

# *Mechanical Processing in Hydrogen Storage Research & Development*

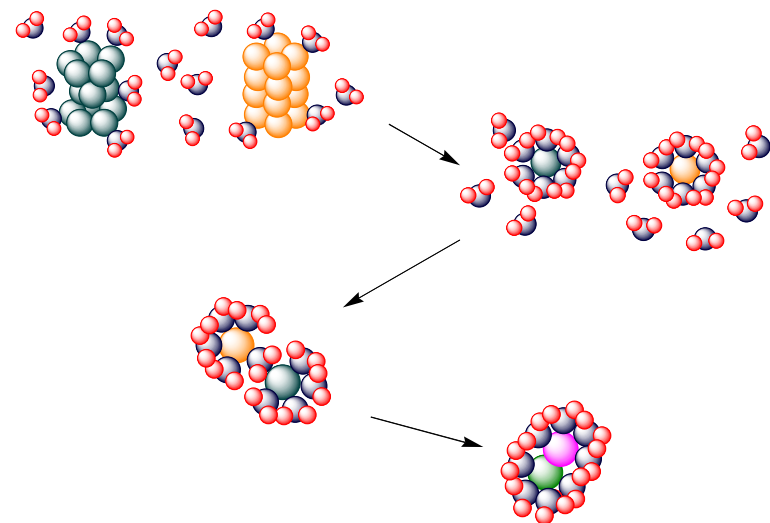


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**Viktor P. Balema**  
Aldrich Materials Science  
*Washington DC, 2009*

# Chemical Transformations

## Solution vs. Solid-State



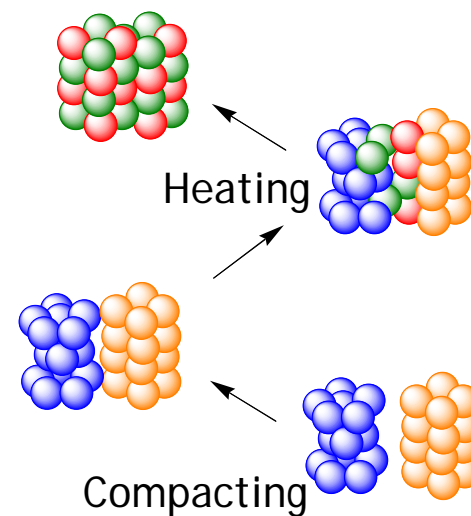
Reactions in Solution - solvent's functions:

1. Destroys crystallinity of solids
2. Mass transfer to and from the reaction zone
3. Absorbs evolving heat
4. Solvation

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### Conventional Solid-State Reactions

1. Poor mass transfer
2. High contact surface area is a must
3. High temperatures to enable diffusion

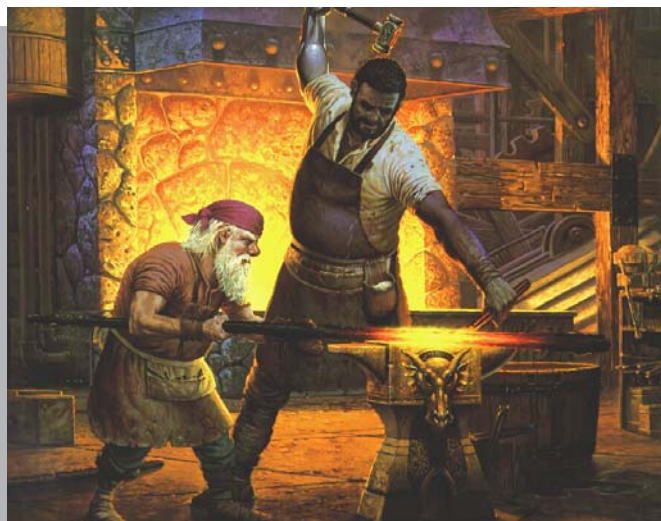


# *Mechanical Alloying*

For millennia, the human race has been using mechanical energy for processing different types of solids by *grinding*, *milling* and *forging*.



*Mechanochemistry - chemical conversion of solids facilitated by mechanical processing, i.e. milling or grinding.*



In the early 60<sup>th</sup>, INCO started industrial production of metal alloys and composite materials by ball-milling. The developed method, called "*mechanical alloying*", brought a new life into the ancient technique ...

**Metal alloys  
and  
intermetallic compounds**

**Hydrogen storage**

**Ceramics  
and composites**

**Nanomaterials**

**Mechanical Alloying**



**Amorphous inorganic  
materials**

**Meta-stable crystalline  
phases**

# Milling and Grinding

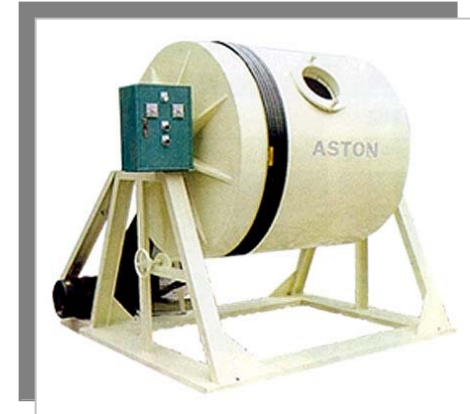
*Spex 8000 Shaker Mill*



*Mortar & Pestle*



*Planetary Mill*



*Ball Mill*



*Attritor Mill*

# Mechanochemical Experiments

## An example

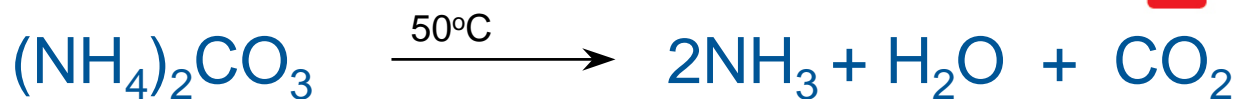
- Solid reactants are ball-milled in a vial sealed under helium using a *Spex 8000* shaker mill
- The powders are analyzed by solid-state NMR, x-ray powder diffraction, DTA/TGA etc. *prior* to any further treatment
- Temperature in the material during milling is  $< 60^{\circ}\text{C}$



