

Mechanical Processing in Hydrogen Storage R&D

Materials Design on Nano & Molecular Scale



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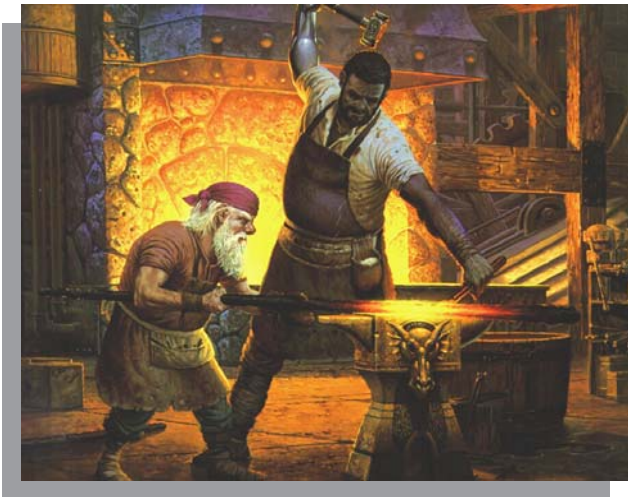
Viktor P. Balema
Aldrich Materials Science
2009 MRS Fall, Boston, MA

Mechanical Processing

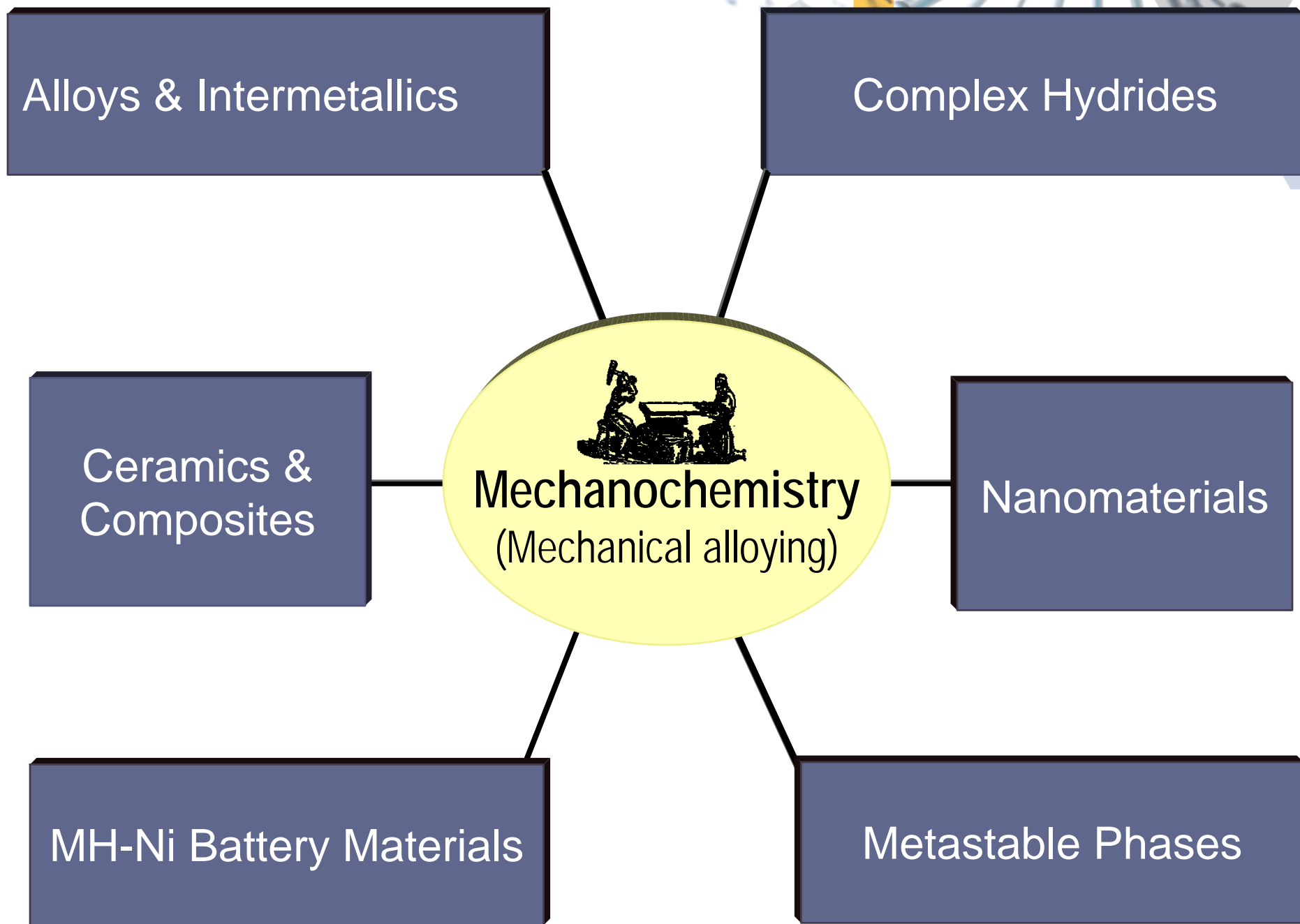
For millennia, the human race has been using mechanical energy for processing different types of solids by *grinding*, *milling* and *forging*.



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



In the early 1960s, INCO started industrial production of metal alloys and composite materials by ball-milling. The developed method, called “*mechanical alloying*”, brought a new life to the ancient technique ...



