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Effect of several metal chlorides on the thermal decomposition behaviour of α -Mg(BH₄)₂

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ABSTRACT

Mechanochemical alloying of Mg(BH₄)₂ with small amounts of metal chlorides (PdCl₂, TiCl₃, VCl₃, MoCl₃, RuCl₃, CeCl₃ and NbCl₅) results in the formation of transition metal doped nanocomposites with different hydrogen desorption properties. The thermal decomposition properties of ball-milled as well as doped α -Mg(BH₄)₂ have been studied. An amorphization reaction of Mg(BH₄)₂ is induced by ball milling, nevertheless a partial recrystallization of the alpha phase takes place after heating up to 150 °C. The effect of ball milling Mg(BH₄)₂ with each additive has been investigated in detail by using differential scanning calorimetry, thermogravimetric analysis and X-ray diffraction. The onset temperature of Mg(BH₄)₂ is lowered by more than 100 °C through the addition of Nb- or Ti chloride. Moreover, a mixed Ti-Nb-nanocomposite was also synthesized and investigated. The onset temperature of hydrogen evolution during decomposition of the mixed Ti-Nb-nanocomposite is considerably lowered by up to 125 °C.

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1. Introduction

Complex hydrides and especially light metal borohydrides have been studied as hydrogen storage materials because of their very high gravimetric and volumetric hydrogen densities [1,2]. An interesting candidate is Mg(BH₄)₂ due to its gravimetric hydrogen density of 14.9 mass % and the small overall enthalpy change of approximately 40 kJ mol⁻¹ H₂, which suggests potential reversibility within the desired range of desorption temperatures [3,4]. However, the main disadvantages of Mg(BH₄)₂ as hydrogen store are the high absorption/desorption kinetic barriers and stable intermediates preventing the reversibility of the material as well as reasonable low sorption temperatures so far. Hence, intensive research efforts have been carried out in order to elucidate the reaction mechanisms of Mg(BH₄)₂ and to identify potential reaction pathways for a reversible reaction as well as intermediate

phases [5–13]. Kinetic barriers of Mg(BH₄)₂ have recently been decreased by confinement of the complex hydride in micro-porous scaffolds like a carbon matrix [14] and/or by the addition of a dopant [15,16].

It is well known that transition metal chlorides show catalytic activity for complex hydrides. For instance, TiCl₃ [17] as well as ScCl₃, PrCl₃ and CeCl₃ [18] have considerably improved the performance of NaAlH₄. More recently the enhancement of the hydrogen sorption properties of Ca(BH₄)₂ by addition of both TiCl₃ and NbCl₅ has been investigated [19] and Rongeat et al. [20] have shown the strong effect of the presence of chlorides on the synthesis and decomposition of Ca(BH₄)₂. Additionally, Au et al. [21] and Kostka et al. [22] have reported the results of using various metal compounds as additives to modify LiBH₄ for reversible hydrogen storage.

The aim of this experimental work is to reduce the desorption temperature and to systematically study the effect

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of different metal chlorides on the dehydrating behaviour of $\text{Mg}(\text{BH}_4)_2$.

2. Experimental section

$\text{Mg}(\text{BH}_4)_2$ was synthesized by a direct wet chemical synthesis [23] from pre-milled MgH_2 (98%, Alfa-Aesar) and $\text{Et}_3\text{N}\cdot\text{BH}_3$ (97%, Sigma Aldrich). MCl_x (PdCl_2 , VCl_3 , MoCl_3 , RuCl_3 , CeCl_3 and NbCl_5 , with purity > 99%) were purchased by Alfa-Aesar whereas TiCl_3 (98%) was purchased by Acros, and used as received. All samples were handled in a glove box filled with a recirculated argon atmosphere where the water and oxygen concentrations were kept below 1 ppm.

High-energy ball milling was carried out by using a Fritsch P6 planetary mill. One gram of each mixture of $\text{Mg}(\text{BH}_4)_2$ and the corresponding amount of metal chloride (5 mol%) was charged together with one 20 mm diameter and seven 10 mm diameter silicon nitride balls into a vial of the same material under an argon atmosphere. The ball-to-powder ratio was approximately 25:1. The milling was performed at 600 rpm for 1 h and was interrupted for 10 min after 30 min of milling to avoid temperature rising. Then ca. 100 mg of the sample were kept and the rest was milled for additional 11 h at the same conditions.