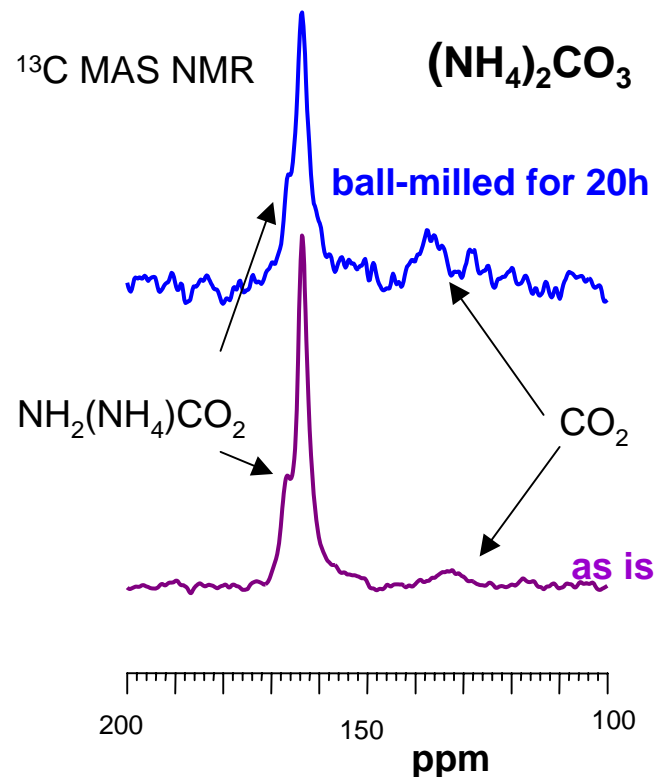
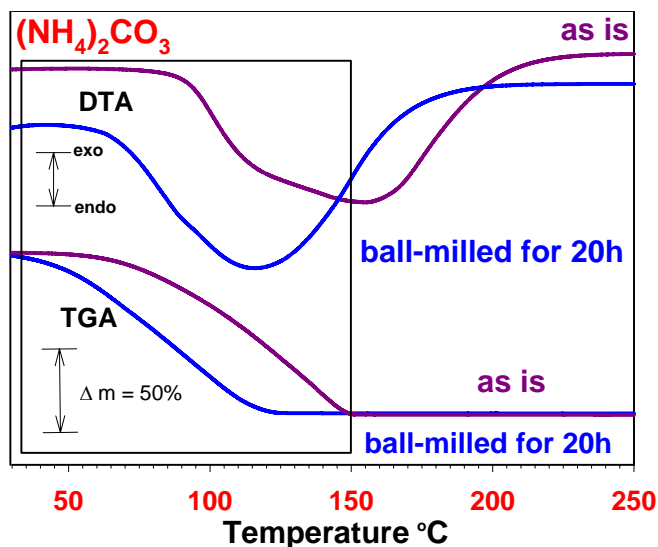
6

*Spex 8000 shaker mill*

# Milling Temperature



- Ball-milling: Spex 8000 mill/Helium
- DTA/TGA: 10°C/min, Argon
- $^{13}\text{C}$  MAS NMR room temperature



Temperature in the materials during milling in Spex-mill is  $< 60^\circ\text{C}$

# Hydrogen Storage Mechanosynthesis



V. P. Balema et al., *J. Alloys Compds.* 313, 69 (2000)



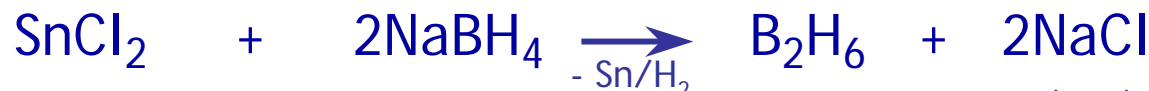
Z. Xiong et al. *Nature Materials* 7, 138 (2008)



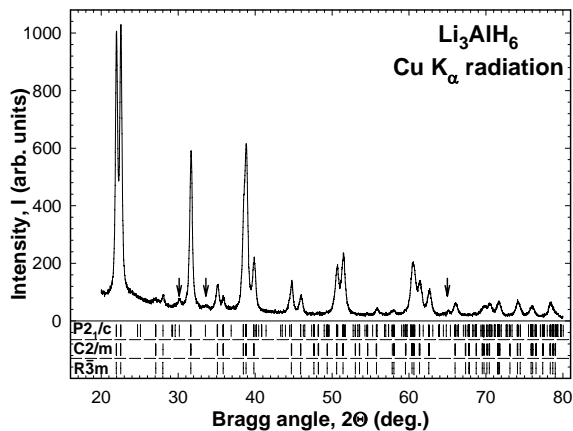
M. Mamathab et al. *J. Alloys Compds.* 407, 78 (2006)  
V. P. Balema et al. *unpublished*



