Mechanical Processing in Hydrogen Storage R&D

Materials Design on Nano & Molecular Scale

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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 …
Mechanochemistry
(Mechanical alloying)

- Alloys & Intermetallics
- Complex Hydrides
- Ceramics & Composites
- Nanomaterials
- MH-Ni Battery Materials
- Metastable Phases
Milling and Grinding

Spex 8000 Shaker Mill

Planetary Mill

Attritor Mill

Mortar & Pestle

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°C
Ball-milling reduces the total capacity of Ir$_3$Ti from 280 mAh/g to 105 mAh/g but its electrochemical capacity triples. Material’s structure changes from Cr$_3$Si (A-15) to CsCl.


Ball-milling reduces decomposition temperature of pure LiAlH$_4$ and Li$_3$AlH$_6$ by 20 °C.
Hydrogen Storage

“The major breakthrough in the field of hydrogen storage.”

\[ \text{[AlH}_4\text{]}^- \quad \xrightarrow{\text{ball-milling}} \quad [\text{AlH}_6]^3\text{-} \]

5.2wt.% H₂

Hydrogen Storage
Materials Modification

MH

S. Chaudhuri et al.
JACS 128, 11404 (2006)

-e-

R. Zidan et al.
Chem. Com. 3717 (2009)

MALH₄

S. Chaudhuri et al.
JACS 128, 11404 (2006)

M₃AlH₆

M = Li, Na

MH

J. M. Bellosta et al.,
Chem. Com. 4732 (2005)

V. P. Balema et al.,

MH + Al + H₂
Hydrogen Storage
Mechanosynthesis

\[ \text{LiAlH}_4 \rightarrow \text{Li}_3\text{AlH}_6 \]
\[ \text{LiH} \rightarrow \text{LiH}_2\text{NBH}_3 \]
\[ \text{H}_3\text{NBH}_3 \]

\[ \text{MgH}_2 + \text{B}_2\text{H}_6 \rightarrow \text{Mg(BH}_4\text{)}_2 \]

\[ \text{MgCl}_2 + 3\text{LiAlH}_4 \rightarrow \text{LiMg(AH}_4\text{)}_3 \]
V.P. Balema et al. unpublished

\[ \text{SnCl}_2 + 2\text{NaBH}_4 \rightarrow \text{B}_2\text{H}_6 + \text{H}_2 + \text{Sn} \]
Mechanosynthesis

Possible Scenarios

Contact time: 30 \( \mu \)s
Pressure: 3.3 GPa

Elastic deformation

Plastic deformations

Shear deformations

Fracture, amorphization, chemical reactions
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.

**Mechanosynthesis**

Possible Scenarios

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**Bridgeman’s anvil**

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

**Pressure:** up to 10 GPa

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3 GPa, $\Theta = 180^\circ$, $h\nu$

solid state

2-5 GPa, $\Theta = 80-120^\circ$

-120 °C, solid state

$\sim 3$ GPa

solid state

1-10 GPa, $\Theta = 4 - 360^\circ$

solid state

polymerization
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.
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Appendix

Additional Slides
Milling Temperature

$\text{(NH}_4\text{)}_2\text{CO}_3 \xrightarrow{60^\circ\text{C}} 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$

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

$\text{(NH}_4\text{)}_2\text{CO}_3 \rightarrow \text{NH}_2(\text{NH}_4)\text{CO}_2$

Other Mechanically Induced Processes

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

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


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