Rapid solid-state transformation of tetrahedral $[AlH_4]^-$ into octahedral $[AlH_6]^{3-}$ in lithium aluminohydride

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Polycrystalline $LiAlH_4$ transforms into polycrystalline Li_3AlH_6 and Al during short time (5 min) ball-milling with 3 mol% $TiCl_4$ at room temperature; solid-state rearrangement of tetrahedral $[AlH_4]^-$ into octahedral $[AlH_6]^{3-}$ at ambient conditions was previously unknown; this transformation does not occur during ball-milling of pure $LiAlH_4$ or in the presence of 3 mol% $TiCl_4$ without mechanochemical treatment.

High capacity solid-state storage of hydrogen is becoming increasingly important as fuel cell power plants approach broad use in automotive and electrical utility applications. Overall hydrogen content of two alkali metal aluminohydrides, $LiAlH_4$ and $NaAlH_4$ (10.5 and 7.3 wt% H_2, respectively), is amongst the highest for about 70 known complex hydrides[1] reviving recent interest to them as potential ultra-high capacity hydrogen storage solids.[2–6] Temperature induced transformation of lithium aluminohydride ($LiAlH_4$) into lithium hexahydroaluminate (Li_3AlH_6) has been known for almost three decades.[7] However, the processes occurring in pure $LiAlH_4$ during its thermal decomposition were understood only recently.[8,9] According to results obtained by Bastide *et al.*[8] and Dymova *et al.*,[9] $LiAlH_4$ is quite stable in the solid state below its melting temperature but rapidly transforms in the melt, where rearrangement of the tetrahedral $[AlH_4]^-$ ion into the octahedral $[AlH_6]^{3-}$ ion[10,11] is easily achieved. The stability of the solid $LiAlH_4$ is, therefore, attributed to kinetic restrictions of the solid-state transformation process in the alumohydride anion rather than to thermodynamic reasons (ΔG of the reaction $LiAlH_4 = 1/3Li_3AlH_6 + 2/3Al + H_2$ is -27 kJ mol^{-1}).[12] Recently, a significant reduction of the decomposition temperatures of alkali metal aluminium hydrides doped with transition metal derivatives has been reported.[3–6] It is, however, unclear, whether transition metal dopants reduce melting points of complex aluminium hydrides or act as catalysts of solid-state transformations near the respective melting temperatures.

Here we report on the first observation of the rapid solid-state transformation of lithium aluminohydride into lithium hexahydroaluminate in the presence of a catalytic amount of titanium tetrachloride ($TiCl_4$) during mechanochemical activation at ambient conditions.† A reaction mixture containing 97 mol% $LiAlH_4$ and 3 mol% $TiCl_4$ was ball-milled in a Spex mill under helium for 5 min and then investigated using X-ray powder diffraction (XRD), differential thermal (DTA) and gas-volumetric analyses. According to XRD data, $LiAlH_4$ was completely transformed during the short mechanochemical treatment with a catalytic quantity of $TiCl_4$. Only Bragg peaks corresponding to the crystalline Li_3AlH_6,[13a] Al and LiCl are seen in the X-ray powder diffraction pattern of the reaction mixture (Fig. 1). The DTA trace of the reaction mixture in the temperature range between 380 and 500 K contains one broad endothermic peak between approximately 395 and 485 K with a minimum at 445 K (inset in Fig. 2). The endothermic process occurs at lower temperatures when compared to that observed in the pure mechanochemically prepared Li_3AlH_6[13a] (*ca.* 480–535 K, minimum at 505 K). This lowering of the hydrogen release temperature is, however, in good agreement with previously reported data on reduction of decomposition temperature of transition metal-doped alkali metal aluminohydrides.[3–5] The gas-volumetric analysis of the reaction mixture between 295 and 675 K in vacuum revealed a slow one-step hydrogen evolution at 395 ± 5 K (Fig. 2), *i.e.* at the onset temperature of the endothermic effect observed in the DTA experiment. The amount of released hydrogen, 2.08 wt%, agrees well with the decomposition of Li_3AlH_6 [eqn. (1)], which was formed according to eqn. (2) (the theoretical hydrogen content in the mixture is 2.1 wt%). The intensities of Bragg peaks (Fig. 1) are in quantitative agreement with the amounts of reaction products. Eqn. (2) summarizes transformations of $LiAlH_4$ and $TiCl_4$ during ball-milling [eqns. (3) and (4)]:

$$2Li_3AlH_6 = 6LiH + Al + 3H_2\uparrow \qquad (1)$$

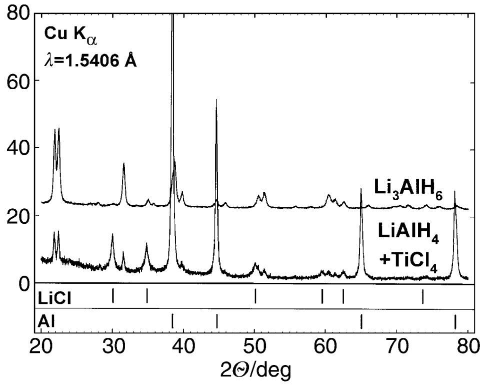

Fig. 1 The X-ray powder diffraction pattern of the reaction mixture obtained during 5 min ball-milling of 97 mol% $LiAlH_4$ and 3 mol% $TiCl_4$ compared with the X-ray powder diffraction pattern of Li_3AlH_6 prepared mechanochemically.[13] Vertical bars at the bottom of the chart indicate positions of Bragg peaks of pure LiCl and Al.