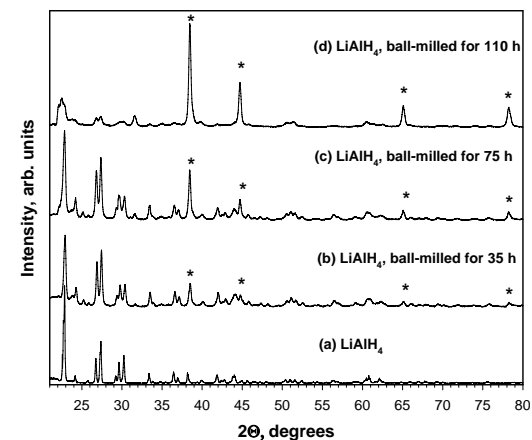
E. Jeon et al. *J. Alloys Compds.* 422, 273 (2006)



V. Volkov et al. *Inorg. Chem. Acta.* 289, 51 (1999)

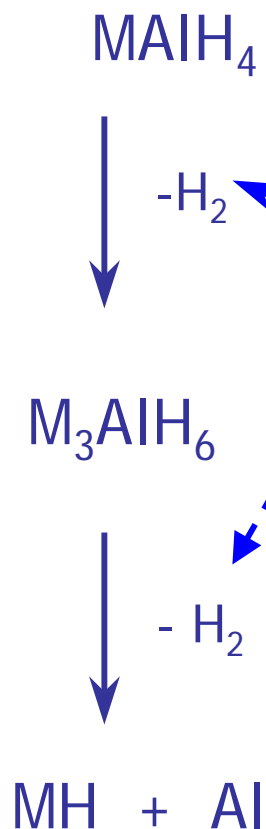


V. P. Balema et al., *J. Alloys Compds.* 313, 69 (2000)

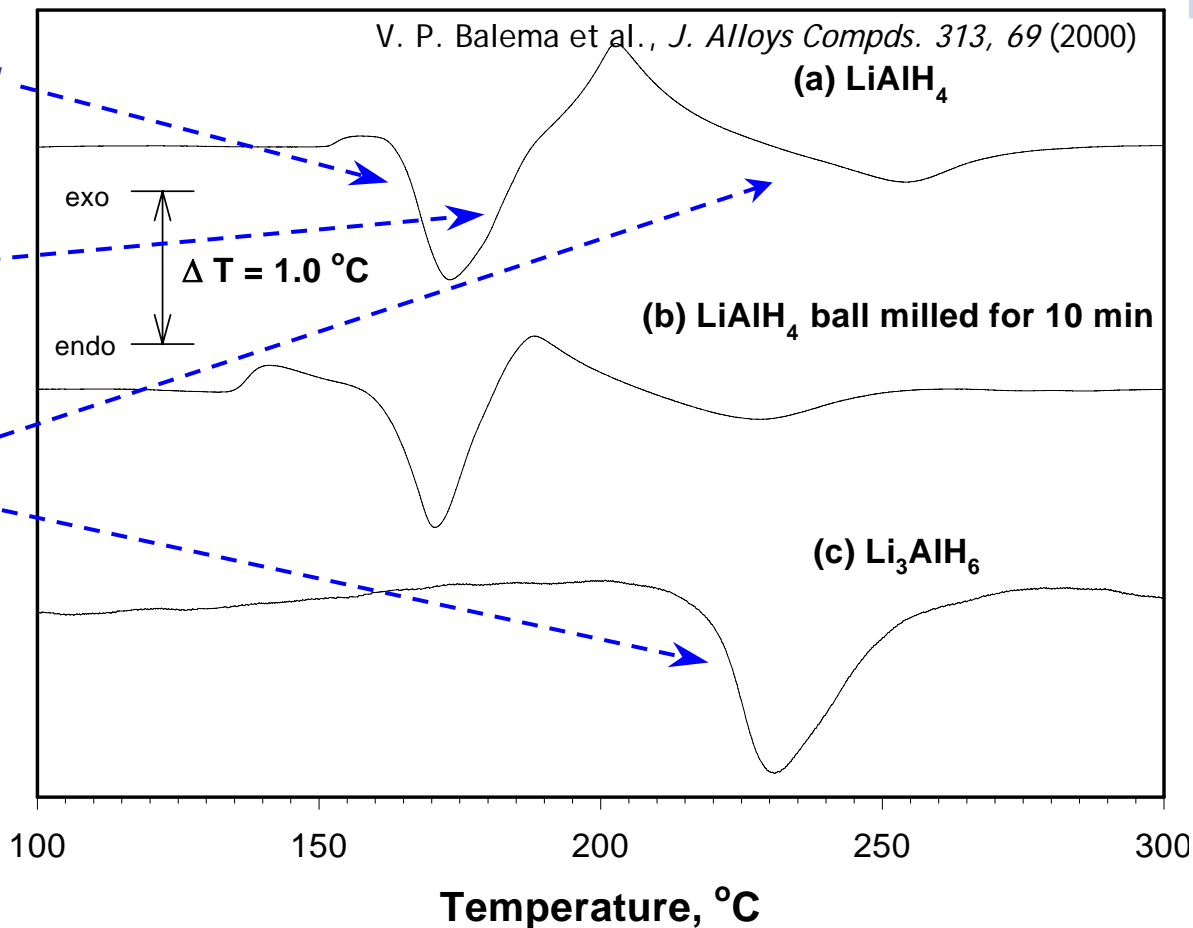


# Hydrogen Storage

## Transformations of Alanates



Melting