Milling and Grinding



Spex 8000 Shaker Mill



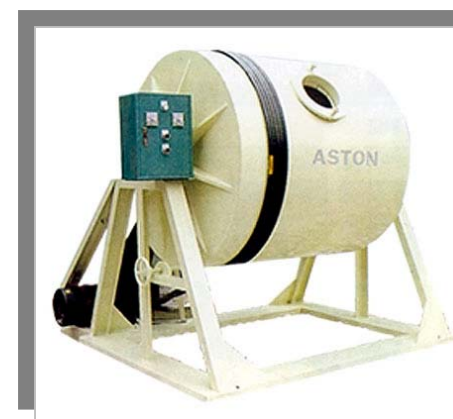
Mortar & Pestle



Planetary Mill



Attritor Mill

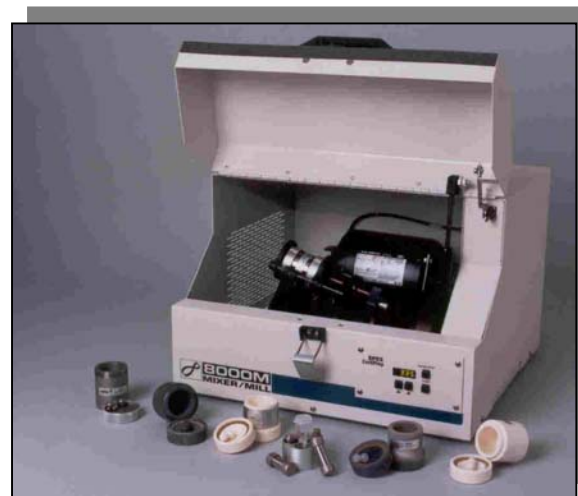


Ball Mill

Mechanochemical Experiments

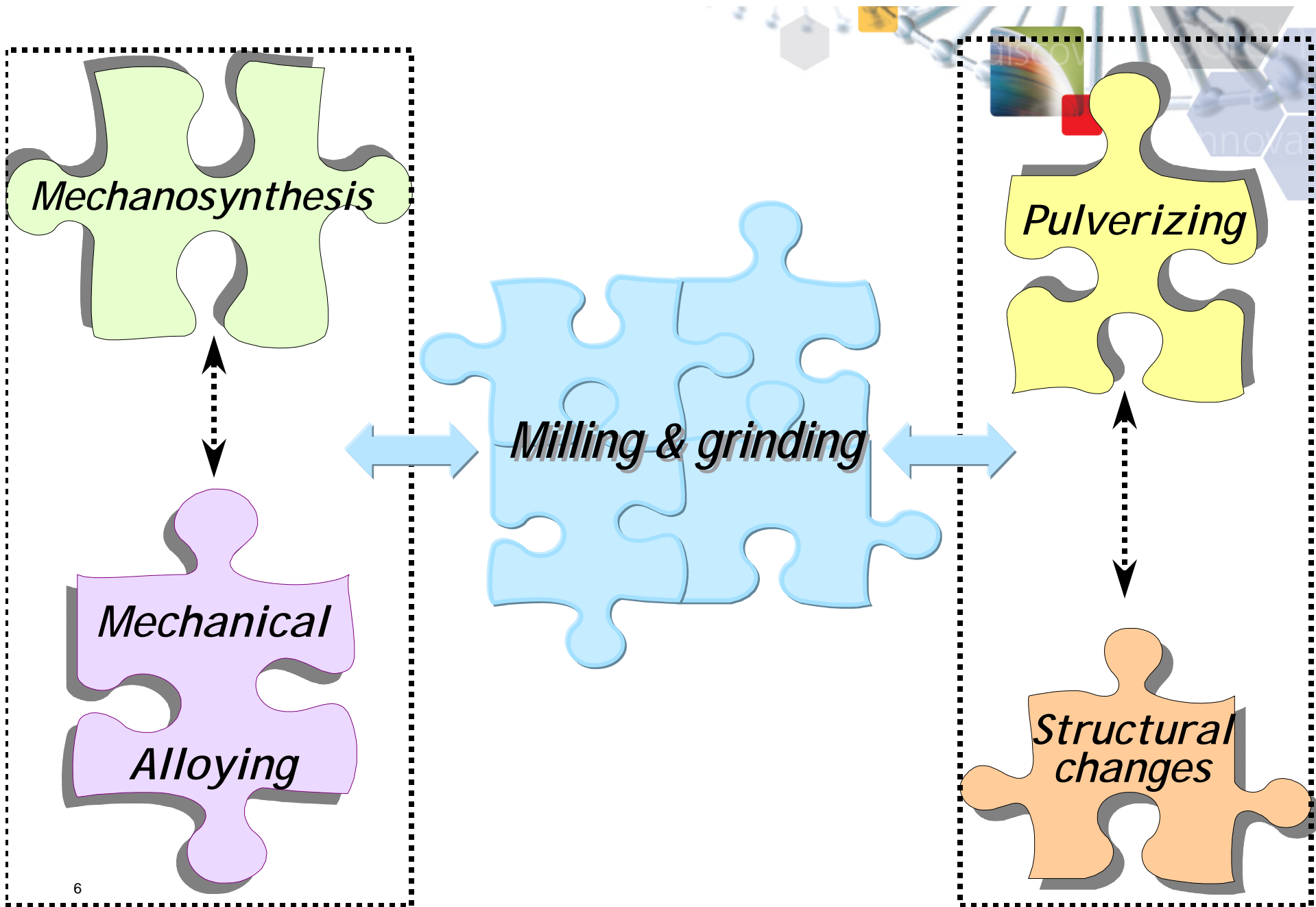
An example

- Solid reactants are ball-milled in a vial sealed under inert gas 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 (in *Spex 8000*): $< 60^{\circ}\text{C}$



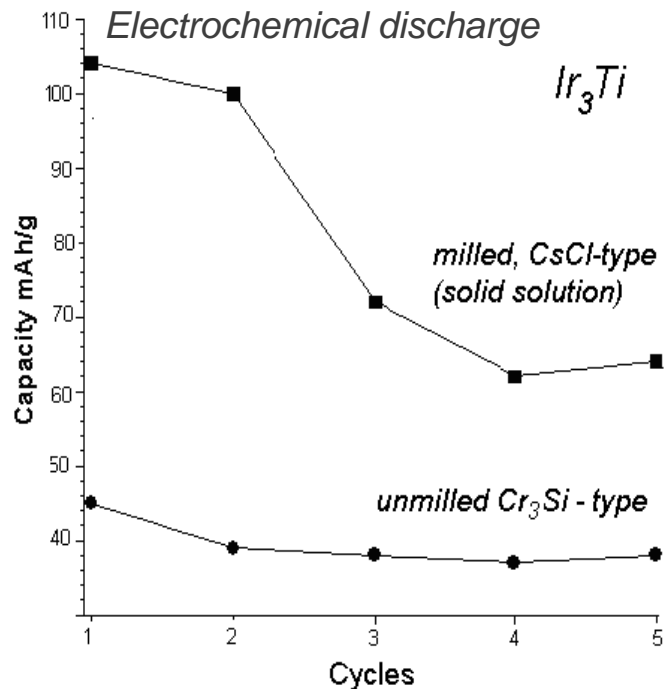
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Spex 8000 shaker mill



