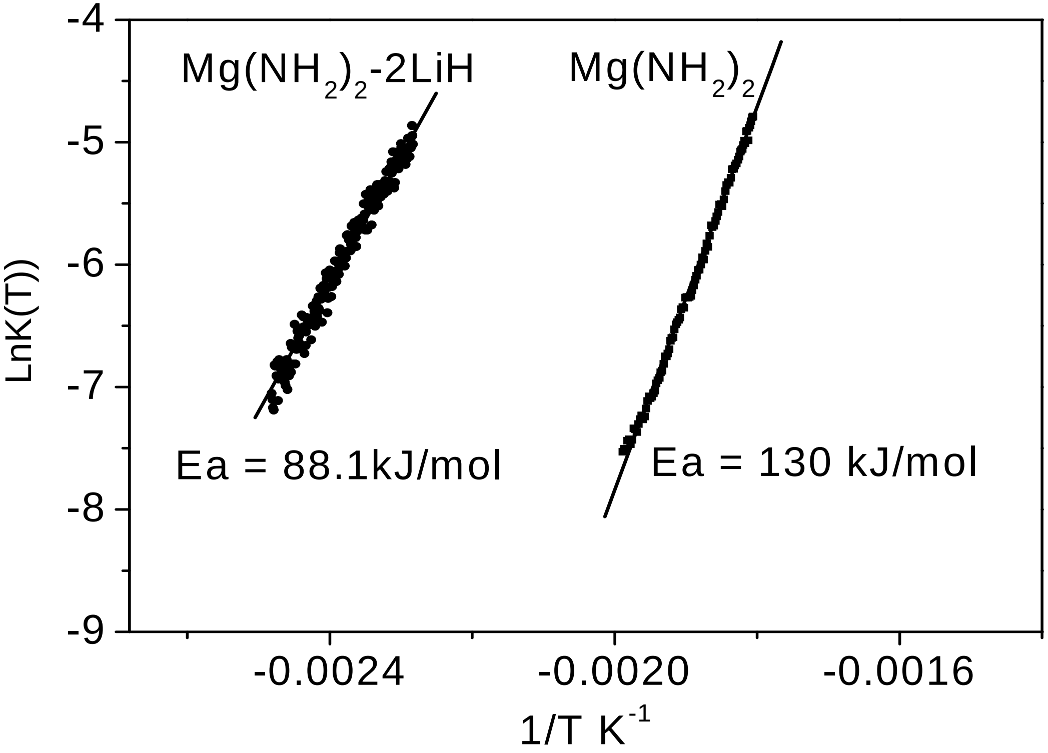
$Mg(NH_2)_2 + 2LiH \rightarrow Li_2Mg(NH)_2 + 2H_2$ & $Mg(NH_2)_2 \rightarrow MgNH + NH_3$



- Hydrogen desorption from the amide and hydride mixture is much faster than ammonia generation from the thermal decomposition of amide alone.
- Linear growth was observed in both reactions at the initial stage

- J Phys Chem B 110 (2006) 14221.