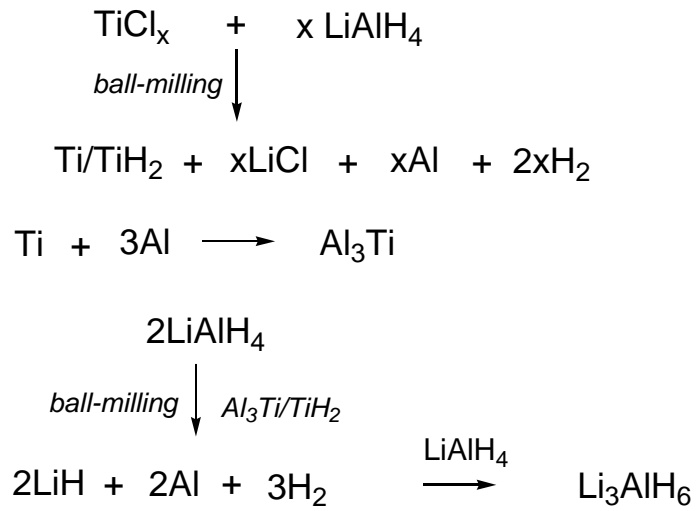
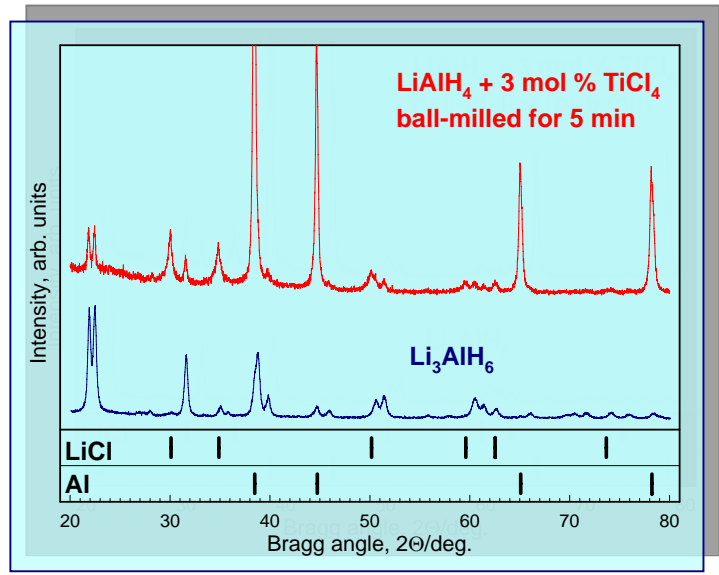
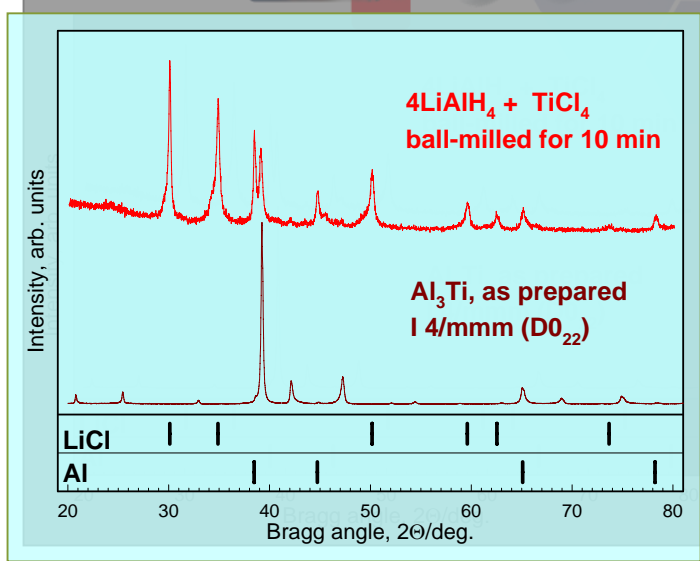
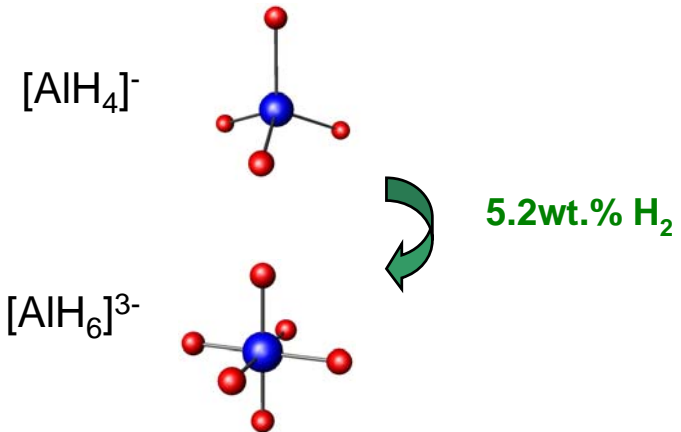
M = Li, Na, K

J. A. Dilts, E. Ashby, *Inorg. Chem.*, 11, 1230 (1972)

# Hydrogen Storage

"The major breakthrough in the field of hydrogen storage."

