

# Amide-hydride Combinations for Hydrogen Storage

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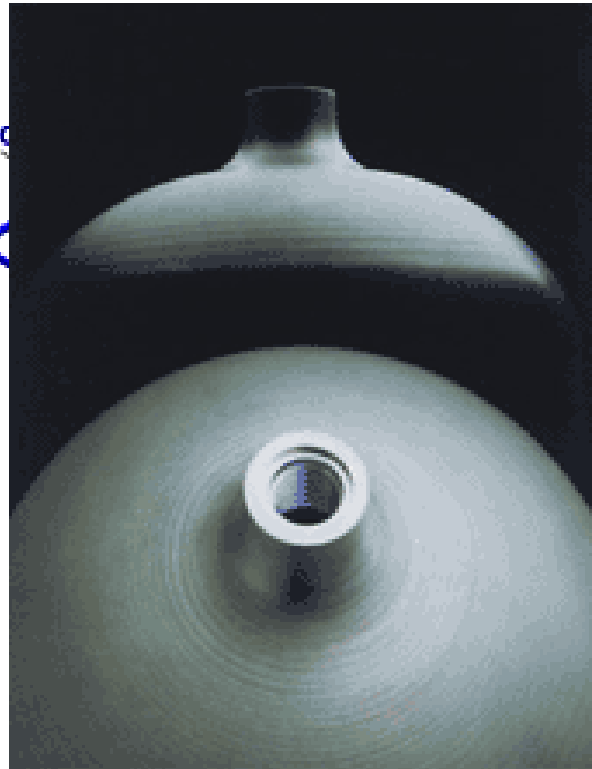
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# Outline

- I. Introduction to Hydrogen Storage**
- II. Hydrogen from Amide-hydride  
Combinations**
- III. Nano-Materials and Catalysts**

# Liquid Hydrogen



Outer Vessel  
Shield  
Inner Vessel  
Heat Exchanger

ambient Air

## Compressed H<sub>2</sub>



Metal hydrides

Conv. metal hydrides  
Alanates -  $\text{NaAlH}_4$   
Borohydrides  
Amide-hydride

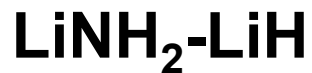
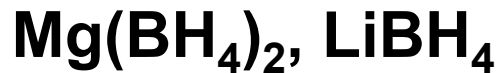
Chemical hydrides

$\text{NaBH}_4\text{-H}_2\text{O}$   
 $\text{NH}_3\text{BH}_3$   
 $\text{MNH}_2\text{BH}_3$

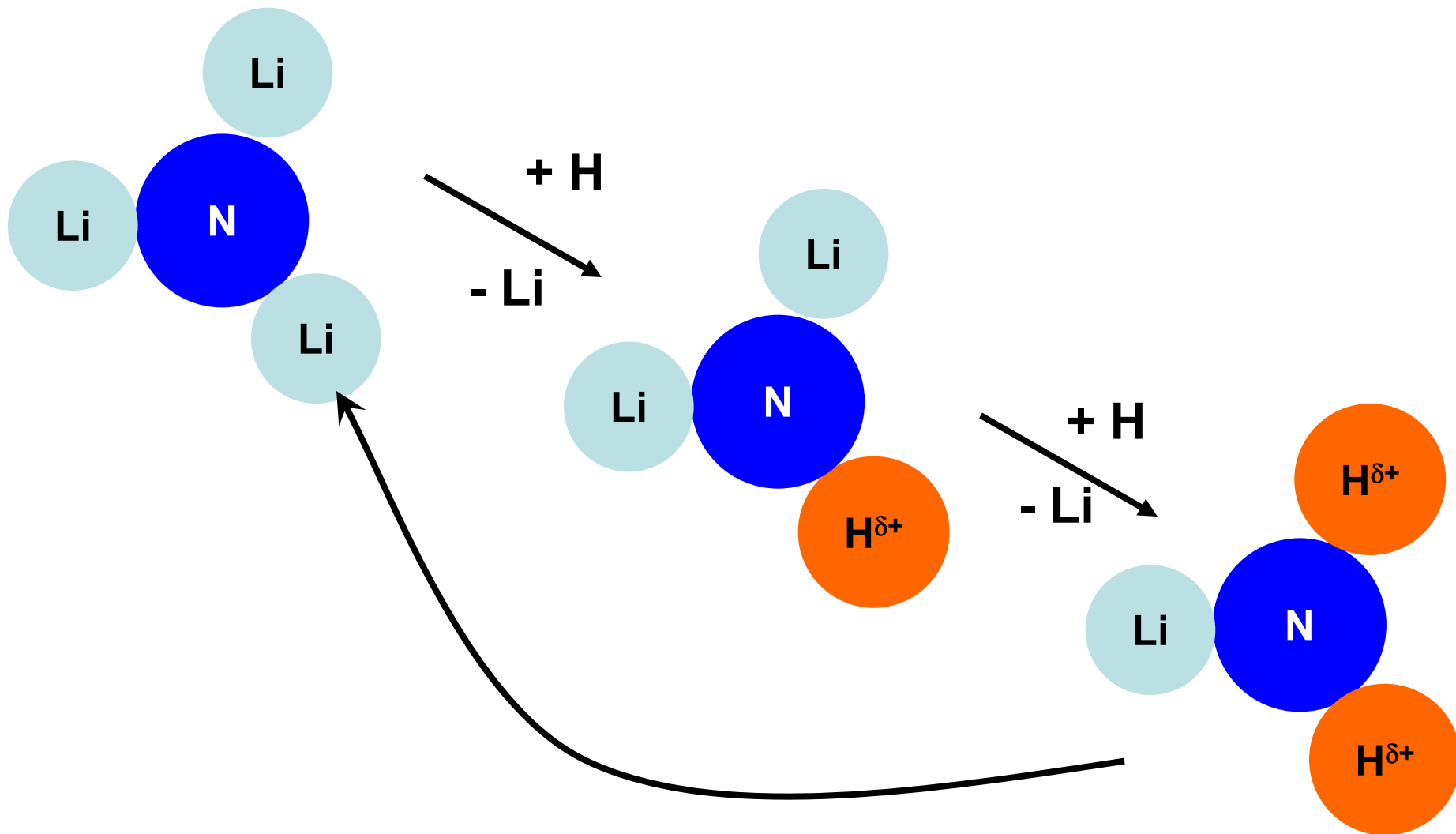
**Solid-state  
Hydrogen Storage**

Sorbents

Carbon Nanotubes  
PANI  
MOFs



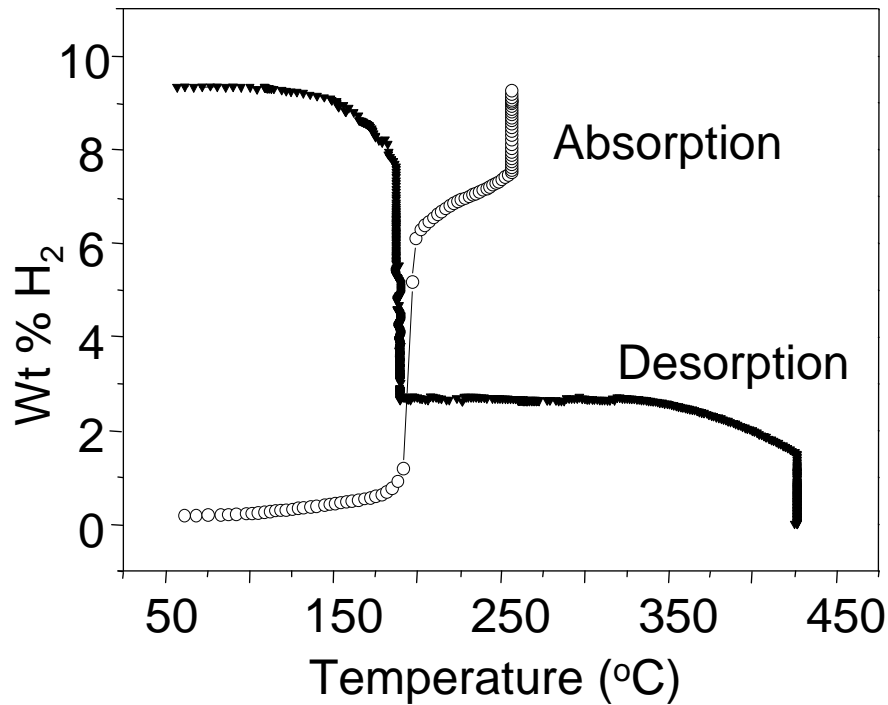
# **II. Hydrogen from Amide-Hydride Combinations**