Rate Constant & Activation Energy



$k_{H2} = 2.01X10^6 e^{-88100/RT}$

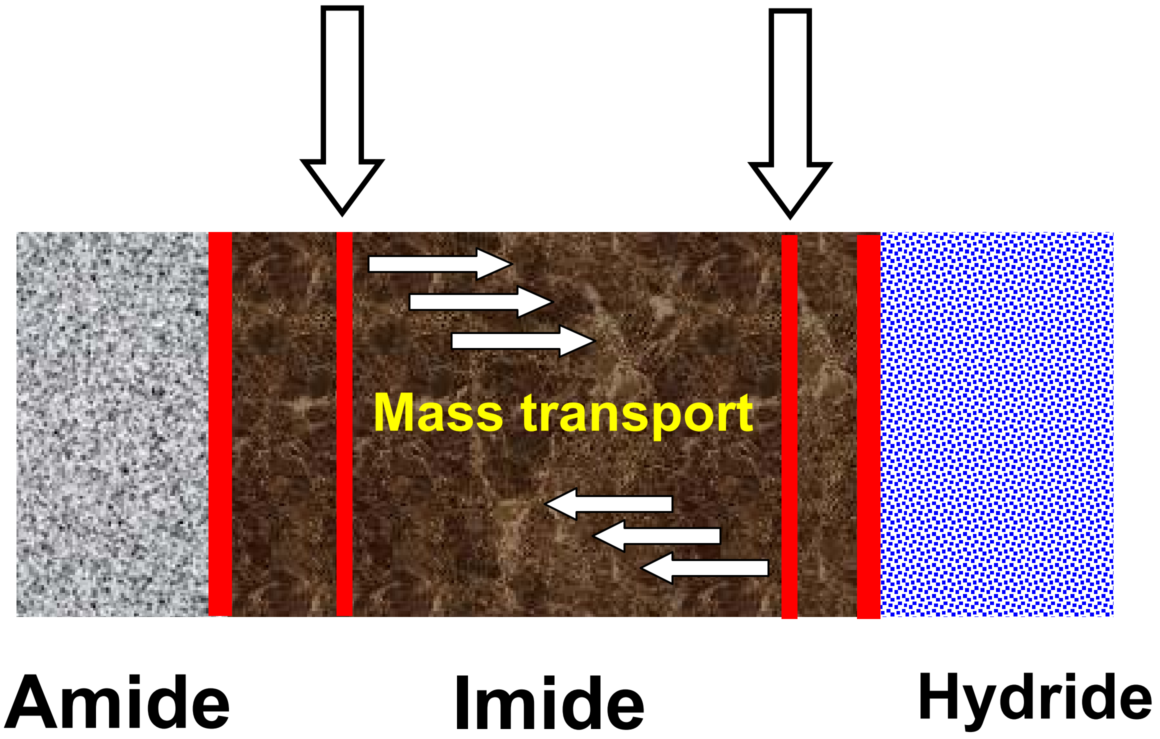
$k_{NH3} = 1.34X10^8 e^{-130000/RT}$

$E_{a\text{-}H2}$ = 88 kJ/mol

$E_{a\text{-}NH3}$ = 130 kJ/mol

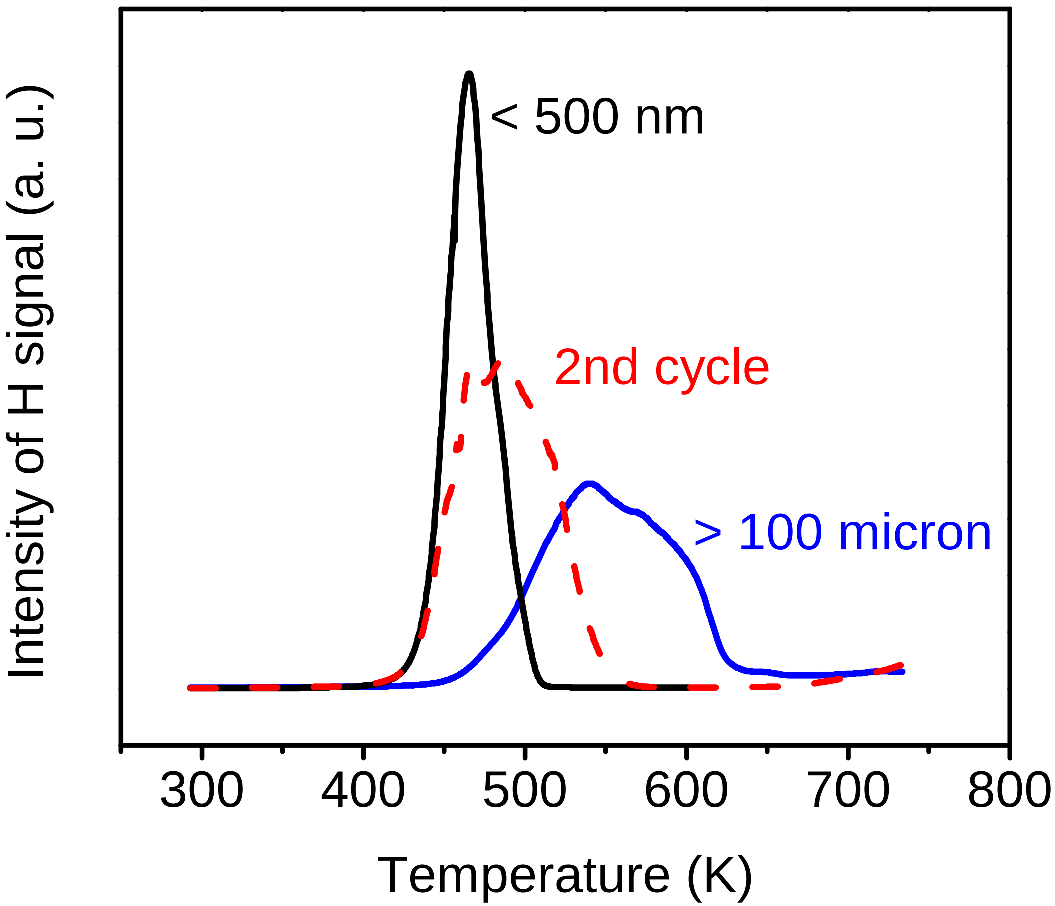
The rate of decomposition of $Mg(NH_2)_2$ is too slow to match that of the H_2 desorption.

Reaction at phase boundaries



Reduce the size of reactants shall increase the contact surface and shorten the ion diffusion path.