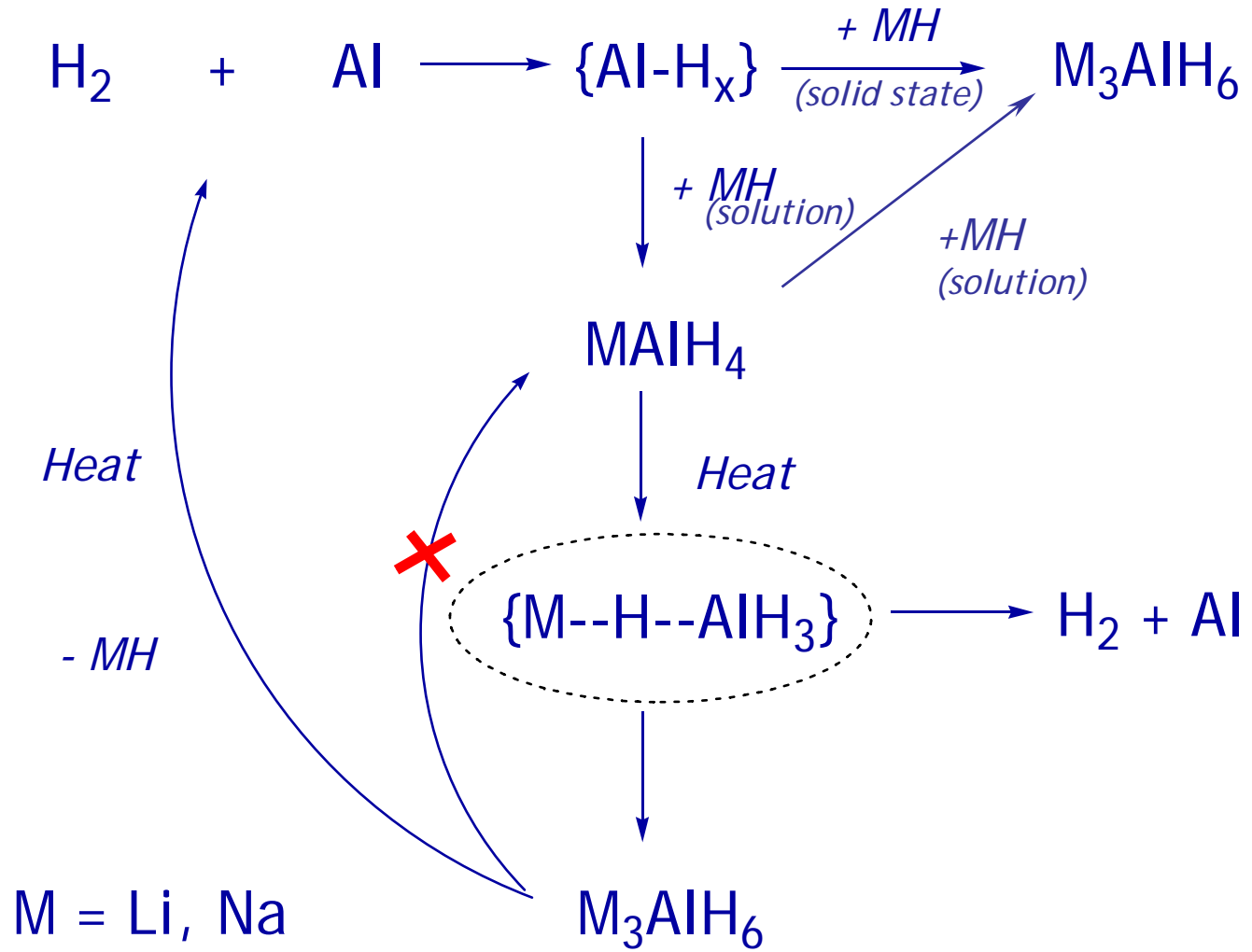
W. Grochala, P.P. Edwards, *Chem. Rev.*, 104, 1283 (2004)



V. P. Balema at al. *Chem. Commun.* 1665, 2000; *J. Alloys Compd.*, 329, 108 (2001); *Phys.Chem.Chem.Phys.* 7, 1310 (2005)