6

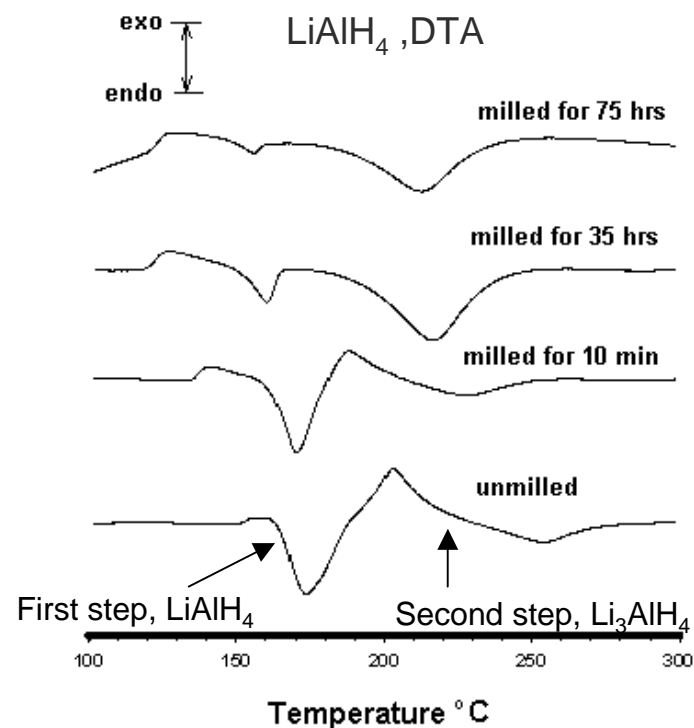
Hydrogen Storage Materials Modification



Ball-milling reduces the total capacity of Ir_3Ti from 280 mAh/g to 105 mAh/g but its electrochemical capacity triples. Material's structure changes from Cr_3Si (A-15) to CsCl.

V. P. Balema et al *J. Alloys Compd.*, 307, 184 (2000)

Ball-milling reduces decomposition temperature of pure LiAlH_4 and Li_3AlH_6 by 20 °C.

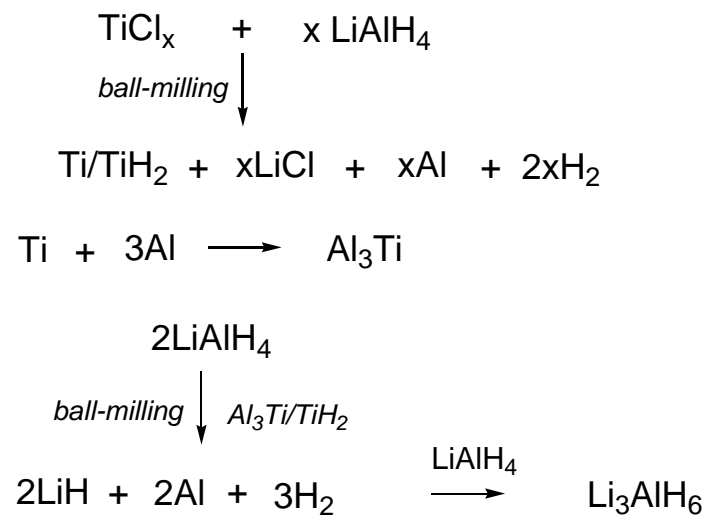
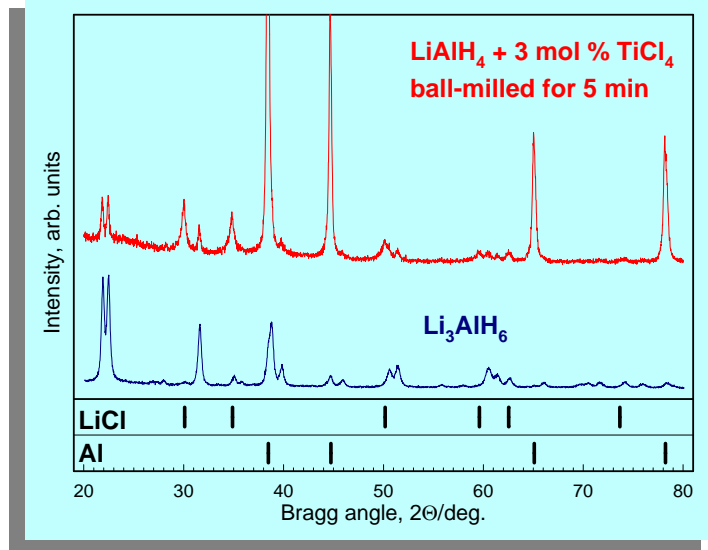
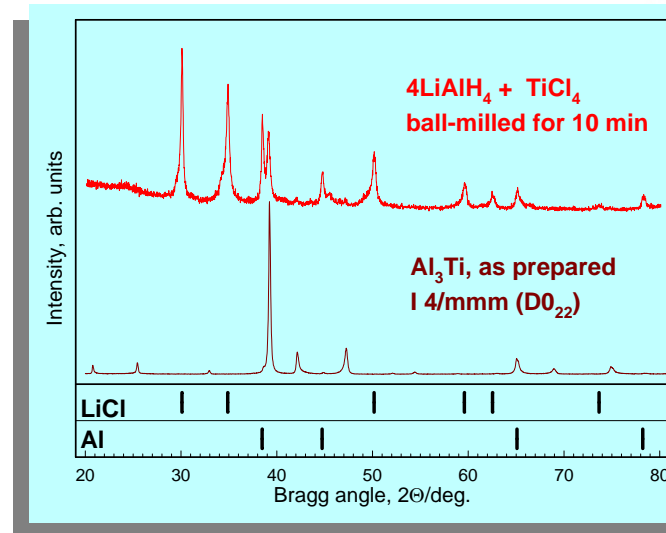
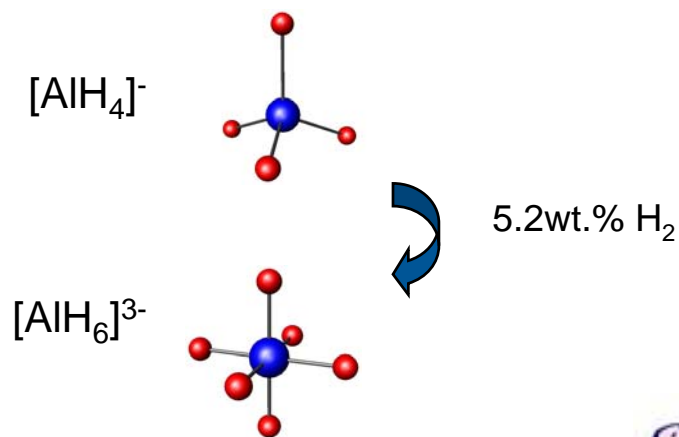