Size Effect

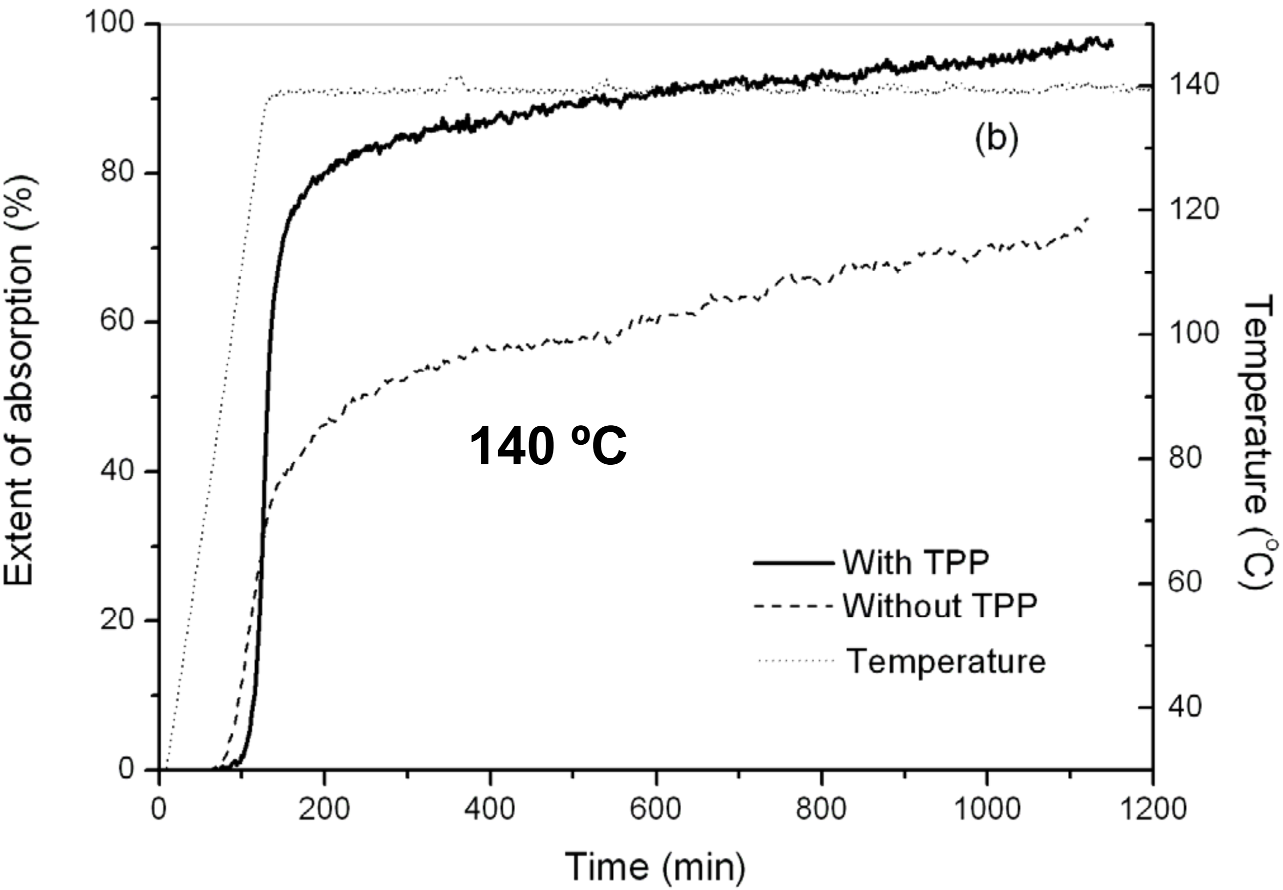


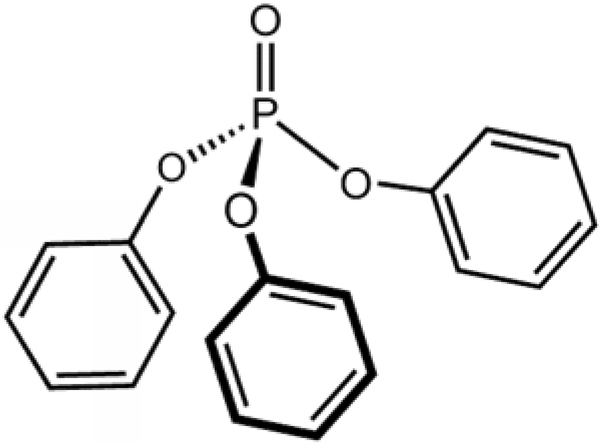
Through energetic ball milling the particle size of material can be reduced to less than 500 nm.

However, particles will aggregate upon repeated hydrogenation & dehydrogenation

- J Phys Chem B 110 (2006) 14221.