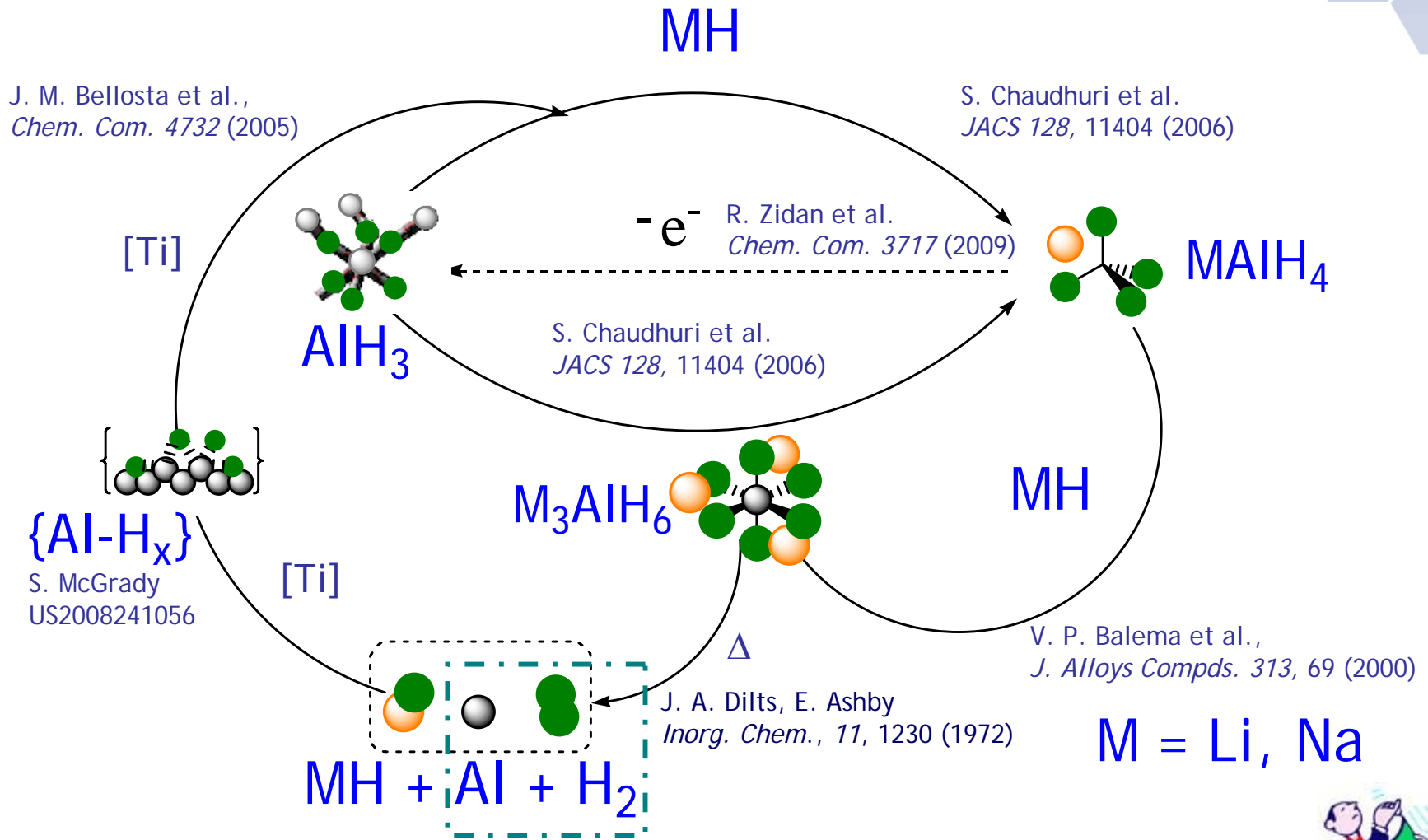
# Hydrogen Storage

## Transformations of Alanates



# Hydrogen Storage

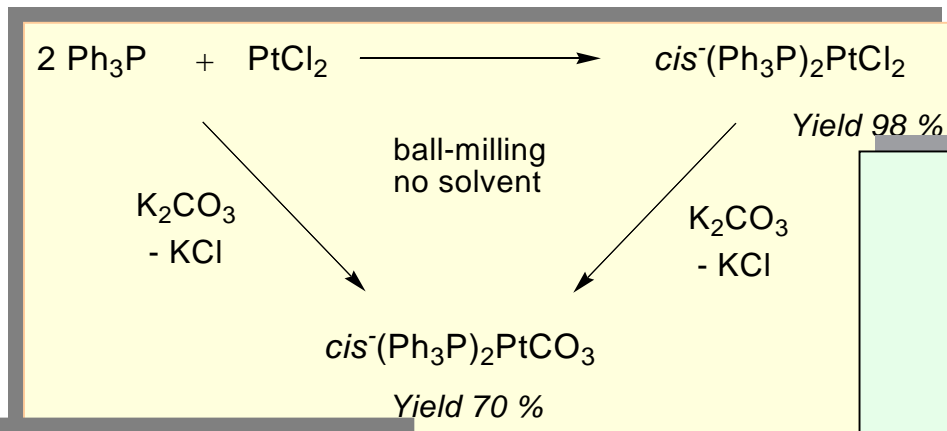
## Transformations of Alanates



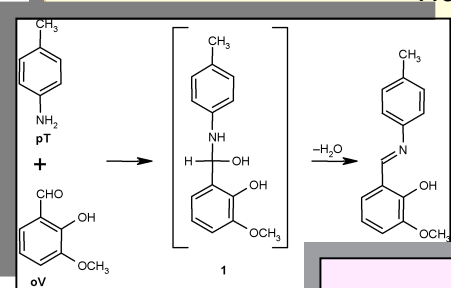
V. Balema, *Material Matters* 2.2, 16 (2007)