V. P. Balema et al *J. Alloys Compd.*, 313, 69 (2000)

Hydrogen Storage

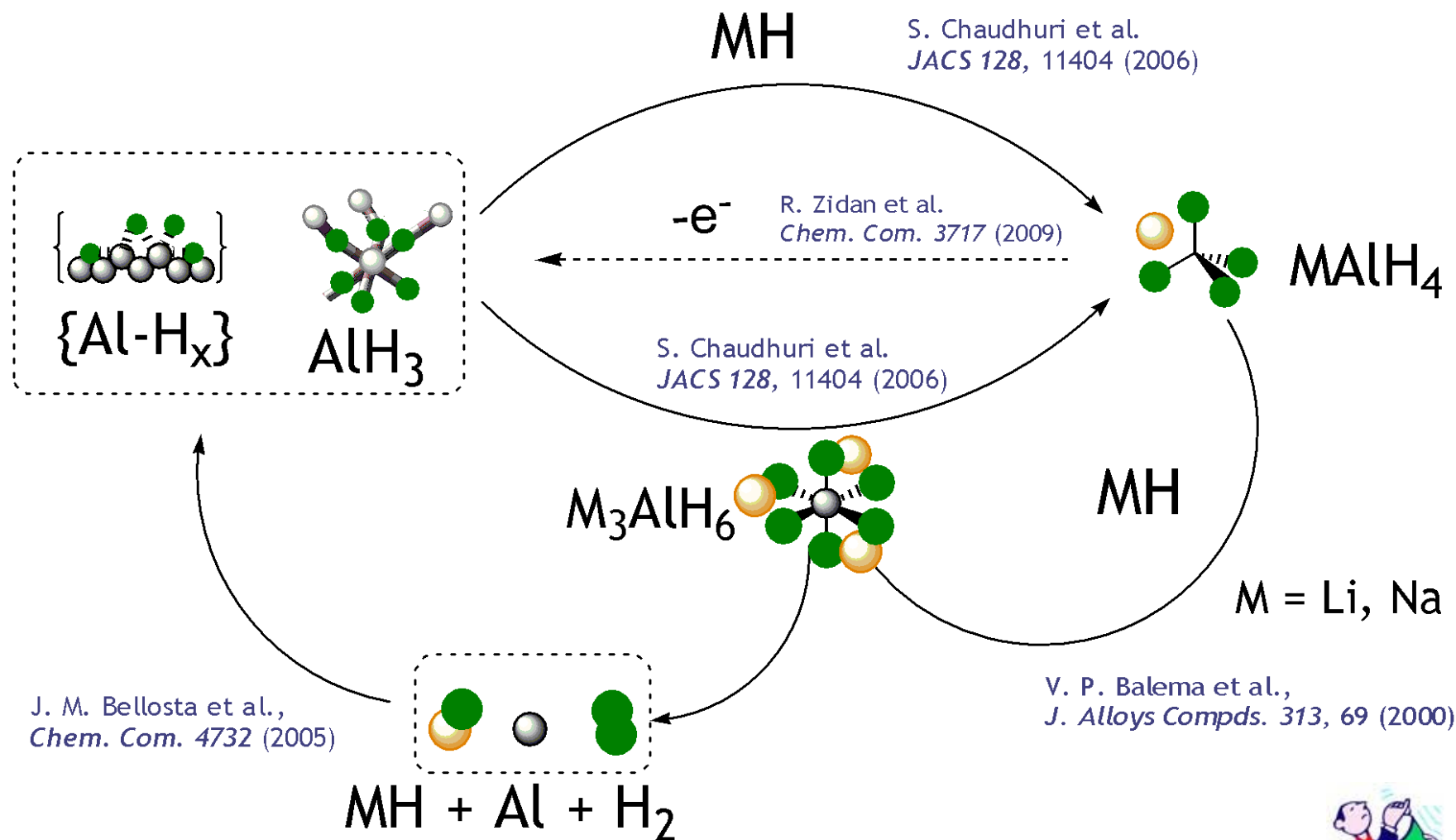
"The major breakthrough in the field of hydrogen storage."

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

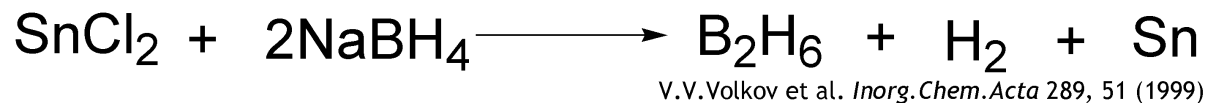
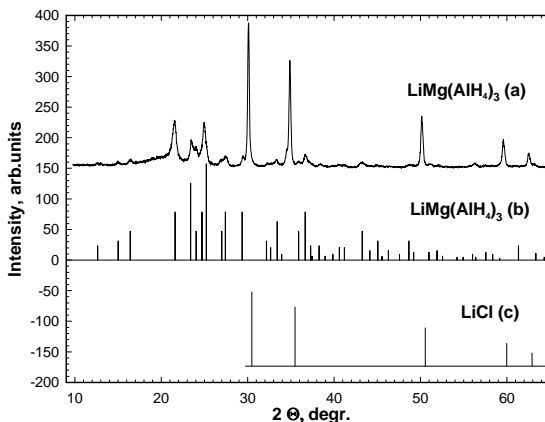
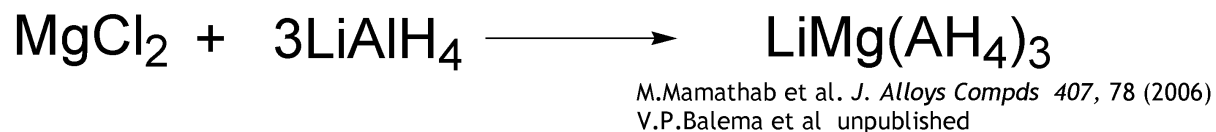
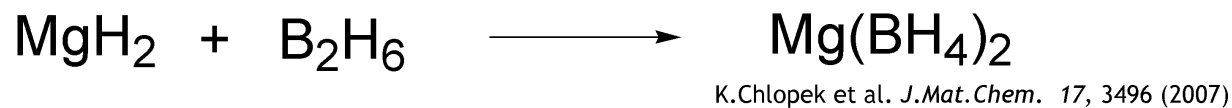
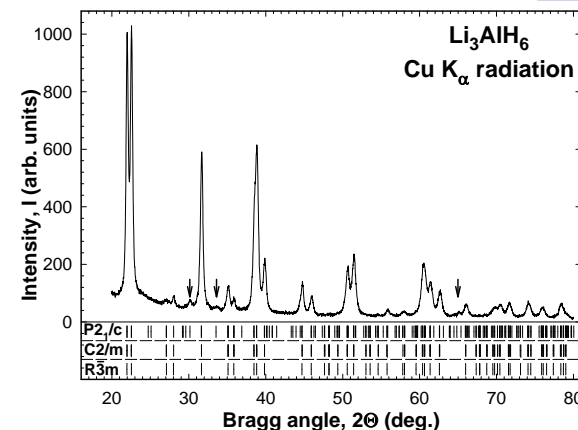
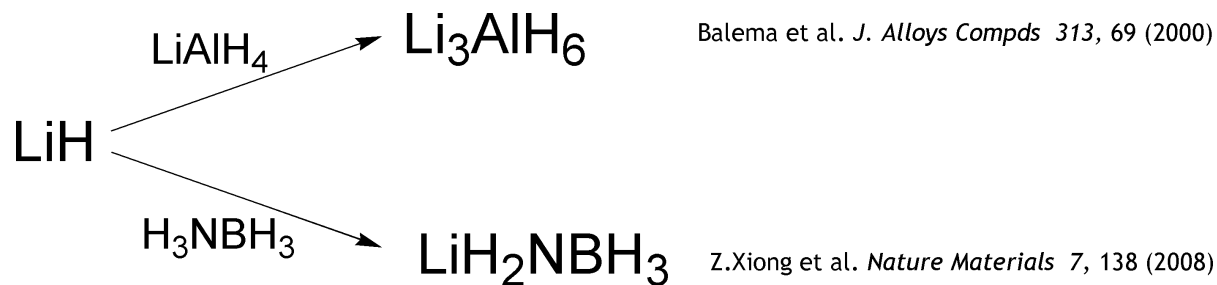