TPP Stabilization

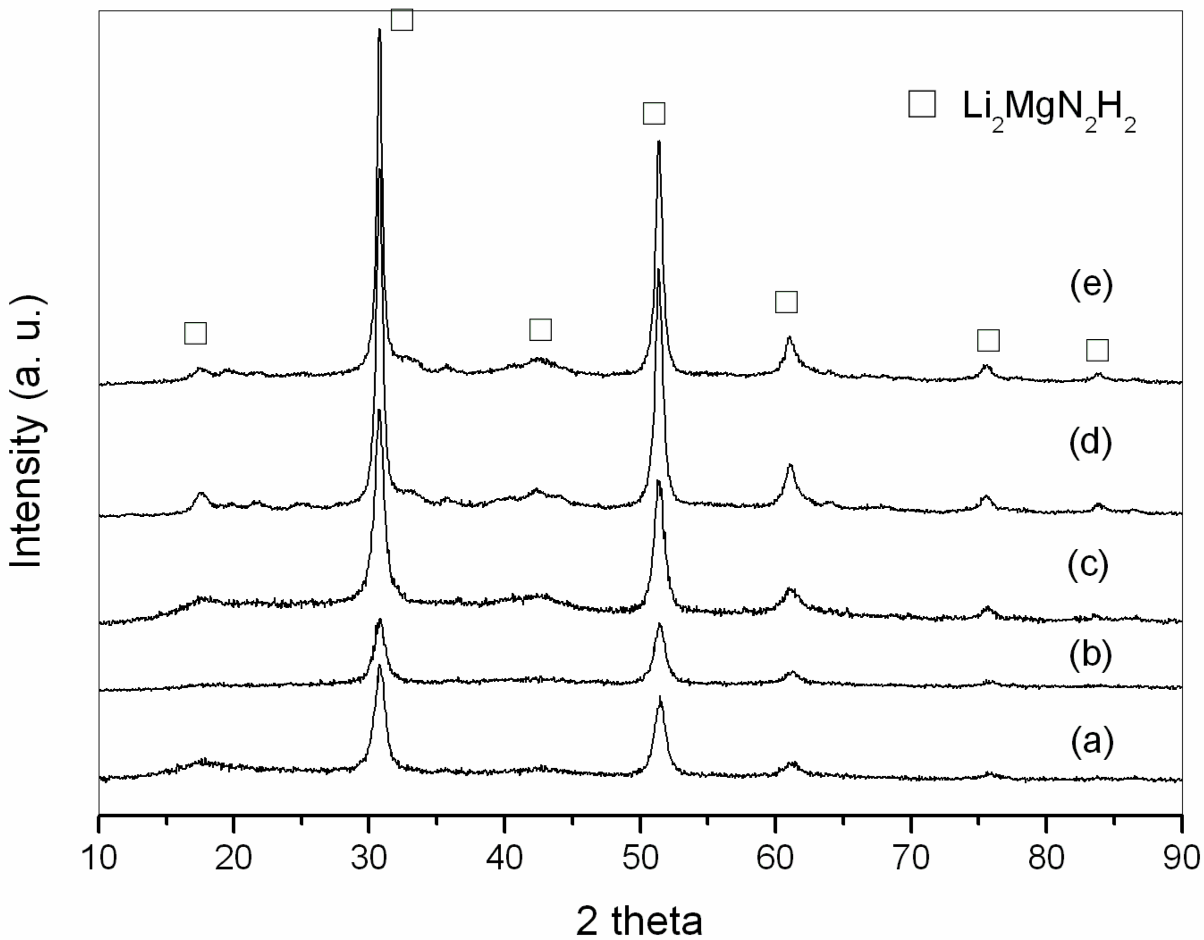




Triphenyl phosphate

- J Mater Chem 19 (2009) 2141

Size of crystalline



2nd dehydrogenation

Pristine

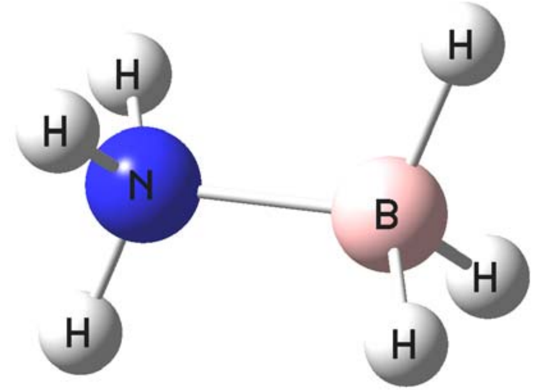
4th dehydrogenation - TPP