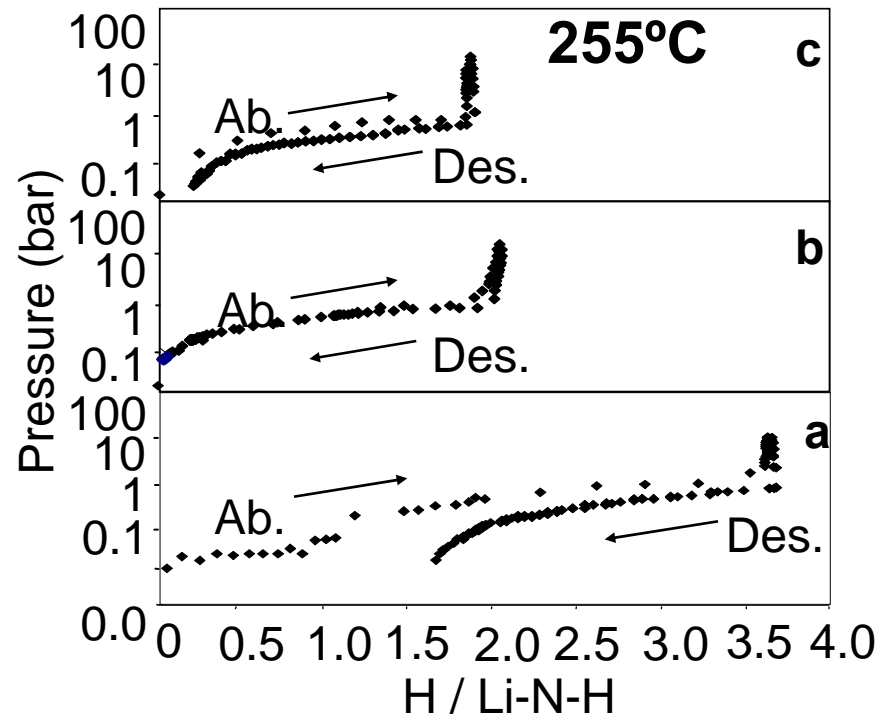


10.5wt%

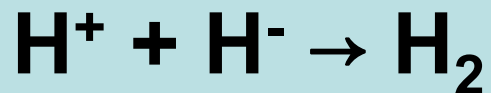
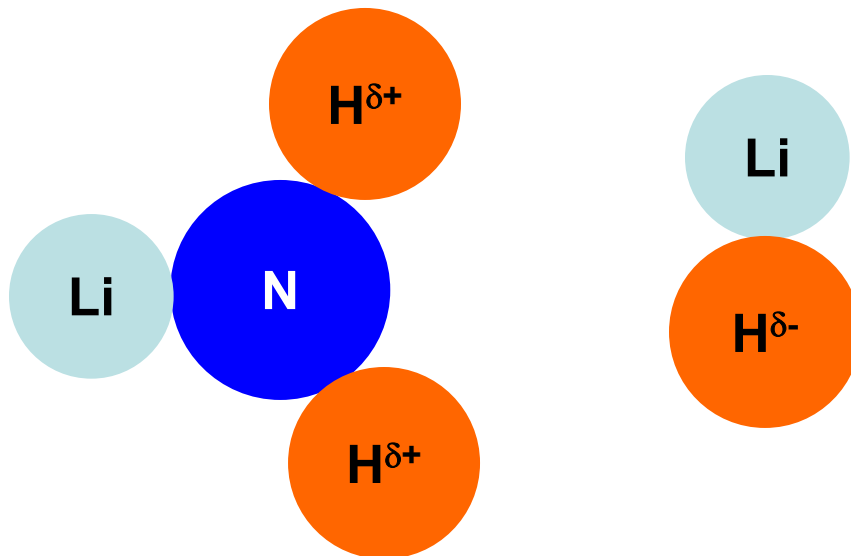
TG



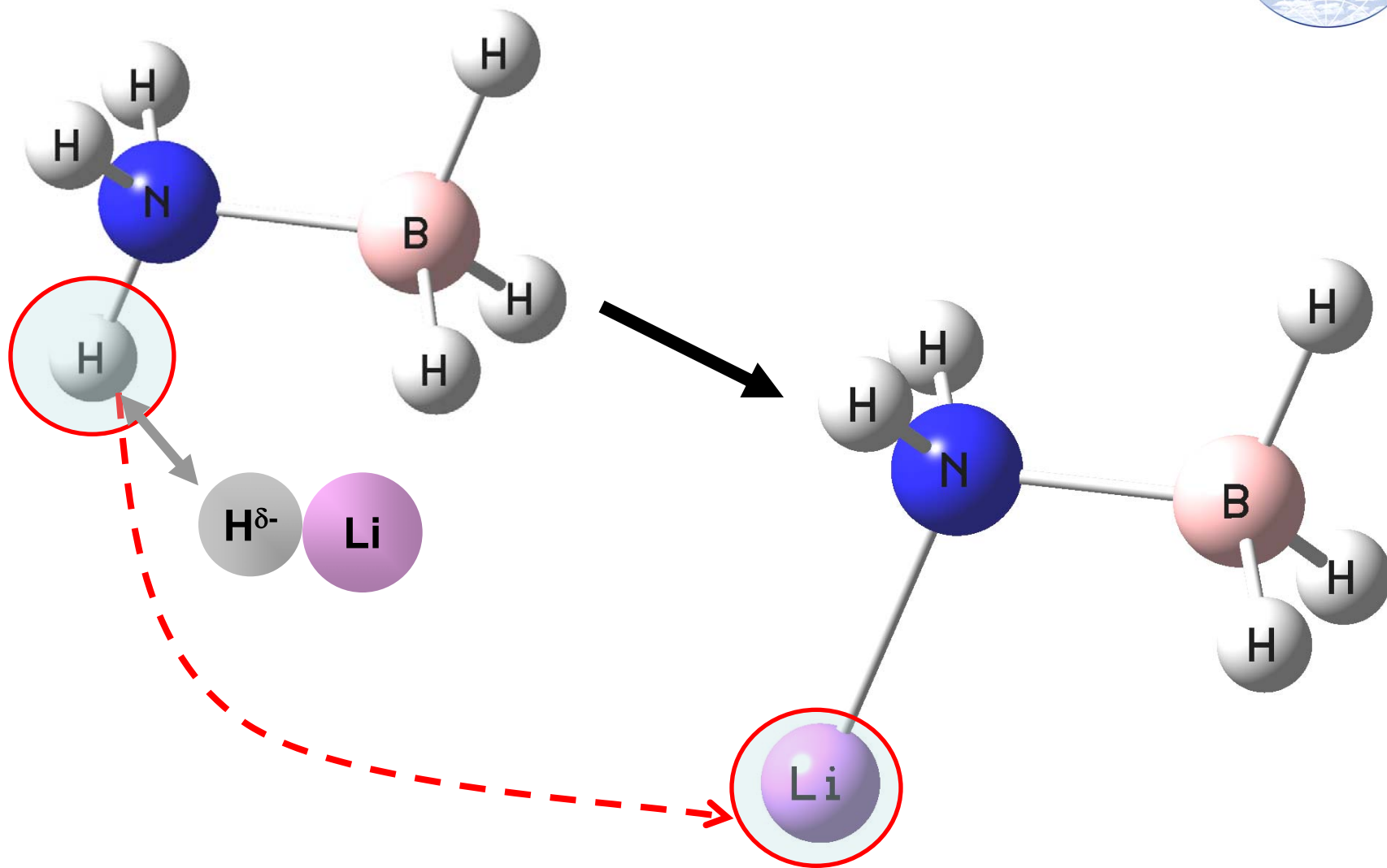
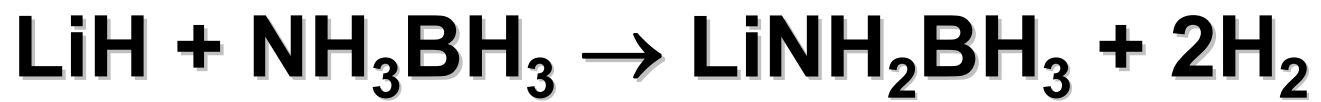
PCT