V. P. Balema et al. *Chem. Commun.* 1665, 2000; *J. Alloys Compd.*, 313, 69 (2001); *Phys. Chem. Chem. Phys.* 7, 1310 (2005)

Hydrogen Storage Materials Modification

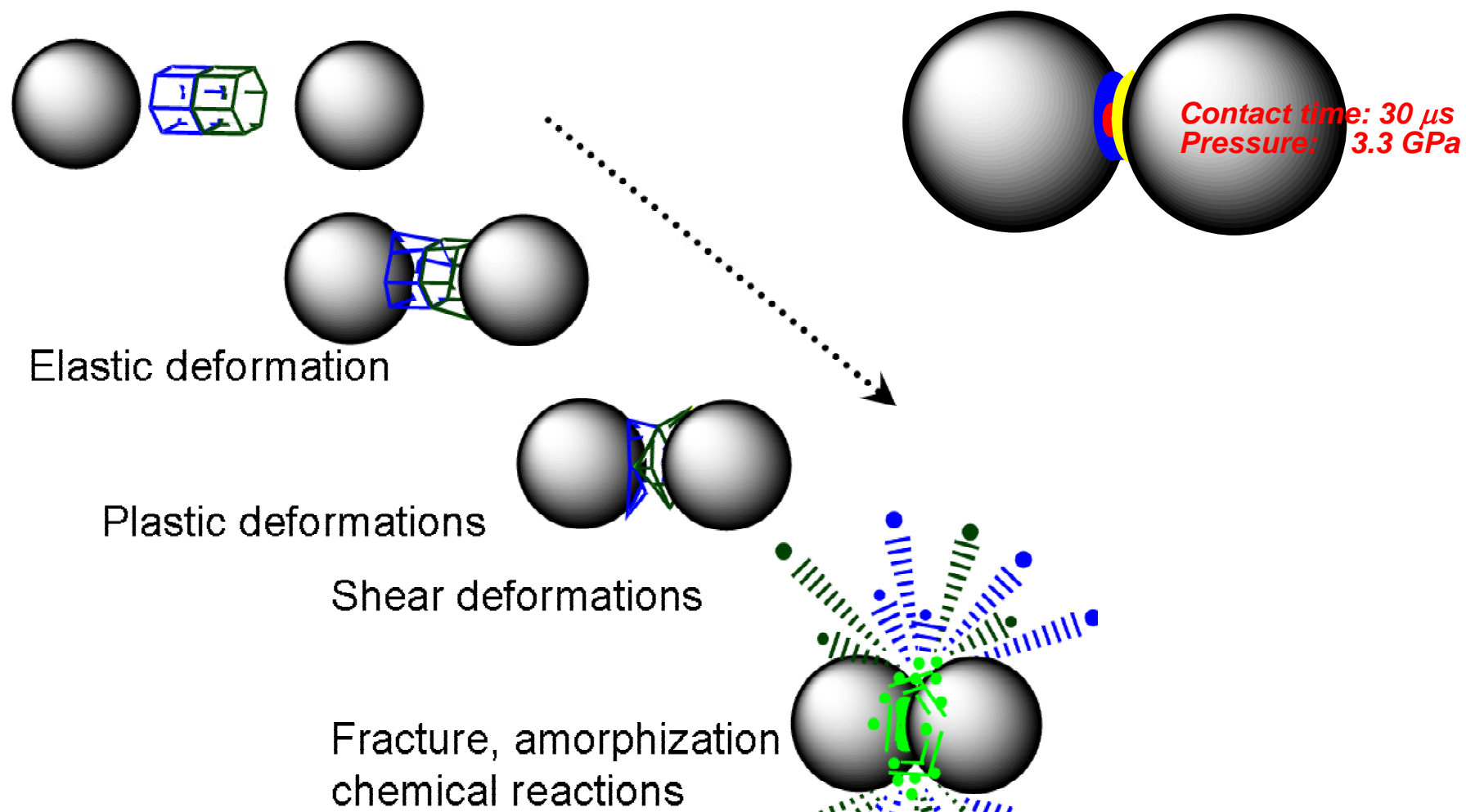


Hydrogen Storage Mechanosynthesis



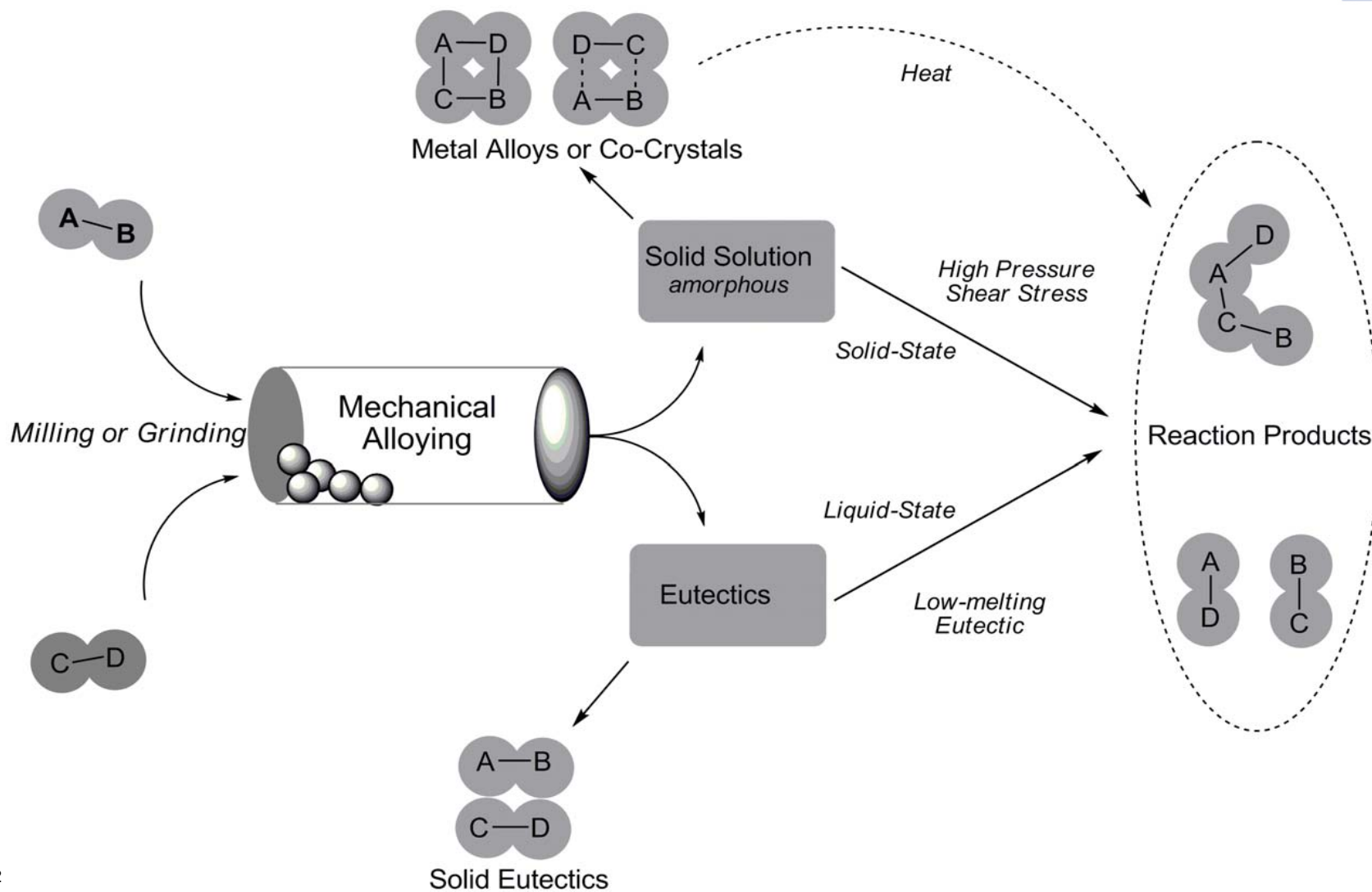
Mechanosynthesis

Possible Scenarios