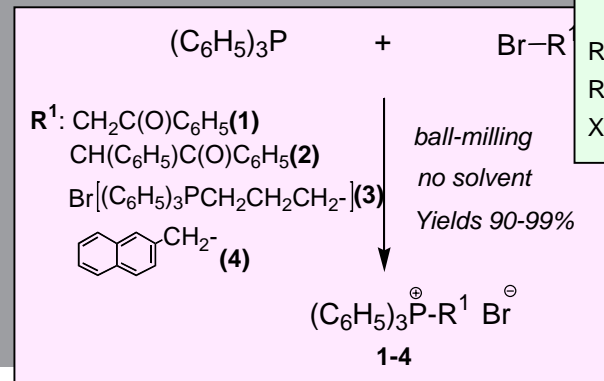
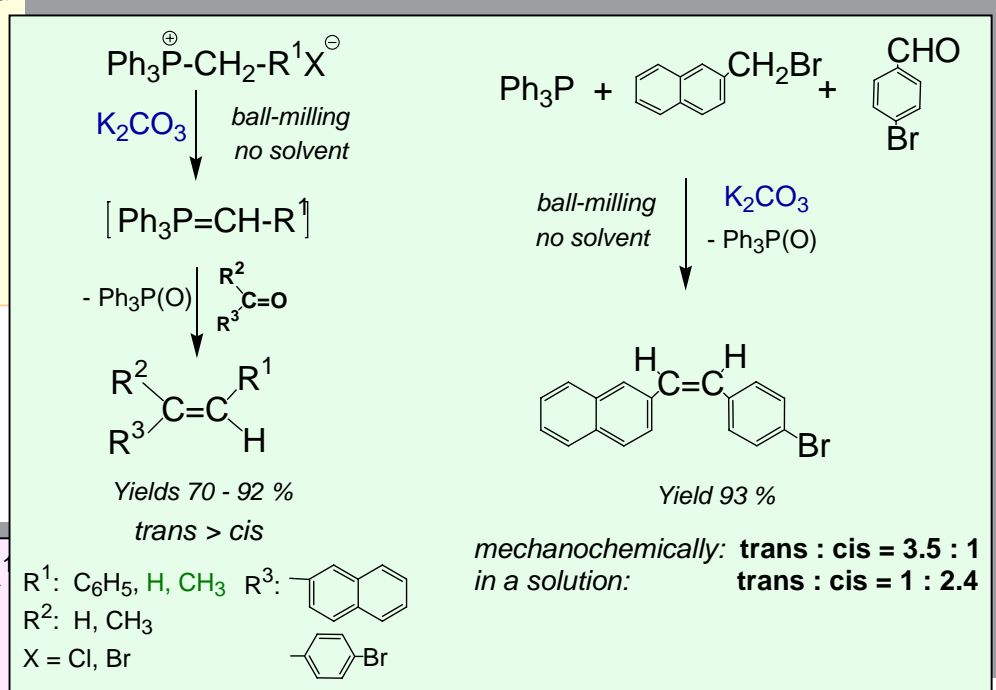
# Other Mechanically Induced Processes



V. P. Balema et al. *Chem. Commun.* 1606 (2002)



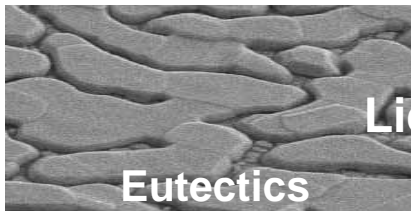
V. Balema et al., *Green Chem.* in print(2002)



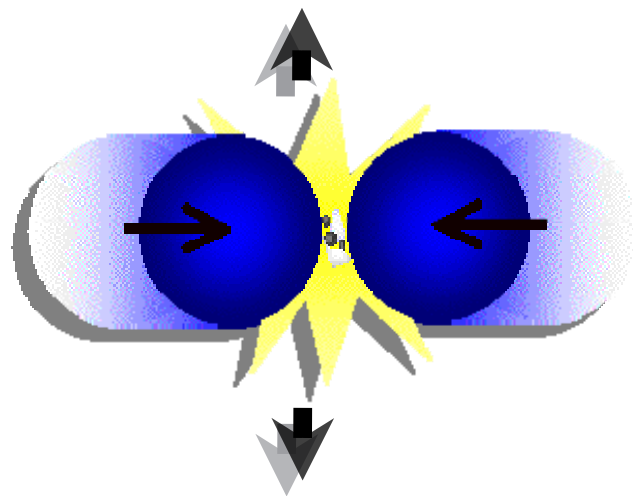
V. P. Balema et al. *JACS* 124, 6244 (2002)