-- *Nature* 420 (2002) 302

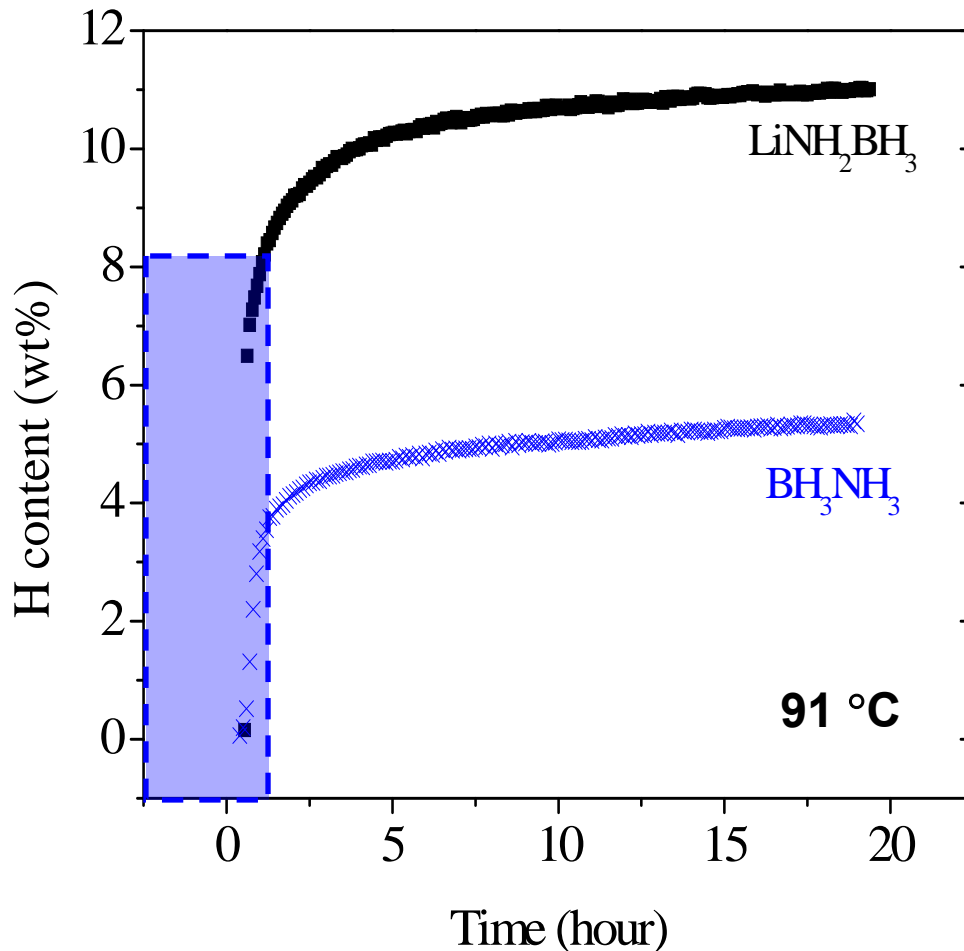


$$\Delta H = - 17.37 \text{ eV}$$





10.9 wt%



- ~ 90 °C
- 2 equiv.  $\text{H}_2$  desorption
- > 10 wt% in 17 hrs.
- ~ 8 wt% in 1st hour
- The rest of  $\text{H}_2$  takes long time to desorb

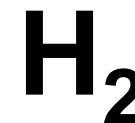
-- *Nature Mater* 7 (2008) 138

# Amide-hydride Combinations

## Amides



## Hydrides



# **III. Nanosized Materials and Catalysts**

## 3.1 Nano-Materials

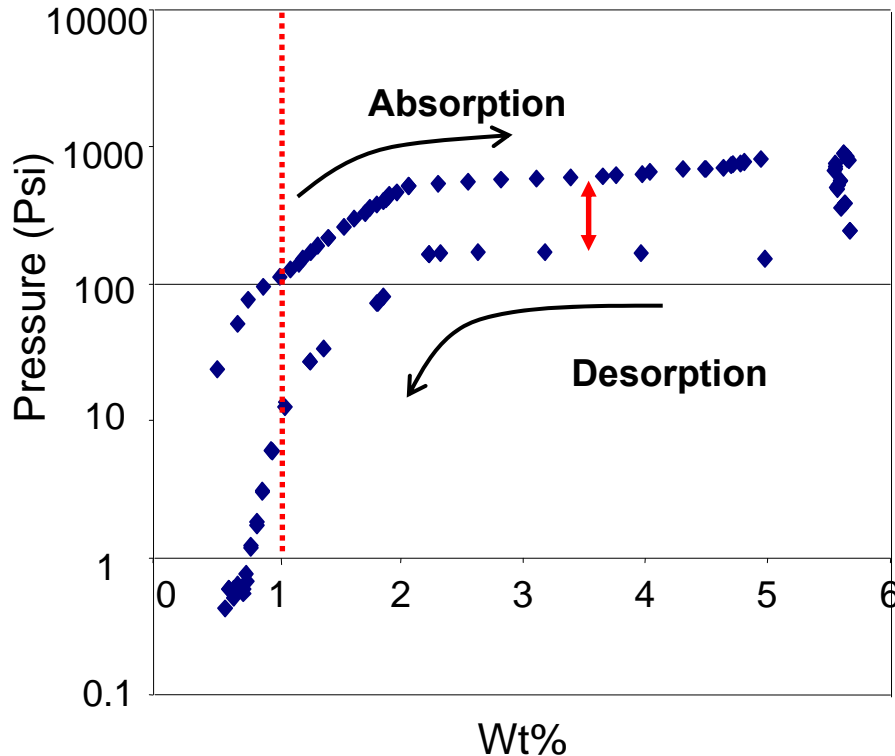


*Ref:*

- *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

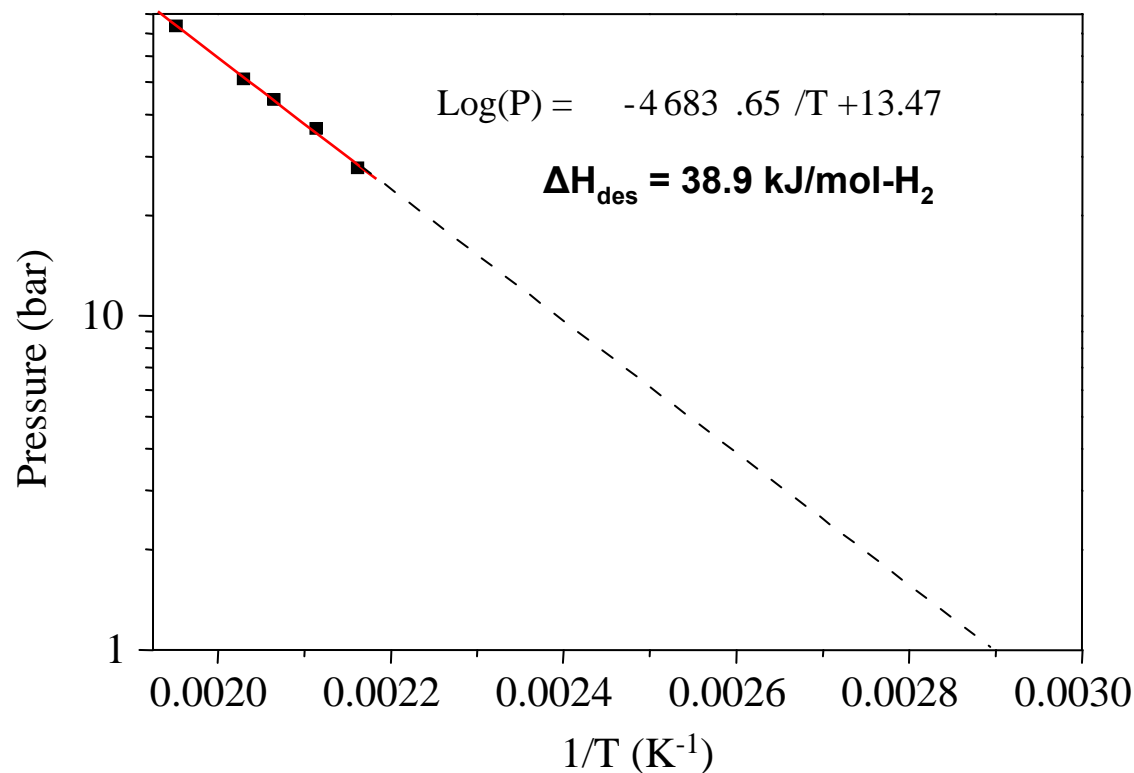
## P-C-T at 180°C



- Relatively high desorption plateau pressure, i. e., at 180°C, 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.