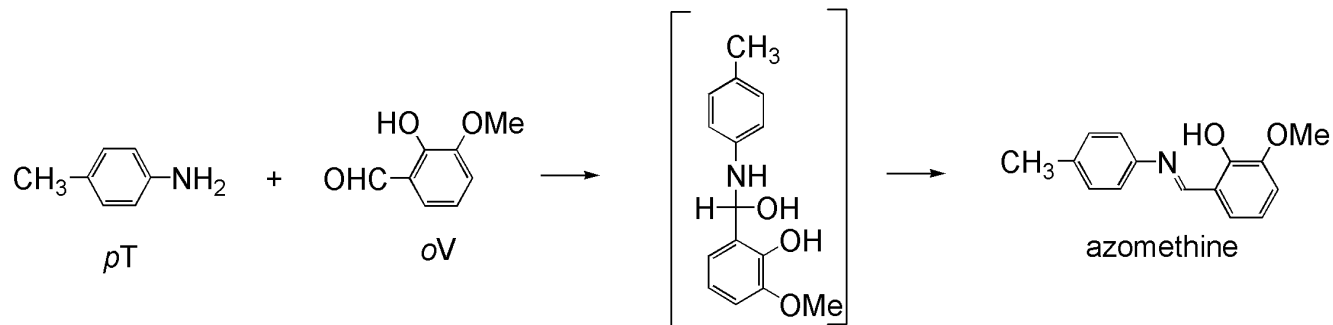
Mechanosynthesis

Possible Scenarios



Mechanosynthesis

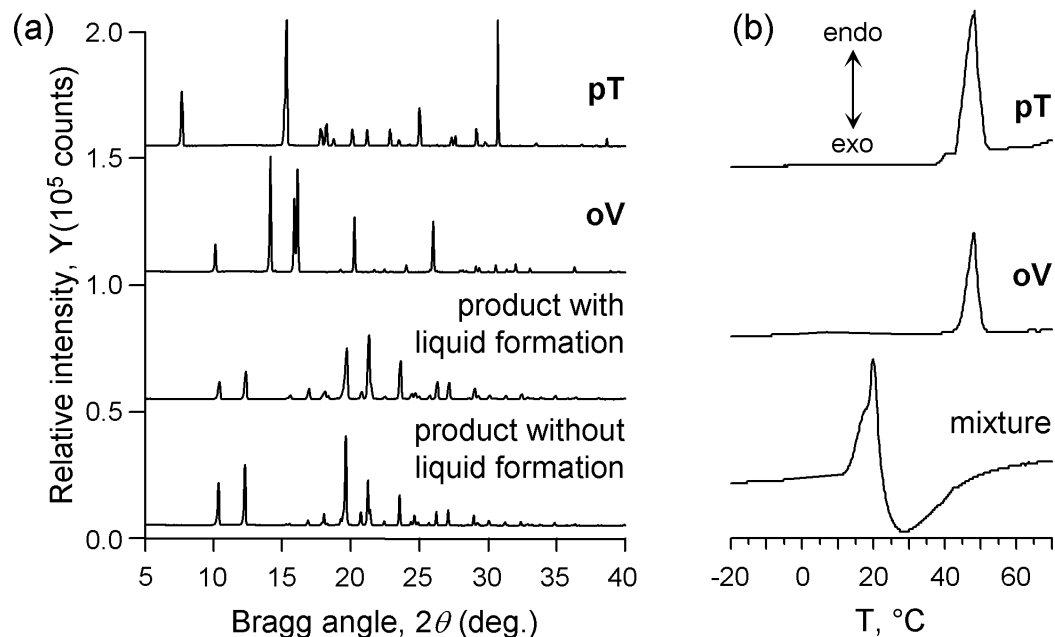
Possible Scenarios



The reaction of *o*-vanillin (oV) and *p*-toluidine (pT) upon grinding at 0 °C and a slow warm up to room temperature appears to proceed in solid state.

