Metal borohydride ammoniates for hydrogen storage

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Solid state hydrogen materials have been investigated intensively during the last decade as a result of their high hydrogen content. This is attractive, because hydrogen is a promising energy carrier in a future society based on renewable energy. However, hydrogen is typically bonded too strongly by covalent/metalllic/ionic bonds in the major part of the known solid state hydrogen storage materials. This gives rise to high operating temperature for hydrogen release and uptake.

Recently, dihydrogen bonds between partly negative hydrogen from for example BH₄⁻ and partly positive hydrogen atoms from for example NH₃ have shown promising properties. Unlike the classical hydrogen bonds, the dihydrogen bonds can react in the solid state via elimination of hydrogen by exchanging the weak H⁺⋯⁻H interactions for strong covalent bonds, and thus may open new routes to rational design of structures and hydrogen release reaction mechanisms [1].

By a newly developed method, we have synthesized a range of halide-free ammine metal borohydride compounds. These compounds and their decomposition mechanisms have been structurally investigated by in situ powder X-ray diffraction at beamline P.02 at Petra III, DESY, Hamburg, Germany with a PerkinElmer XRD 1621 detector system and wavelengths, λ ~ 0.20 Å. The samples were packed in a sapphire (Al₂O₃) single crystal tube (1.09 mm o.d., 0.79 mm i.d.) using a special designed sample holder [2].

In an ammonia atmosphere Mn(BH₄)₂ forms a hexaammoniate, Mn(BH₄)₂·6NH₃. Mn(BH₄)₂·2NH₃ has subsequently been synthesized by mechanochemical treatment of Mn(BH₄)₂·Mn(BH₄)₂·6NH₃ (2:1). The two structures solved from synchrotron powder X-ray diffraction are shown in Figure 1. While Mn(BH₄)₂·6NH₃ releases NH₃ upon heat treatment, Mn(BH₄)₂·2NH₃ releases hydrogen, likely as a result of strong dihydrogen bonds [3].

Figure 1 The crystal structures of Mn(BH₄)₂·2NH₃ (right) and Mn(BH₄)₂·6NH₃ (left). NH₃ (N green, H light gray) coordinates to magnesium (orange) in the crystal structures, while BH₄ (blue tetrahedra) coordinates either to the metal or acts as a counter ion in the solid state. For clarity, hydrogen atoms in the ammonia molecules are not shown in Mn(BH₄)₂·6NH₃.
Rare earth metal borohydride ammoniates, Re(BH$_4$)$_2$·xNH$_3$ (Re = Y, Gd, Dy) have also been investigated, and a series of new structures have been solved [4]. *In situ* SR-PXD data for Gd(BH$_4$)$_2$·6NH$_3$ heated from RT to 160 °C is plotted in Figure 2. It is clearly seen how the concent of NH$_3$ in the crystal structures are lowered upon heat treatment.

![Figure 2](image)

Figure 2 (Left) *In situ* SR-PXD for Gd(BH$_4$)$_3$·6NH$_3$ measured from RT to 200 °C (5 °C/min, p(Ar) = 1 bar, λ = 0.2072 Å) at Petra III. (Right) Integrated intensities of selected reflections. Symbols: □ Gd(BH$_4$)$_3$·6NH$_3$; ● Gd(BH$_4$)$_3$·5NH$_3$; □ Gd(BH$_4$)$_3$·4NH$_3$

References