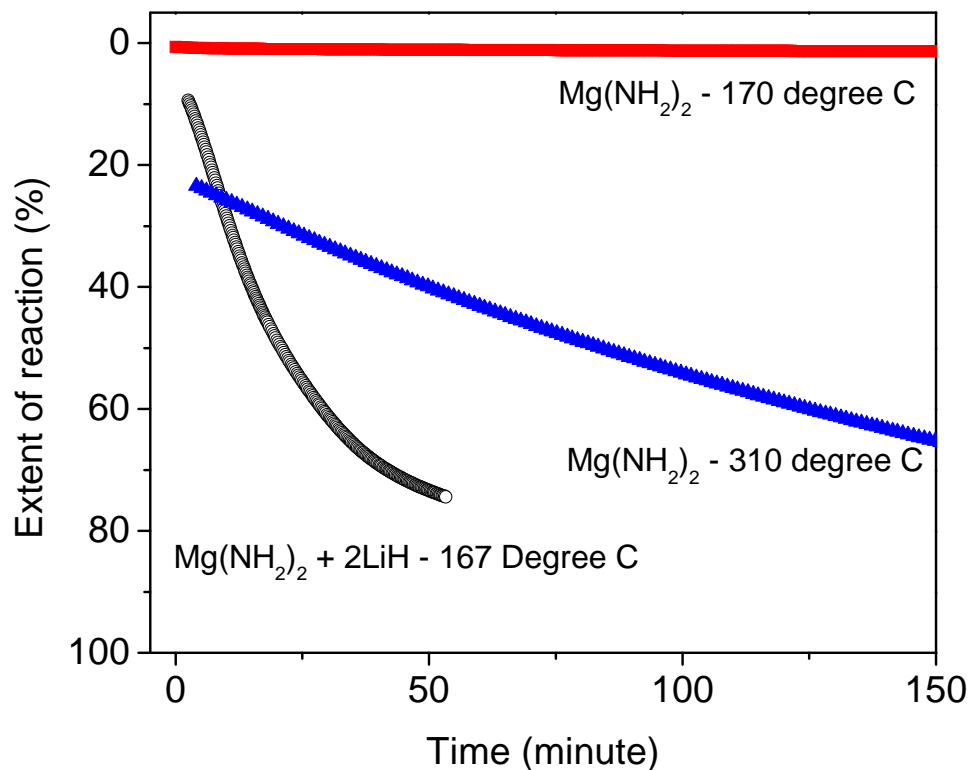
# Thermodynamics



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

-- *J Alloy Comp* 398 (2005) 235.

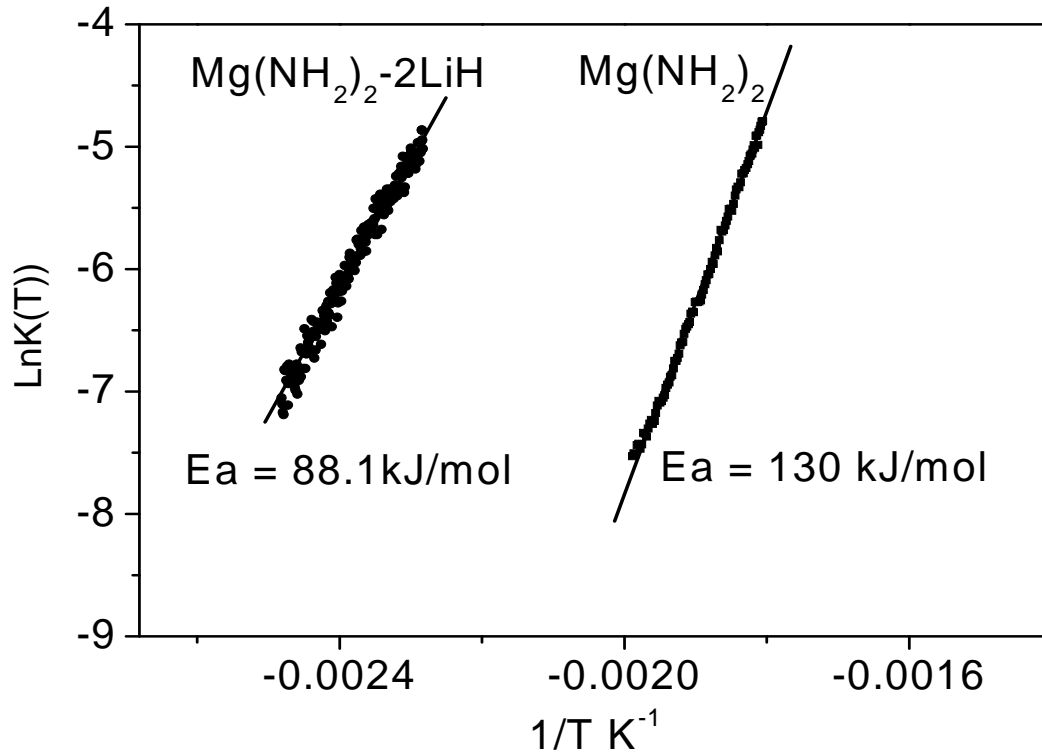
# Kinetics



- 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



$$k_{\text{H}_2} = 2.01 \times 10^6 e^{-88100/RT}$$

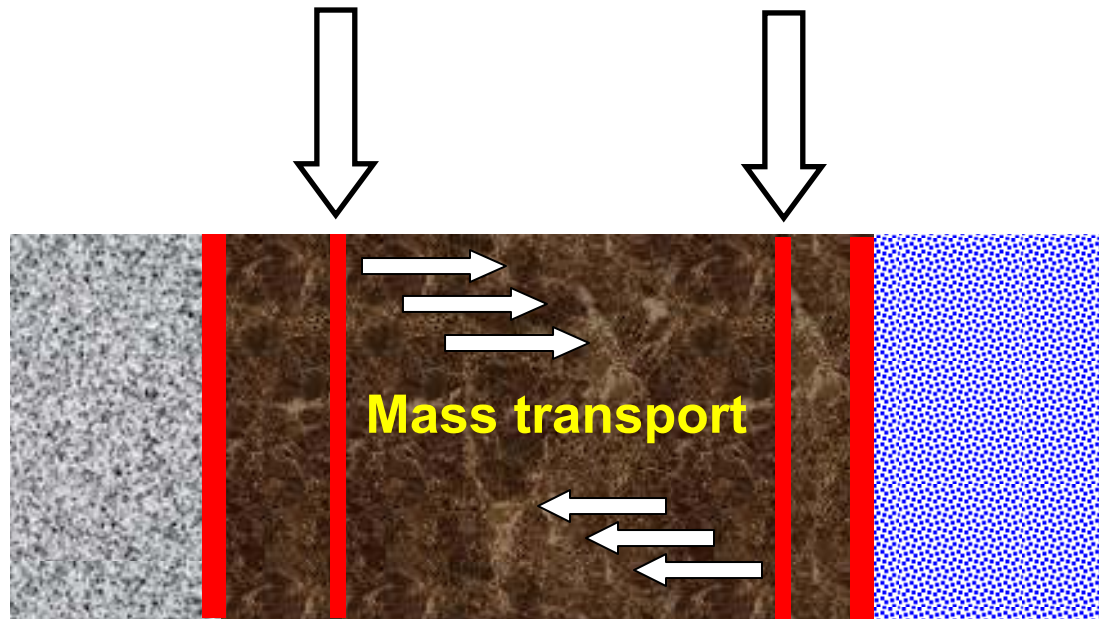
$$k_{\text{NH}_3} = 1.34 \times 10^8 e^{-130000/RT}$$

$$E_{a-\text{H}_2} = 88 \text{ kJ/mol}$$

$$E_{a-\text{NH}_3} = 130 \text{ kJ/mol}$$

The rate of decomposition of  $\text{Mg}(\text{NH}_2)_2$  is too slow to match that of the  $\text{H}_2$  desorption.