In fact, it occurs in a liquid eutectic, which remains hidden behind solid reactants and the reaction product.

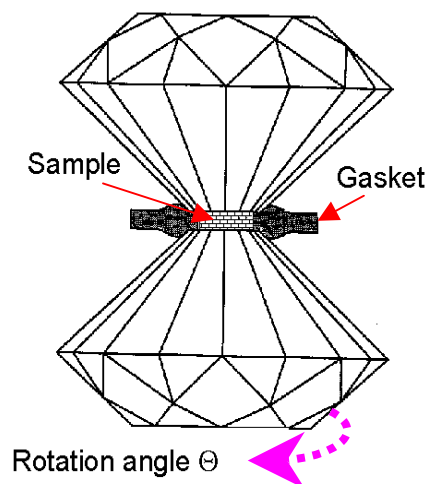
Low melting eutectics also form when *triphenylphosphine* is ball-milled with *4-bromobenzophenone* as well as in many other cases.



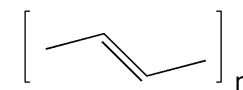
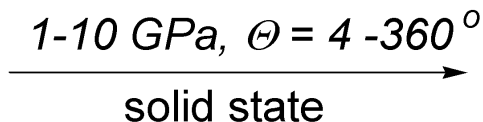
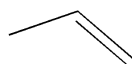
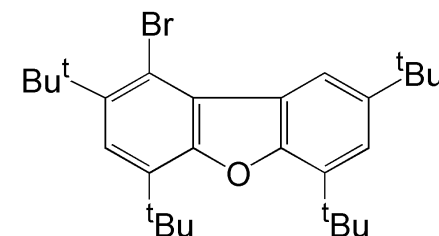
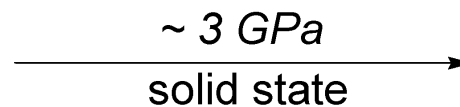
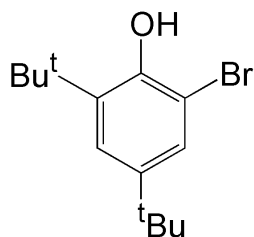
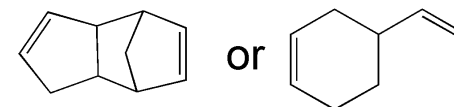
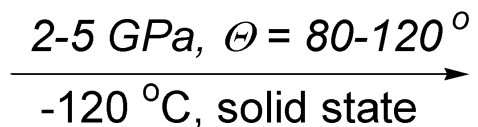
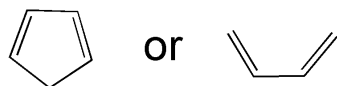
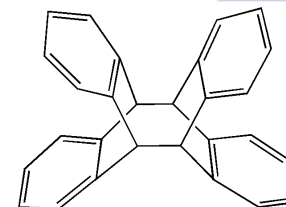
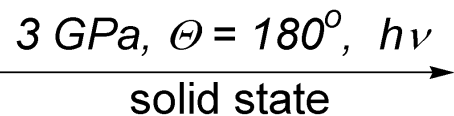
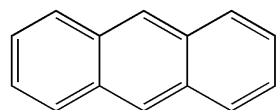
V.P. Balema et al. *Chem. Commun.* 724 (2002);
New J. Chem. 2009, ASAP article

Mechanosynthesis

Possible Scenarios



Bridgeman's anvil



polymerization

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

Pressure: up to 10 GPa

Conclusions



- Mechanical processing is an extremely useful tool for nano-scale design of novel materials including hydrogen storage materials.
- Most likely, a majority of mechanically-induced transformations proceed through similar stages.
- Mechanical processing enhances interactions between different solids, provides mass transfer and energy required for physicochemical and/or chemical transformations.
- The knowledge acquired in one area of mechanochemistry helps better understand other mechanically-induced processes in solids.

Acknowledgment



Experiments:

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Dr. Marek Pruski

Special thanks:

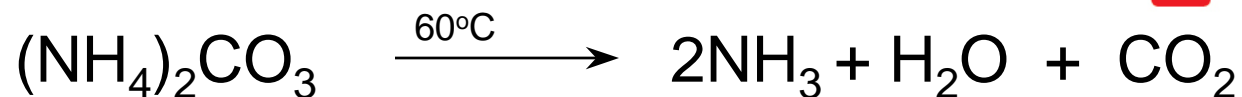
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Dr. Karl A. Gschneidner