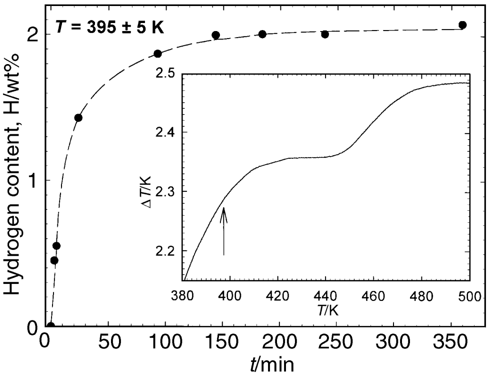

Fig. 2 The results of gas-volumetric analysis at 395 ± 5 K of the reaction mixture obtained during 5 min ball-milling of 97 mol% $LiAlH_4$ with 3 mol% $TiCl_4$. The inset shows the DTA trace of the same reaction mixture. The vertical arrow on the inset indicates the onset of the endothermic process.

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$$0.97LiAlH_4 + 0.03TiCl_4 = 0.283Li_3AlH_6 + 0.12LiCl + 0.687Al + 0.03[Ti] + 1.091H_2\uparrow \quad (2)$$

$$4LiAlH_4 + TiCl_4 = 4LiCl + 4Al + [Ti] + 2H_2\uparrow \quad (3)$$

$$3LiAlH_4 + [Ti] = Li_3AlH_6 + 2Al + [Ti] + 3H_2\uparrow \quad (4)$$

The formation of lithium chloride, aluminium and a Ti-containing micro-crystalline phase with unknown composition during 5 min ball-milling of lithium aluminohydride and titanium tetrachloride was confirmed by mechanochemical treatment of stoichiometric amounts (4 : 1) of $LiAlH_4$ and $TiCl_4$ [eqn. (3)].[13b] No Bragg peaks corresponding to either $LiAlH_4$ or Li_3AlH_6 were detected from XRD data. Furthermore, the gas-volumetric analysis of the obtained reaction mixture [eqn. (3)] did not reveal observable hydrogen gas evolution up to 925 K.

To verify that the titanium catalyzed solid state transformation of $LiAlH_4$ into Li_3AlH_6 proceeds only during mechanochemical activation, the mixture containing 97 mol% of lithium aluminohydride and 3 mol% of titanium tetrachloride was thoroughly ground in a mortar under helium for 10 min. Although slight changes of the reaction mixture color from grayish-white to gray were observed, XRD did not indicate the formation of detectable amounts (*i.e.* 5 vol% or more) of Li_3AlH_6 during grinding. Weak Bragg peaks corresponding to polycrystalline LiCl and Al were found in the X-ray diffraction pattern of the reaction mixture after grinding, and therefore, the observed color changes were likely associated with the reduction of $TiCl_4$ by $LiAlH_4$ according to eqn. (3). Furthermore, our experiments with pure $LiAlH_4$ revealed that this complex hydride is stable during ball-milling without $TiCl_4$ for up to 35 h.

Currently, several different models describing the observed rapid solid-state rearrangement of $LiAlH_4$ (*i.e.* tetrahedral $[AlH_4]^-$ ion) into Li_3AlH_6 (*i.e.* octahedral $[AlH_6]^{3-}$ ion) in the presence of $TiCl_4$ during mechanochemical treatment at ambient conditions are being considered. One of the most likely mechanisms explaining the catalytic effect of $TiCl_4$ can be its reduction to a highly reactive nanocrystalline or amorphous titanium phase [eqn. (3)], which subsequently mechanically alloys into the crystal lattice of $LiAlH_4$. The following destabilization of the host crystal lattice caused by the presence of titanium leads to the formation of metastable 'melt-like' hydride phases, where the rearrangement of the tetrahedral $[AlH_4]^-$ ion into the octahedral $[AlH_6]^{3-}$ ion becomes kinetically possible. Although the nature of intermediate phase(s) is presently unclear, it is feasible that they are similar to the metastable high-pressure γ-$LiAlH_4$ with hexa-coordinated $[AlH_6]^{3-}$ ion,[10,15] and their formation becomes possible due to mechanically induced strain in the presence of titanium catalyst.

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Notes and references

† All experiments described in this communication were carried out in a glove box in a purified helium atmosphere and in a hardened-steel vial sealed under helium. The X-ray diffraction experiments were performed under helium in a sample holder covered by X-ray transparent polymer film. The differential thermal analysis was carried out in an argon atmosphere at ambient pressure using commercially available equipment. The heating rate during DTA measurements was 10 K min^{-1}. The gas-volumetric experiments were performed using a standard Sievert's type apparatus.

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13 (*a*) Solvent free Li_3AlH_6 was prepared by ball-milling of 0.80 g (0.1 mol) LiH and 1.90 g (0.05 mol) $LiAlH_4$ in a helium atmosphere for 5 h. *Crystal data*: for Li_3AlH_6 monoclinic, space group $P2_1/c$, a = 5.667(1), b = 8.107(2), c = 7.917(2) Å, β = 92.17(1)°, V = 363.5(2) $Å^3$, M = 53.8, Z = 4, T = 298 K . The obtained lattice parameters are in excellent agreement with the previously reported data[14] for conventionally prepared Li_3AlH_6; (*b*) ball-milling of stoichiometric amounts of $LiAlH_4$ and $TiCl_4$ was carried out in a Spex mill in a hardened-steel vial sealed under helium. According to XRD, the reaction mixture contains polycrystalline LiCl, Al and an unidentified intermetallic $Ti_{1-x}Al_x$ phase.

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