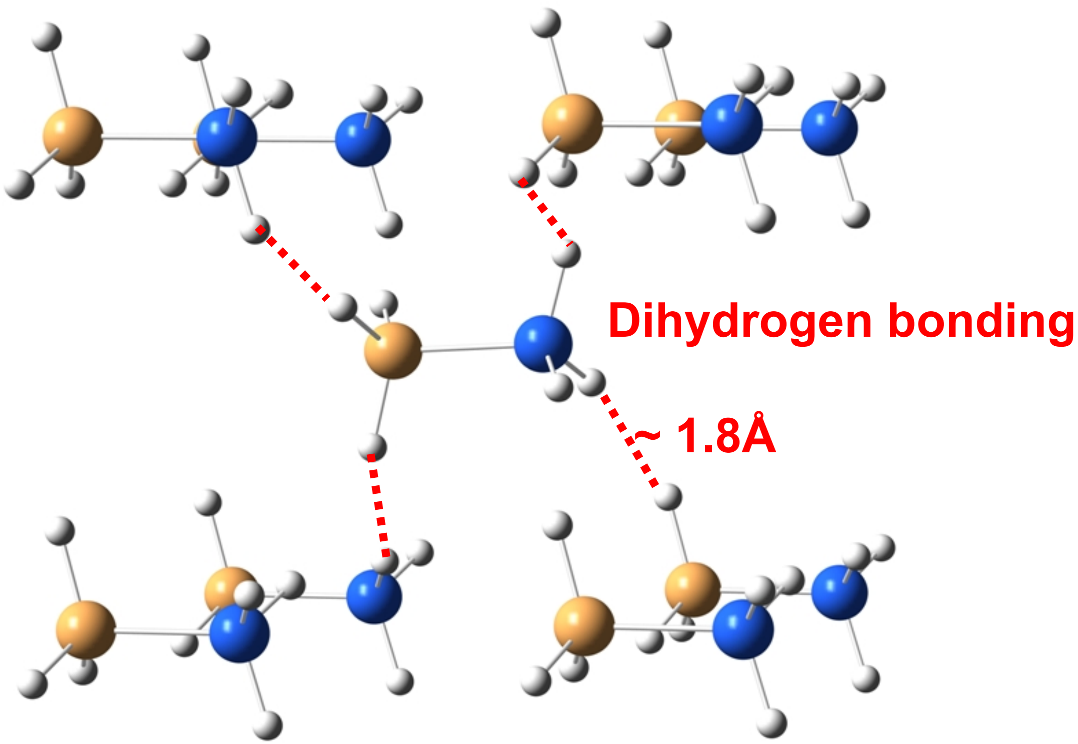
2nd hydrogenation -TPP

1st dehydrogenation -TPP

- J Mater Chem 19 (2009) 2141

3.2 Nanosized Catalysts

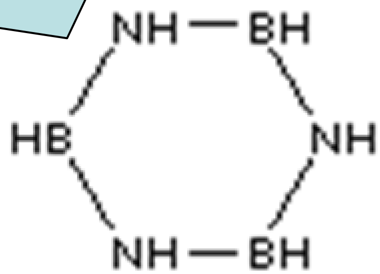




Thermal Dehydrogenation of Ammonia Borane (AB)

