Mechanical Processing in Hydrogen Storage Research and Development

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Introduction

Storing hydrogen in solids—hydrides, composite materials or metal-organic frameworks—offers a unique opportunity for its convenient and safe use in automotive, portable and other applications. Unfortunately, none of the materials currently on the market satisfy the needs of end users, which explains the growing interest and investments into hydrogen storage related research and development.\(^1,2\)

Throughout this issue, leading experts in the field discuss recent experimental results and ideas associated with hydrogen storage applications. Complementing these reports, the article below addresses an experimental approach, which proved to be indispensable in basic and applied hydrogen storage R&D\(^2\)—the preparation and modification of hydrogen rich molecular and ionic materials using high-energy mechanical milling.

Mechanically Induced Conversion of Metal Hydrides

Although mechanical milling has been routinely used in processing of solids for hundreds of years, systematic studies into its chemical effects began relatively recently.\(^3\) By the end of 20th century, mechanical processing by milling, also known as mechanical alloying or mechanochemistry, matured into an experimental technique routinely used in the preparation of metal alloys, ceramics and composites.\(^4\) It has also become indispensable for the preparation and processing of hydrogen rich solids, including metal hydrides.\(^2,4\)

Usually, mechanochemical experiments are carried out in a planetary or vibro-mill in a tightly sealed container (Figure 1) that can be loaded and unloaded under inert gas in a glove box.
In a typical procedure, pure solids or mixtures are charged into a milling vial and ball-milled for a defined period of time. The material is then recovered from the vial and investigated using an appropriate solid-state analytical technique such as x-ray or neutron diffraction, magic angle spinning solid-state nuclear magnetic resonance (MAS NMR), IR- or UV-spectroscopy, thermal analysis, and others. It is worth noting that MAS NMR has recently proven to be particularly efficient in monitoring chemical processes in metal hydrides\textsuperscript{5,6} and other solids.\textsuperscript{7}

**Metal Hydrides**

Use of the mechanochemical technique enabled the discovery of chemical processes that can take place in metal hydrides in the solid state. It turns out that solid-state chemistry of aluminum- and boron-based hydrides is quite as rich as their chemistry in solution. For example, ball milling of alkali metal aluminohydrides with binary alkali metal hydrides allows for a convenient preparation of hexahydroaluminates, which are hardly accessible through the wet-chemistry synthetic routes.

Moreover, it became evident that numerous chemical reactions in metal—aluminum or boron—hydrogen systems do not, in fact, require a liquid phase and can be successfully run under solvent-free conditions (Eqs. 1–6).
MH + AlH₃ $\rightarrow$ MAIH₄ \hspace{1cm} (1)⁸,⁹
2MH + 2Al + 3H₂ $\rightarrow$ 2MAIH₄ \hspace{1cm} (2)¹⁰,¹¹
MAIH₄ + 2MH $\rightarrow$ M₃AlH₆ \hspace{1cm} (3)¹²,¹³
M₃AlH₆ + 2AlH₃ $\rightarrow$ 3MAIH₄ \hspace{1cm} (4)⁸,⁹

$M = \text{Li, Na}$

TiCl₃ + 3LiBH₄ $\rightarrow$ Ti(BH₄)₃ + 3LiCl \hspace{1cm} (5)¹⁴
UCl₄ + 4LiBH₄ $\rightarrow$ U(BH₄)₄ + 4LiCl \hspace{1cm} (6)¹⁴

The mechanochemical technique has also helped to identify some of the titanium-species that form during doping of alkali metal aluminohydrides or magnesium hydride with Ti-salts (Eqs. 7,8).¹⁵–¹⁷ Another result of mechanochemical studies is the discovery of Ti-catalyzed decompositions of LiAlH₄ at room temperature upon mechanical milling.¹⁸

nMAIH₄ + TiClₙ $\rightarrow$ nMCl + Al + TiAl₃ + [TiH]ₓ(traces) + H₂ \hspace{1cm} (7)¹⁵,¹⁶

$M = \text{Li, Na; } n = 3,4$

MgH₂ + TiCl₃ $\rightarrow$ MgCl₂ + TiH₂ \hspace{1cm} (8)¹⁷

Along with fundamental studies into the solid-state reactivity of metal and boron hydrides, solvent-free mechanochemistry has been successfully used in the preparation of binary and complex metal hydrides (Eqs. 9–12) as well as low molecular weight gases such as the extremely toxic diborane (Eq. 13). The latter can also form as a by-product in other mechanically induced processes involving alkali metal borohydrides and transition metal salts¹⁴ (for more examples see the article by G. Soloveichik on page 11).