# Reaction at phase boundaries



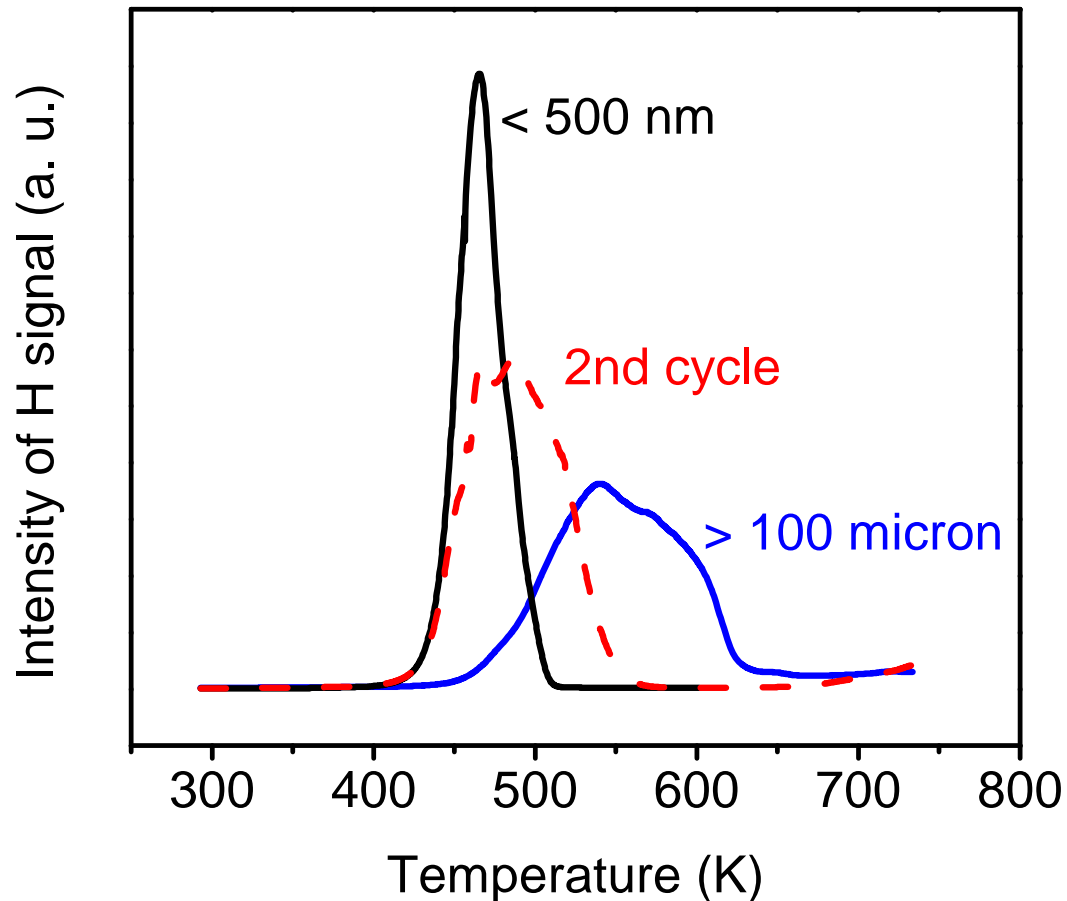
**Amide**

**Imide**

**Hydride**

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

# Size Effect

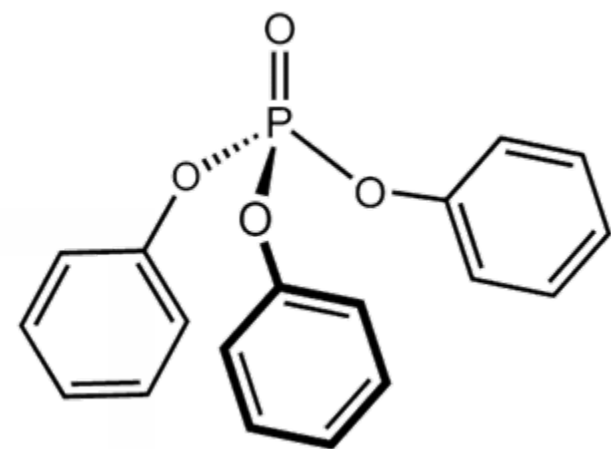


Through energetic ball milling the particle size of material can be reduced to less than 500 nm.

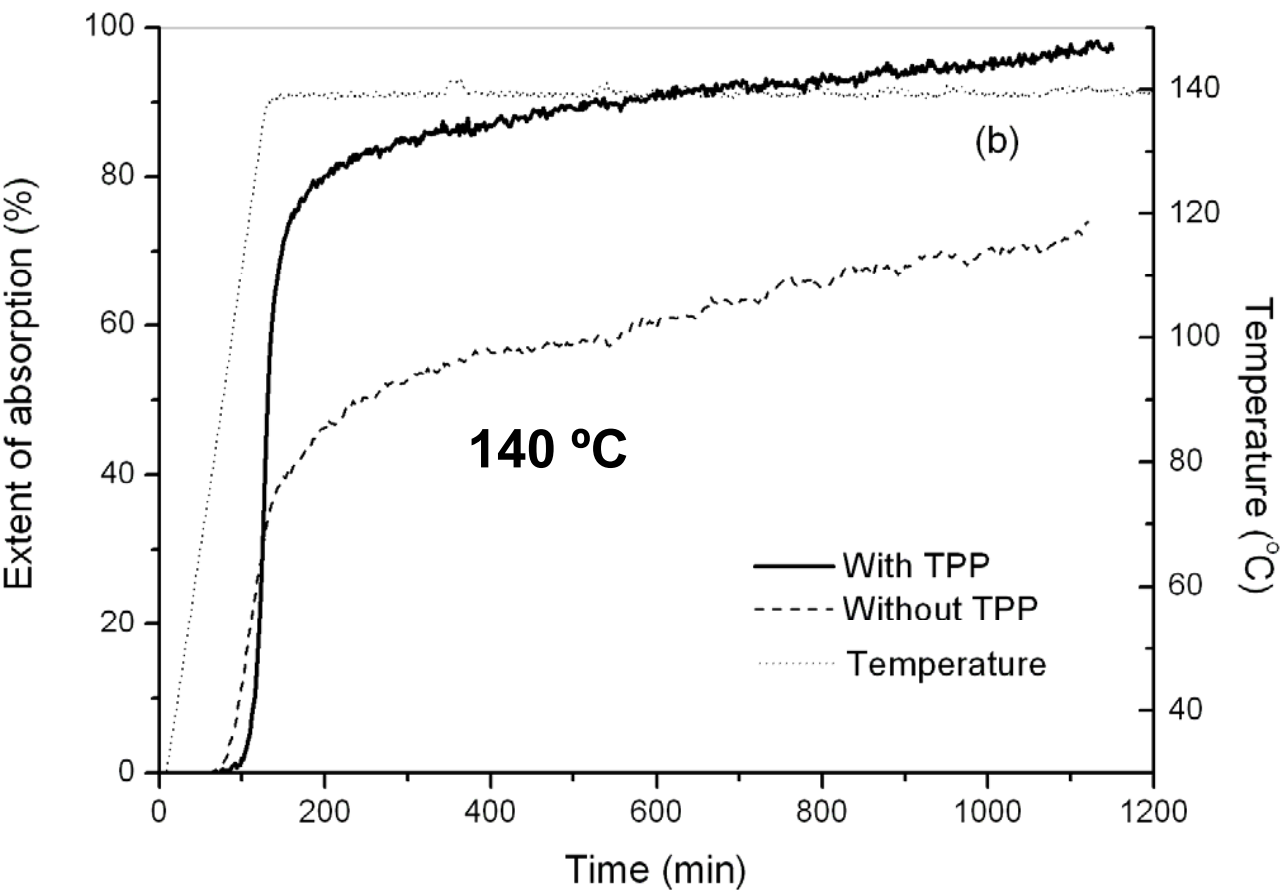
However, particles will aggregate upon repeated hydrogenation & dehydrogenation

- *J Phys Chem B* 110 (2006) 14221.