110°C $n\ BH_3NH_3 \rightarrow (BH_2NH_2)_n + n\ H_2$

150°C $n\ BH_2NH_2 \rightarrow (BHNH)_n + B_3H_3N_3H_3 + n\ H_2$

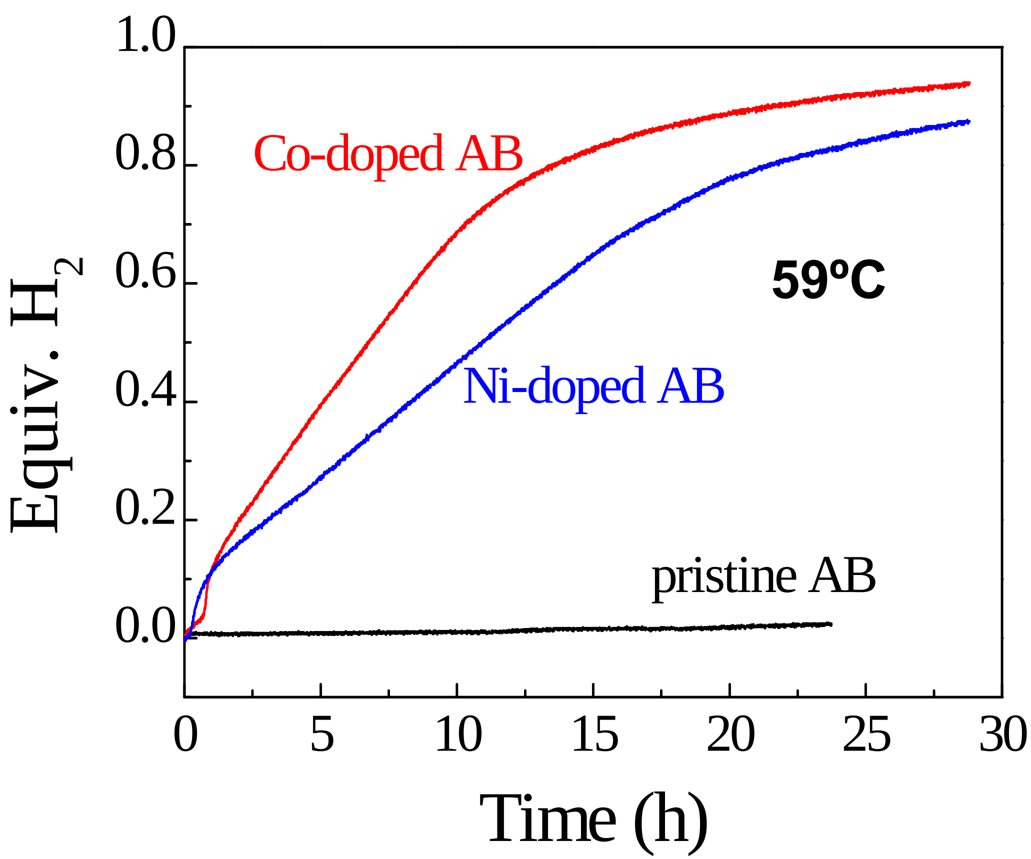


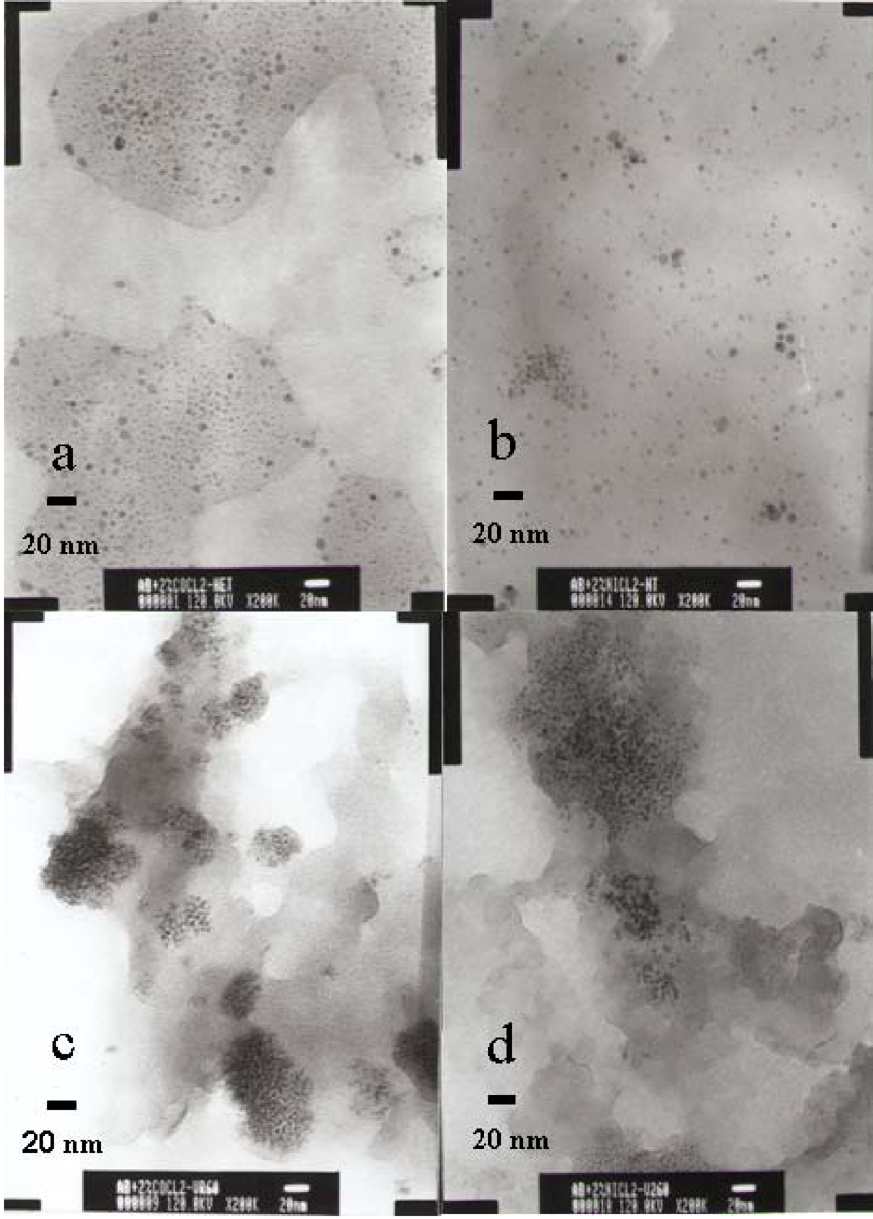
500°C $BHNH \rightarrow BN + H_2$

$BH_3NH_3 \rightarrow BN + 3H_2$ **19.5 wt.%**

- Wolf G et al *Thermochimica* **2000**, 343, 19.
- Gutawska A & Autrey T et al *Angew Chem* **2005**, 44, 3578
- Stephens FH & Baker RT et al *Dalton Trans* **2007**, 25, 2613