V. P. Balema et al., *Chem. Commun.* 724 (2002)

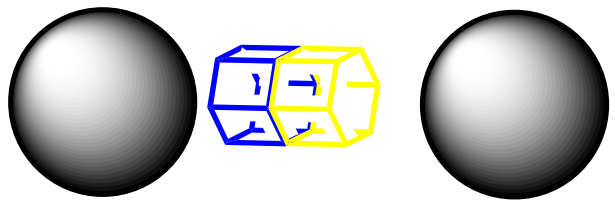




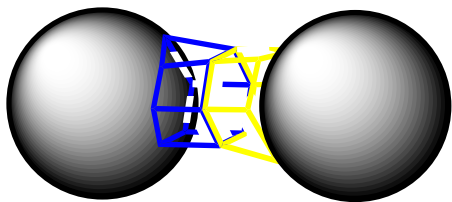
## Liquid-Phase reactions



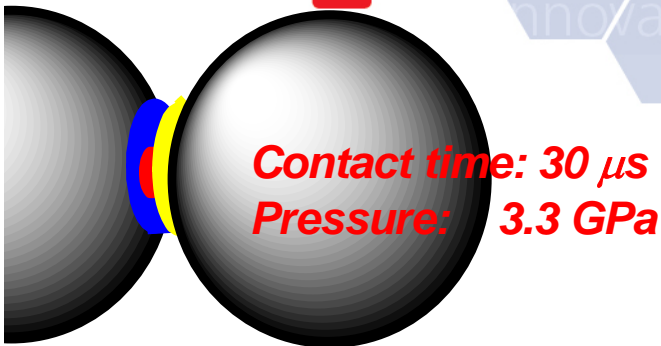
# Mechanically Induced Transformations



*Elastic deformation*

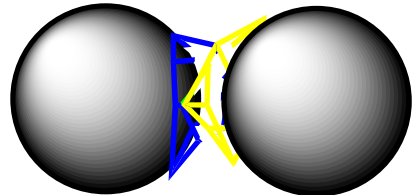


*Shear deformations*

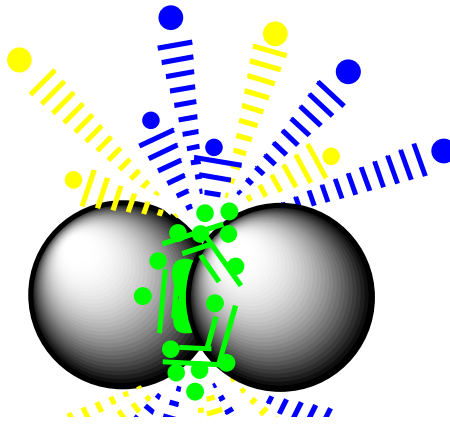


**Contact time: 30  $\mu$ s**  
**Pressure: 3.3 GPa**

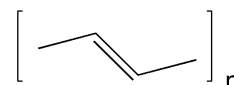
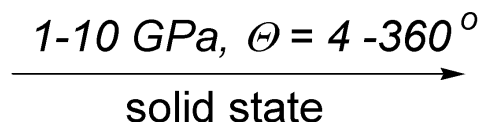
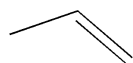
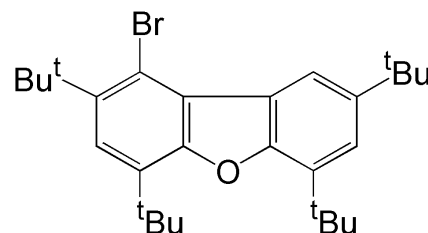
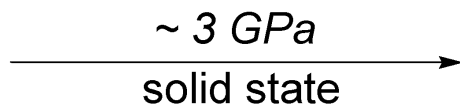
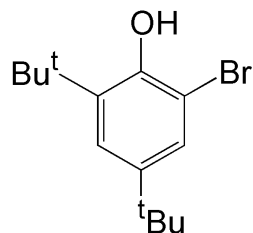
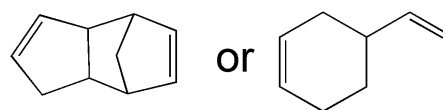
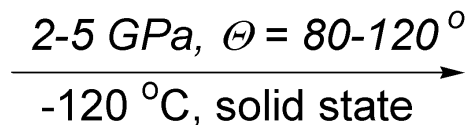
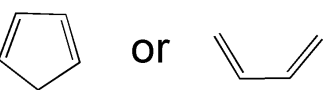
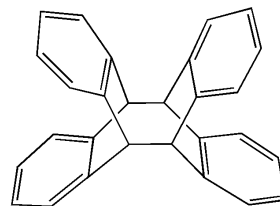
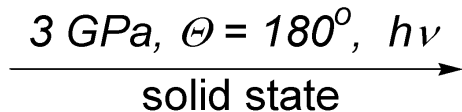
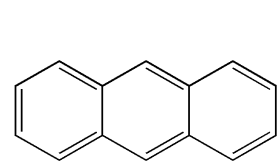
*Plastic deformations*



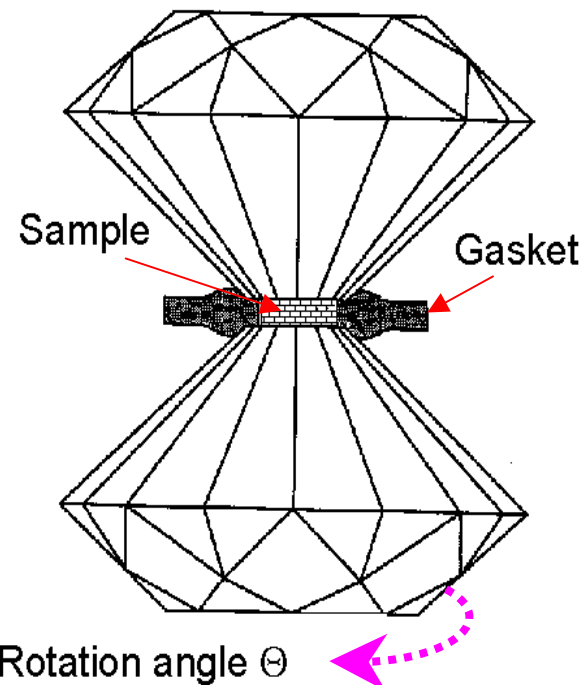
*Fracture and Amorphization*



# Mechanically Induced Transformations



polymerization



## Bridgman's anvil

*Material:* diamond, boron nitride, ball-bearing steel.

*Sample:* 5 -10 mg

*Pressure:* up to 10 GPa

# Conclusions

- Mechanochemistry holds the promise of becoming an enable technique for a number of technologies including Hydrogen Storage.
- Ball-milling facilitates chemical conversion of metal hydrides.
- Complex *multi-step* processes can be carried out by milling solids without solvent.
- Most likely, mechanically induced transformations *are not* thermally driven events.
- Mechanical activation is a complex process, which mechanism should be evaluated on a case-by-case base.

# Acknowledgment



## Experiments:

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