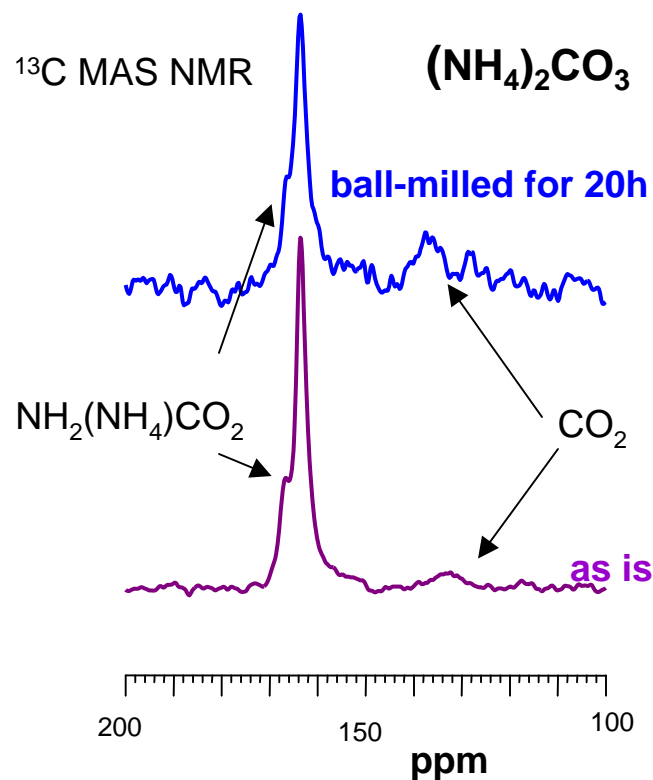
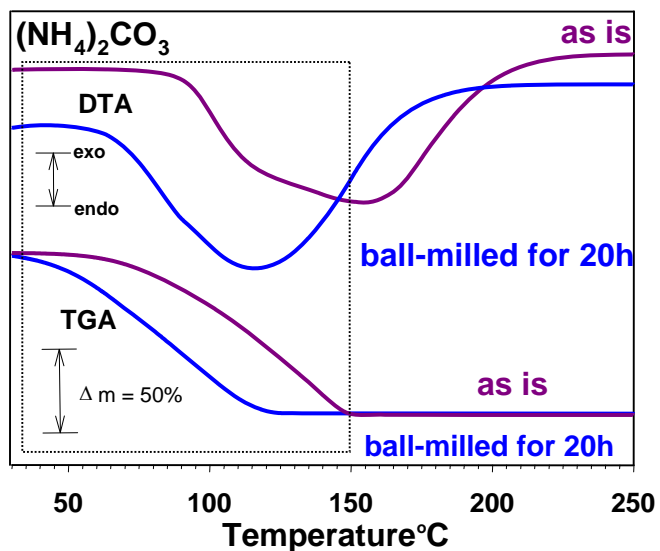
Appendix

Additional Slides

Milling Temperature

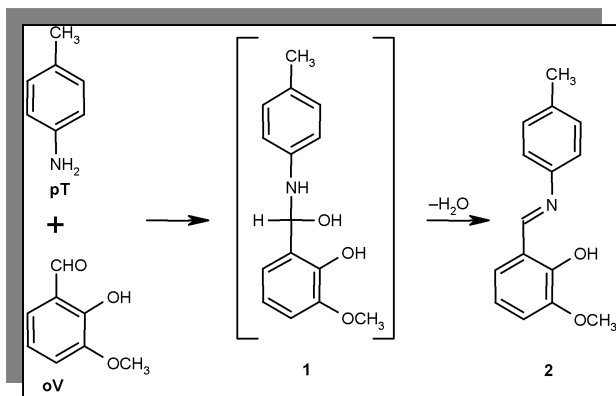


- Ball-milling: Spex 8000 mill/Helium
- DTA/TGA: 10°C/min, Argon
- ^{13}C MAS NMR room temperature

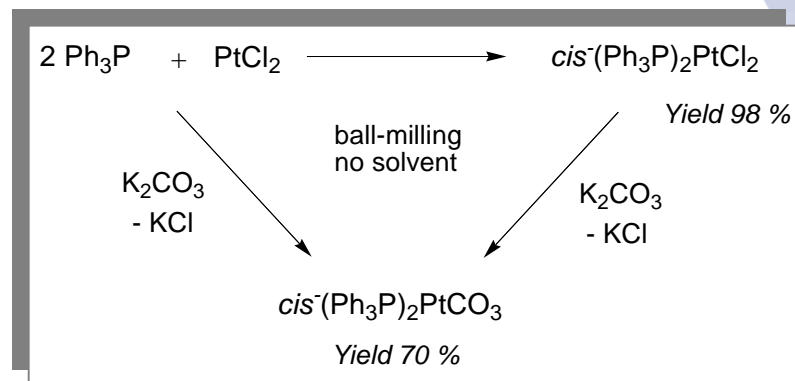


¹⁰
V. P. Balema et al. *Phys.Chem.Chem.Phys.* 7, 1310 (2005)

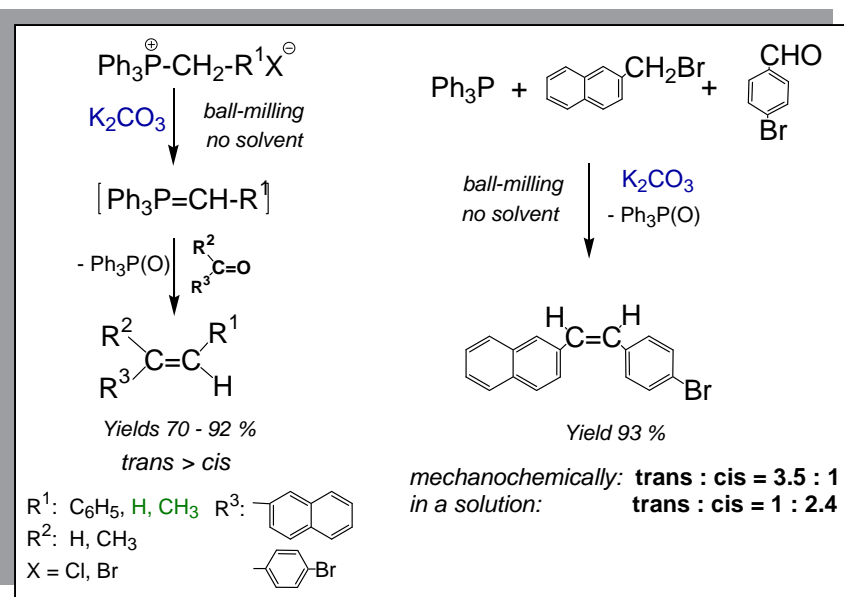
Other Mechanically Induced Processes



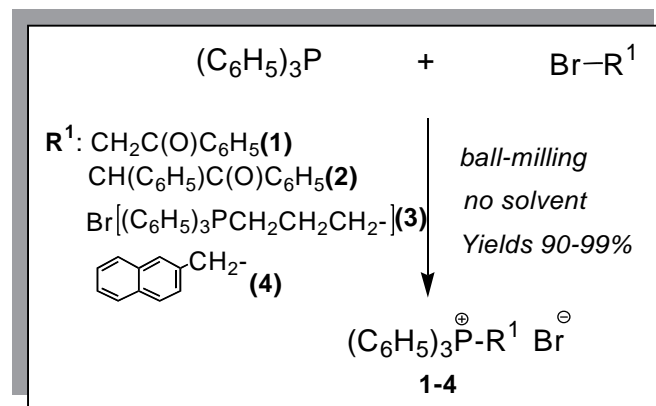
V. Balema et al., *New J. Chem.* 2009, ASAP articles



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