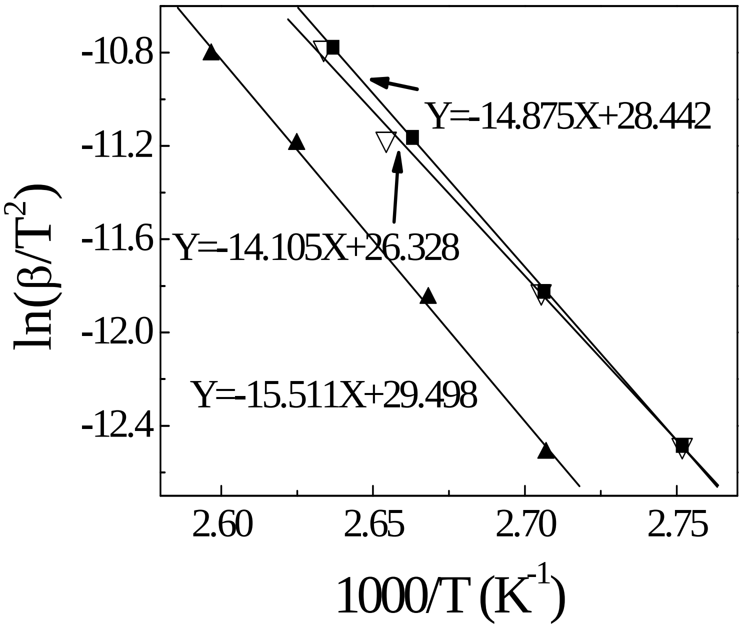
Doping 2 mol% Co or Ni catalyst leads to considerably decreased temperature and shorted induction period





Kinetic Parameters

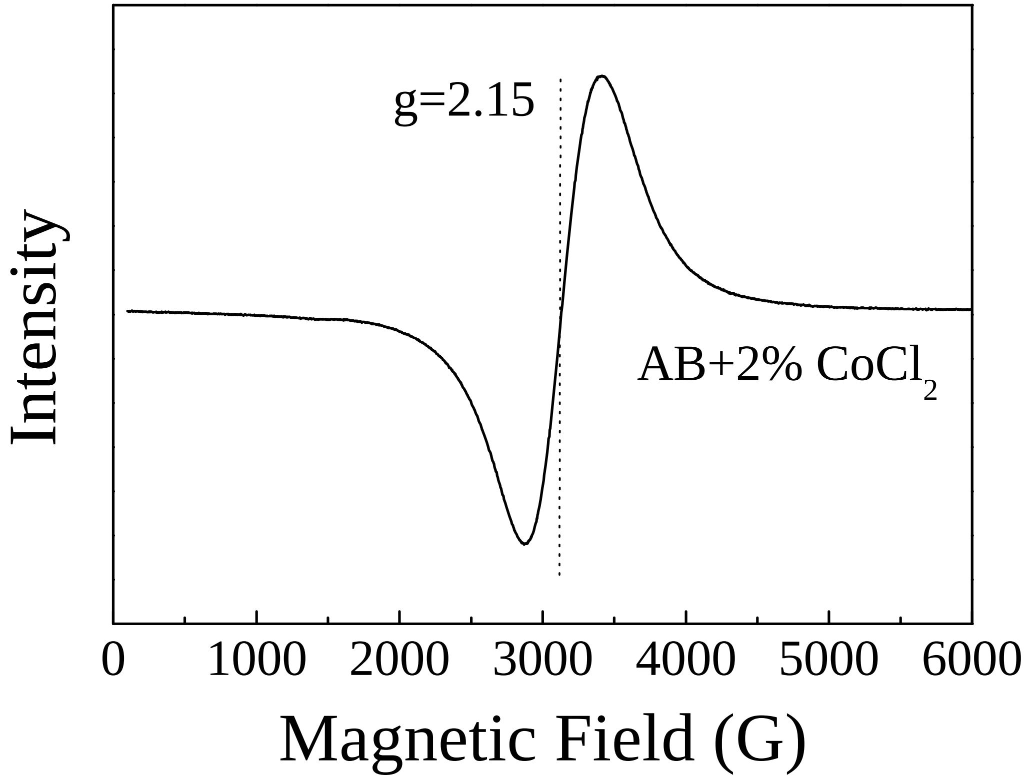
	E_a kJ mol^{-1}	A min^{-1}	k(80 ºC) min^{-1}
Pristine AB	129.0	$1.00*10^{17}$	$8.14*10^{-3}$
AB+2%Co	117.3	$3.83*10^{15}$	$1.68*10^{-2}$
AB+2%Ni	123.5	$3.35*10^{16}$	$1.78*10^{-2}$



By introducing Co or Ni, the rate constant of dehydrogenation is ca. doubled than AB without catalyst.