# TPP Stabilization

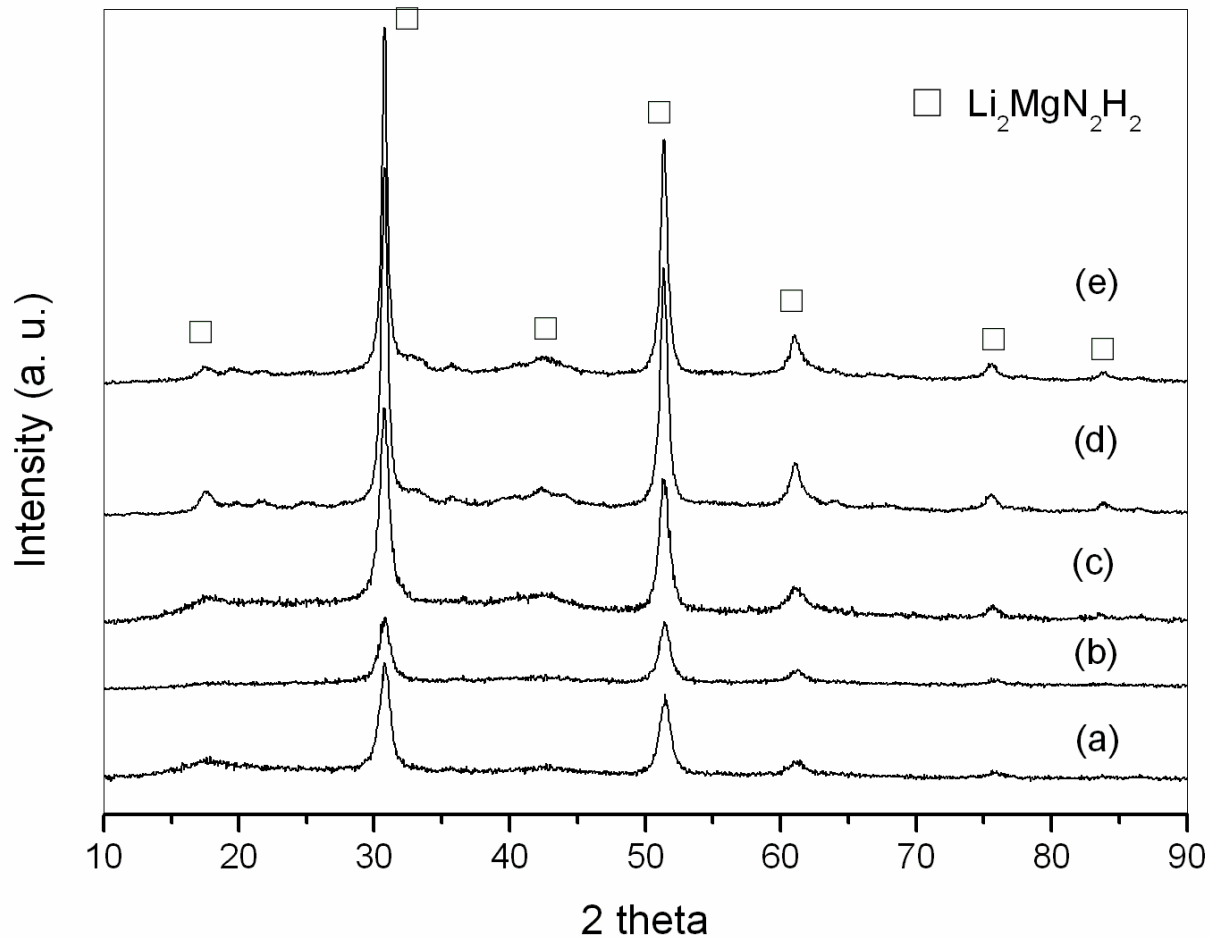


Triphenyl phosphate



- *J Mater Chem* 19 (2009) 2141

# Size of crystalline



2<sup>nd</sup> dehydrogenation

Pristine

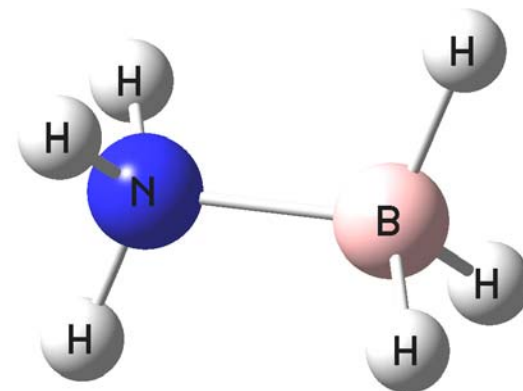
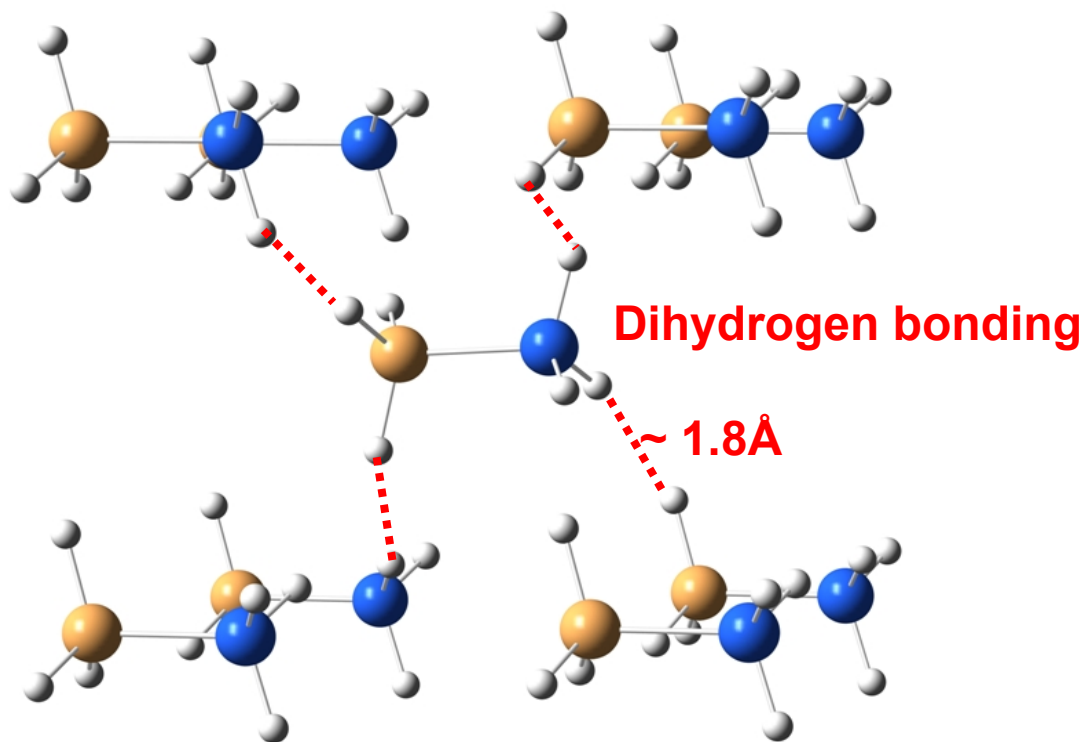
4<sup>th</sup> dehydrogenation - TPP