M + H₂ $\rightarrow$ MHₓ \hspace{1cm} (9)¹⁹

$M = \text{Mg, Ti, Zr, Nb } x=1–2$

MgCl₂ + 3LiAlH₄ $\rightarrow$ LiMg(AlH₄)₃ + 2LiCl \hspace{1cm} (10)²⁰

3LiAlD₄ + AlCl₃ $\rightarrow$ 4AlD₃ + 3LiCl \hspace{1cm} (11)²¹

MgH₂ + Co $\rightarrow$ MgCoH₅ \hspace{1cm} (12)²²

2NaBH₄ + SnCl₂ $\rightarrow$ 2NaCl + Sn + 2H₂ + B₂H₄ \hspace{1cm} (13)¹⁴

A number of other mechanically induced transformations involving metal alloys, amides, nitrides, and nano-materials has been published during the last decade. Due to the limited size of this publication, they will be discussed in the future.

**Mechanism of Mechanochemical Reactions**

Even a brief glimpse at the previous paragraphs is sufficient to realize the extreme diversity and complexity of solid-state processes that can occur in a crystalline solid trapped between
steel or ceramic balls, colliding in a tightly-closed vial. Indeed, high-energy ball-milling brings about a broad variety of defects including cracks, pores, dislocations, vacancies, new surfaces, grain, twin boundaries, and others. Prolonged milling can also destroy crystallinity of the material leading to its complete or partial amorphization. Changes in a solid crystalline material under mechanical stress start with its elastic deformation, which disappears once the load is lifted. If, however, the load increases, the elastic deformation transforms into an irreversible plastic deformation, which is followed by the fracture and/or amorphization of the material. Plastic deformations normally occur under shear stress, parallel to the face of the material, as opposed to brittle fractures that take place under normal stress perpendicular to the face (Figure 2).

Figure 2. Changes in the material trapped between colliding balls in a ball mill.

Thus, physicochemical effects of mechanical milling include breaking crystallinity, creating new surfaces, and mass transfer (mixing).

The constant formation of a new surface and mass transfer are major factors responsible for the enhanced reactivity of metals toward hydrogen under ball-milling (Eq. 9). At the same time, these effects cannot be solely responsible for solid-to-solid reactions discussed previously as well as for the transformations in other molecular and ionic solids shown in Figure 3.24–26
These studies revealed that mechanochemical reactions in molecular and ionic solids are not temperature-driven processes. In a number of cases, the temperature increase in the material during milling is well below their melting or decomposition points. In addition, the theoretical analysis of a ball-milling process in a commercial Spex-type shaker mill revealed a moderate temperature effect (~60 °C). According to the same study, the pressure generated in the solid, trapped between two colliding balls, can rise as high as several GPa, thus facilitating genuine ultra-high pressure activated processes.

Some additional insight into the nature of mechanically induced chemical reactions is provided by the photochemical dimerization of anthracene (Figure 4). It occurs readily in solution but does not take place in the solid state because of the unfavorable orientation of anthracene molecules in the crystal. No photochemical reaction is observed when crystalline anthracene is subjected to high hydrostatic pressure up to 10 GPa. However, once external pressure is combined with a shear stress, the photochemical reaction becomes possible. Apparently, the high pressure combined with the shear stress not only reduces the distance between molecules but also changes their orientation in the solid, thus making the reaction possible.

Figure 3. Mechanically induced reactions of organic and metal-organic solids.

Figure 4. Photochemical dimerization of anthracene.
In conclusion, mechanochemistry has proven to be an extremely useful tool for the preparation of novel materials as well as for the investigation of chemical transformations that can take place in solids under solvent-free conditions. Although the exact mechanism of mechanochemical phenomena should be determined on a case-by-case basis, it appears that mechanochemical processes in solids are primarily driven by structural changes and high pressure, generated in the material during milling. The crystal structure, lattice energy, and chemical reactivity of the material govern the magnitude of the energy input required for such processes to occur.

References