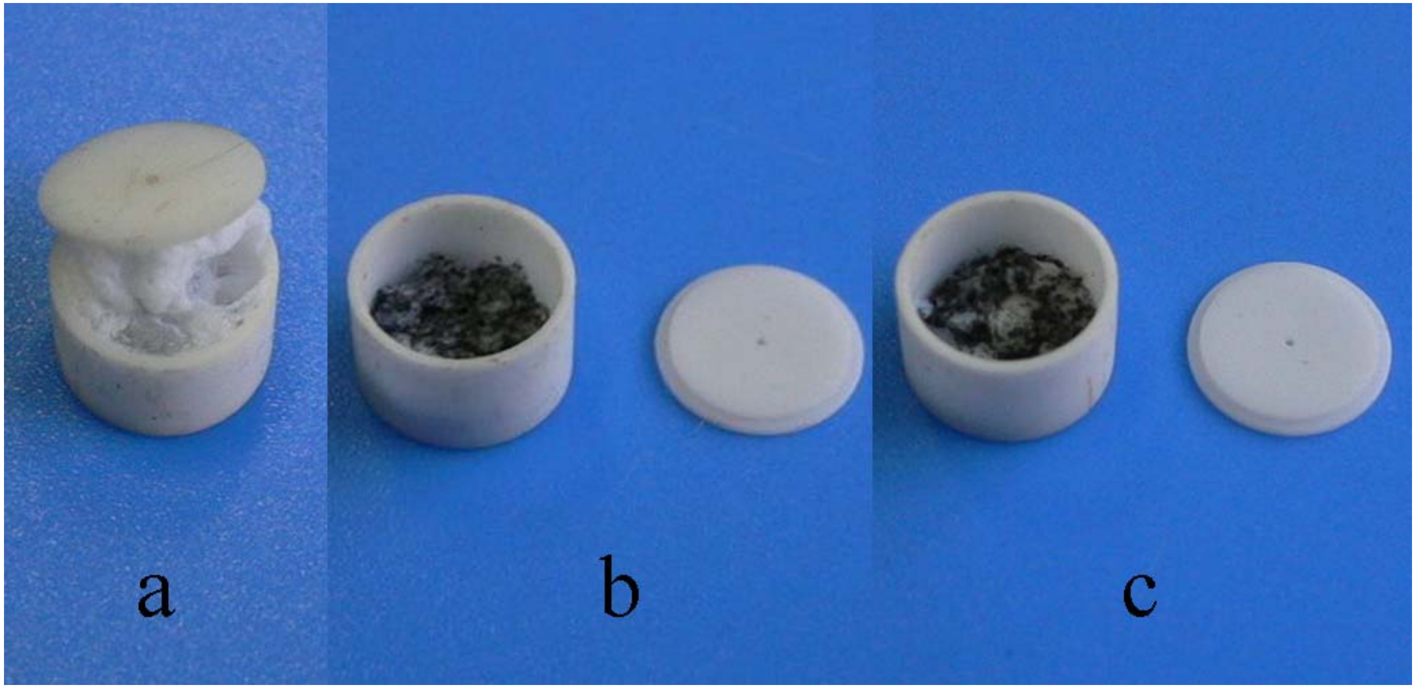
- Chem Mater 21 (2009) 2315

Chemical State of Catalyst



ESR measurement of the Co-AB sample after dehydrogenation shows that Co is in a partially reduced state rather than metallic state. There may be an alloy of Co and B (CoB_2) which is functional to the dehydrogenation.

Sample Foaming



Pristine AB AB + 2 mol% Co AB + 2 mol% Ni

Acknowledgements

Group members	**IPHE Collaborators**
In DICP	Pacific Northwest National Laboratory
Prof. Zhitao XIONG	Abhi Karkamkar
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Dr. Chengzhang WU	
Dr. Hailiang CHU	Rutherford Appleton Laboratory
Mr. Teng HE	William I F David
Ms. Na XU	
Miss Xueli ZHENG	University of Oxford
Mr. Jianhui WANG	Martin Owen Jones,
	Simon R Johnson
	Peter P Edwards
In NUS	
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Miss Wen LI	Rajeev Ahuja
Mr. Weiliang XU	Moysès Araùjo

NGC2009 & CSTC2009