2<sup>nd</sup> hydrogenation - TPP

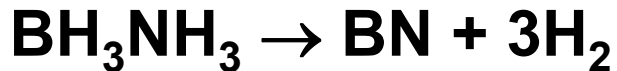
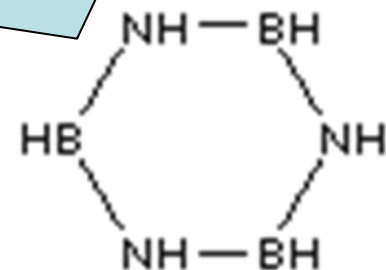
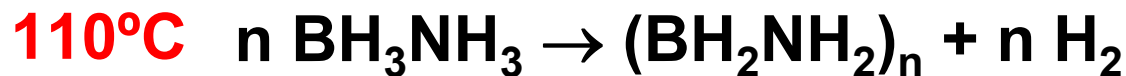
1<sup>st</sup> dehydrogenation - TPP

- *J Mater Chem* 19 (2009) 2141

## 3.2 Nanosized Catalysts



# Thermal Dehydrogenation of Ammonia Borane (AB)

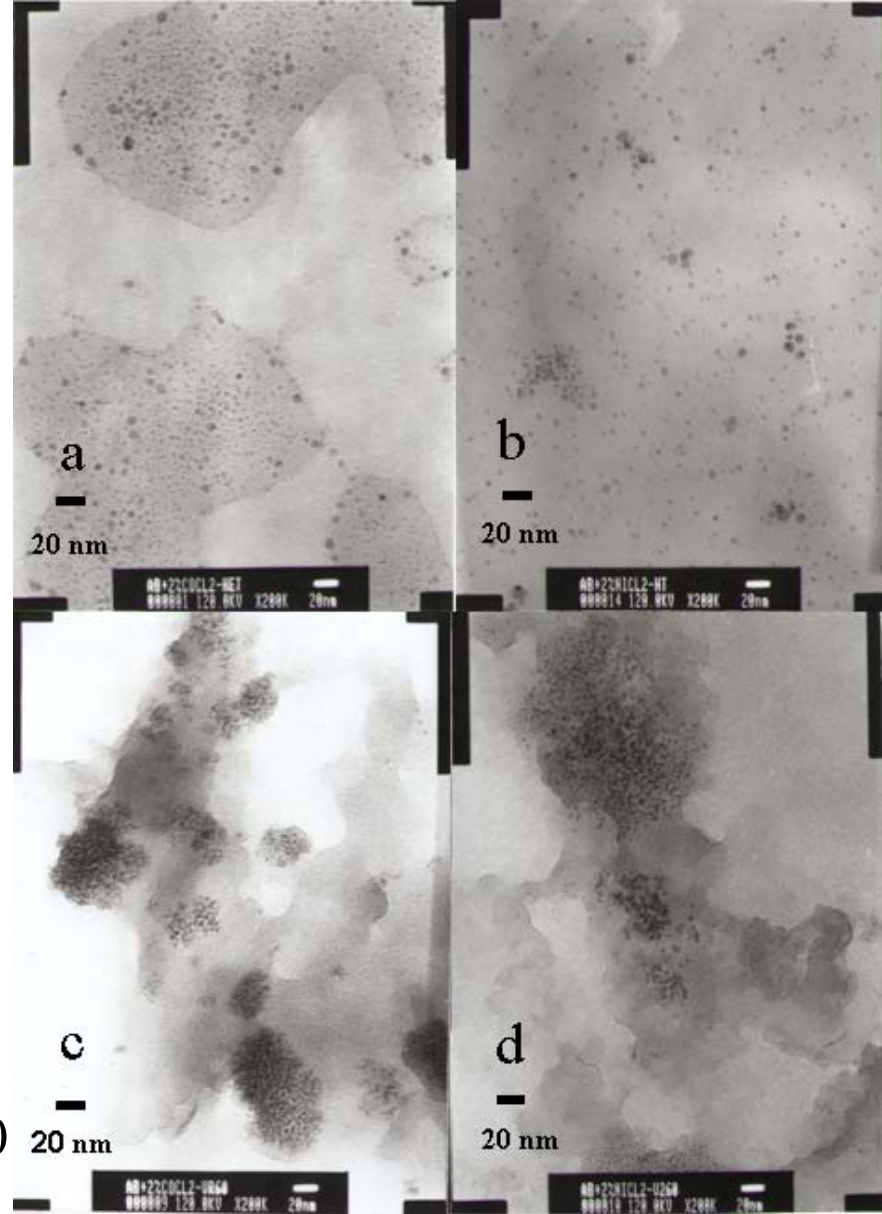
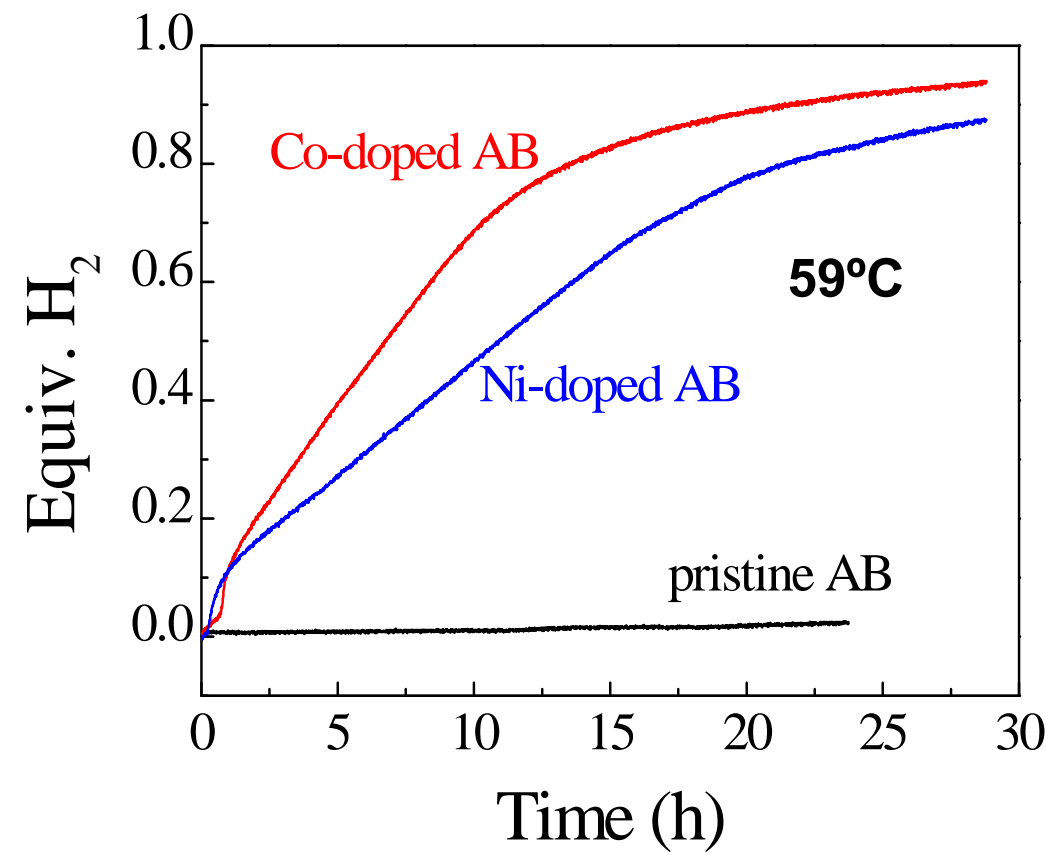


**19.5 wt.%**

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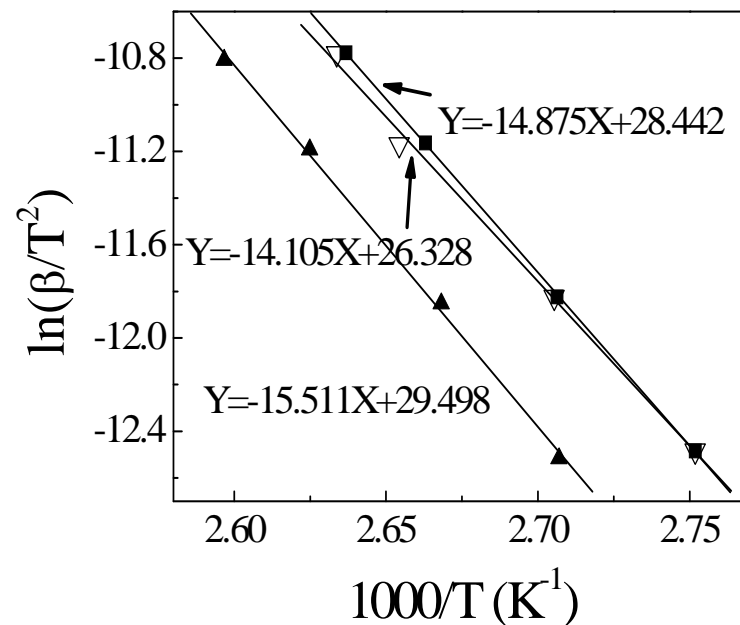
- Wolf G et al *Thermochimica* **2000**, 343, 19.
- Gutawska A & Autrey T et al *Angew Chem* **2005**, 44, 3578
- Stephens FH & Baker RT et al *Dalton Trans* **2007**, 25, 2613

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



# Kinetic Parameters

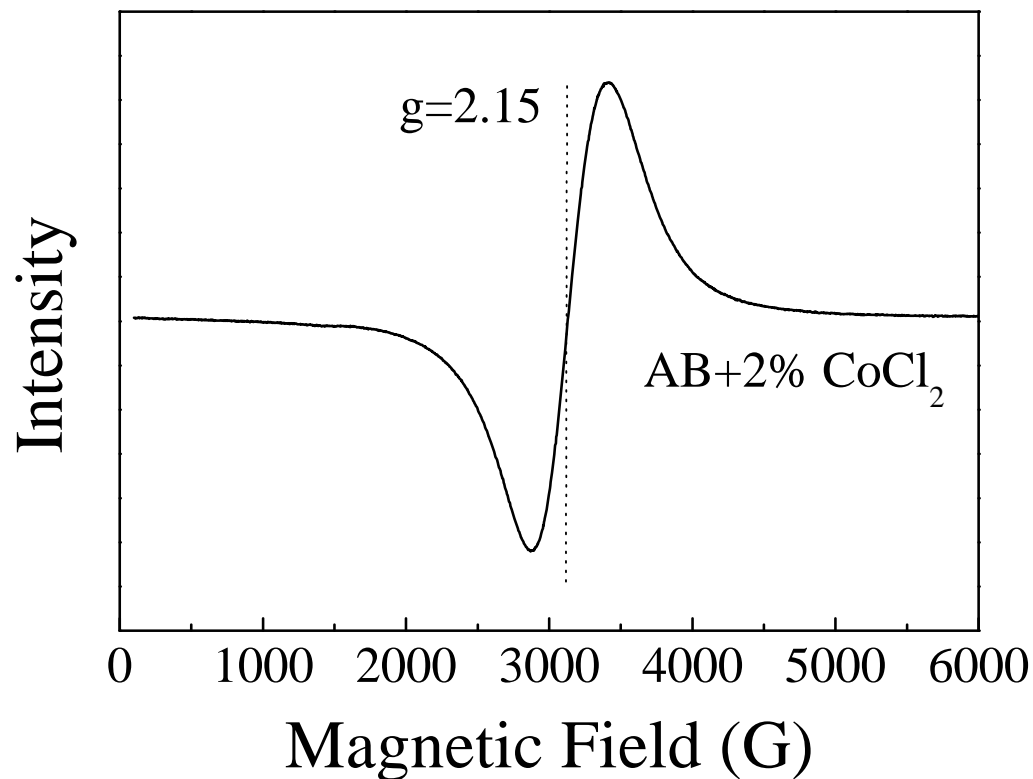
	$E_a$ kJ mol <sup>-1</sup>	$A$ min <sup>-1</sup>	$k(80\text{ °C})$ min <sup>-1</sup>
Pristine AB	129.0	$1.00 \cdot 10^{17}$	$8.14 \cdot 10^{-3}$
AB+2%Co	117.3	$3.83 \cdot 10^{15}$	$1.68 \cdot 10^{-2}$
AB+2%Ni	123.5	$3.35 \cdot 10^{16}$	$1.78 \cdot 10^{-2}$



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

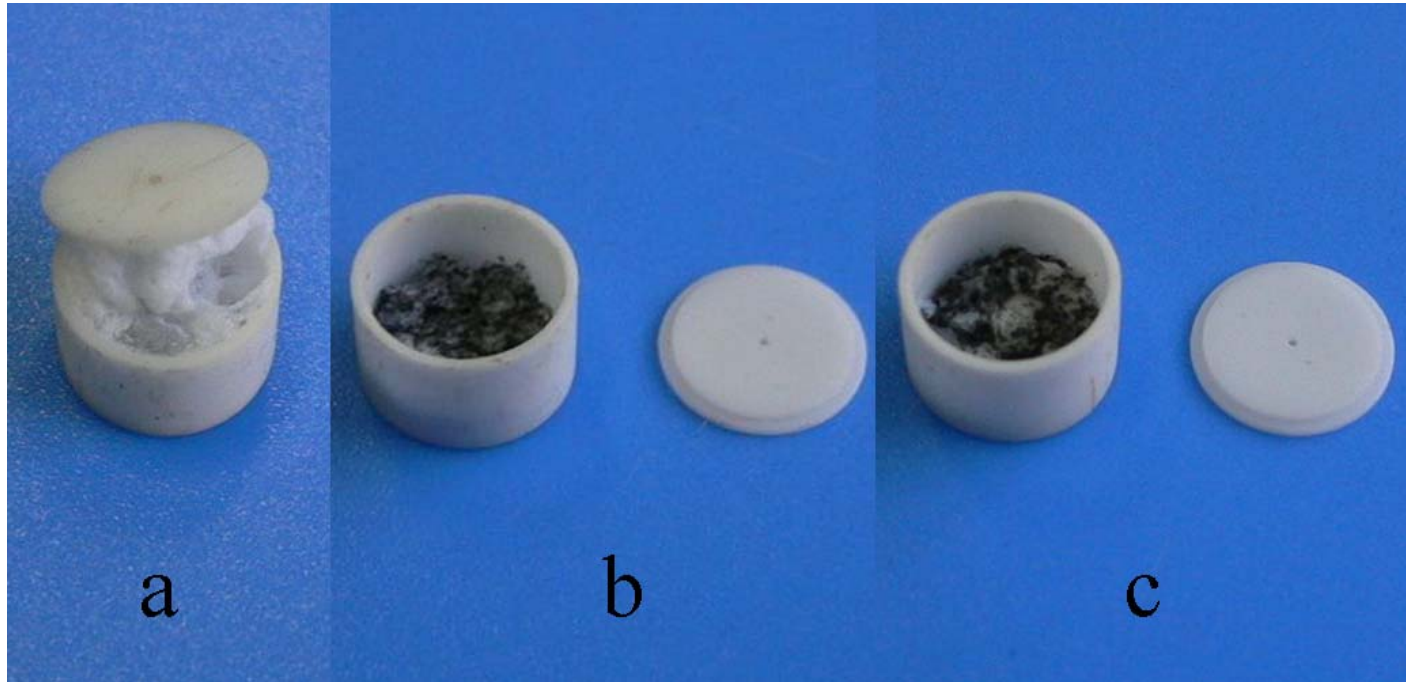
**- Chem Mater 21 (2009) 2315**

# 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<sub>2</sub>) which is functional to the dehydrogenation.**

# Sample Foaming



**Pristine AB**

**AB + 2 mol% Co**

**AB + 2 mol% Ni**

# Acknowledgements

<b>Group members</b>	<b>IPHE Collaborators</b>
<p><u>In DICP</u> Prof. Zhitao XIONG A/P Guotao WU Dr. Chengzhang WU Dr. Hailiang CHU <b>Mr. Teng HE</b> Ms. Na XU Miss Xueli ZHENG <b>Mr. Jianhui WANG</b></p> <p><u>In NUS</u> Mr. Yong Shen CHUA Miss Wen LI Mr. Weiliang XU</p>	<p><u>Pacific Northwest National Laboratory</u> Abhi Karkamkar Thomas Autrey</p> <p><u>Rutherford Appleton Laboratory</u> William I F David</p> <p><u>University of Oxford</u> Martin Owen Jones, Simon R Johnson Peter P Edwards</p> <p><u>University of Uppsala</u> Rajeev Ahuja Moysès Araùjo</p>



**NGC2009 & CSTC2009**