Powder X-ray diffraction patterns were obtained by using a Philips X'PERT diffractometer (Cu $K\alpha$ radiation). The powder was spread on a silicon single crystal and sealed in a glove box by an airtight hood of Kapton foil. *In-situ* XRD studies were performed with the same instrument under a He flow using an HTK 1200 sample holder made by Anton Paar GmbH. The samples were heated from room temperature to 130 °C and temperature was increased stepwise. The data were taken every 20 °C between 130 °C and 420 °C. The measuring time at each temperature step was approximately 1 h.

Simultaneous thermogravimetric analysis and mass spectrometry (TG-MS) was performed by using a Netzsch STA 409 C analyzer equipped with a Balzers quadrupole mass spectrometer for the analysis of the evolved gas. The measurements were performed under a gas flow of 30 ml He min^{-1} and heating rate of 2.5 °C min^{-1} by using open Al_2O_3 crucibles.

High-pressure differential scanning calorimetry (HP-DSC) was performed by using a Netzsch DSC 204 HP placed inside an argon-filled glove box with partial pressures of oxygen and water below 1 ppm. The samples were measured by using Al_2O_3 crucibles and Al_2O_3 lids at 5 bar H_2 and at a heating rate of 5 °C min^{-1} to 500 °C and at a cooling rate of 5 °C min^{-1} to 50 °C.

Elemental analysis of carbon, nitrogen and hydrogen was performed with CE Instruments Flash EA 1112 series analyzer using He as the purge gas. The typical amount of the sample was 1–3 mg.

3. Results and discussion

3.1. As-synthesized and ball-milled $\alpha\text{-Mg}(\text{BH}_4)_2$

It is well-known that magnesium borohydride exhibits two different modifications of the structure depending on the

temperature [24,25]. When $\alpha\text{-Mg}(\text{BH}_4)_2$ is heated to approx. 190 °C (under inert gas or hydrogen atmosphere) an irreversible polymorphic transition to $\beta\text{-Mg}(\text{BH}_4)_2$ takes place indicating that $\alpha\text{-Mg}(\text{BH}_4)_2$ is a metastable modification [23]. Additionally, Li et al. [15] have reported the effect of ball milling on the dehydrating reaction of $\beta\text{-Mg}(\text{BH}_4)_2$, suggesting that first, an amorphization reaction is induced by ball milling and second, further crystallization into $\beta\text{-Mg}(\text{BH}_4)_2$ takes place upon heating to 140 °C for 2 h.

In this work, the dehydrating behaviour of milled $\alpha\text{-Mg}(\text{BH}_4)_2$ was analyzed by using HP-DSC and XRD. Fig. 1 shows the DSC data of the material measured under 5 bar hydrogen and at a heating rate of 5 °C min^{-1} . The main decomposition of milled $\text{Mg}(\text{BH}_4)_2$ occurs between 250 °C and 450 °C, similar to the as-synthesized $\text{Mg}(\text{BH}_4)_2$ [10]. Nevertheless, four endothermic decomposition peaks (b–e) can be assigned to the decomposition of the as-synthesized material, but just three endothermic peaks (b'–d') can be observed in this region for the milled material. The peak corresponding to the phase transformation at around 190 °C (a) is slightly shifted down to lower temperature for the milled material (a') and furthermore, an exothermic peak at 150 °C appears in the DSC curve of the sample after milling during 12 h. In order to determine the origin of this exothermic peak, XRD measurements of the milled sample after heating in the DSC were performed.

Fig. 2 shows the XRD profiles of the borohydride after ball milling during 12 h and after heating up to 175 °C and 200 °C, respectively. As shown in Fig. 2a, the diffraction peaks of $\alpha\text{-Mg}(\text{BH}_4)_2$ disappear after milling while the peaks corresponding to $\beta\text{-Mg}(\text{BH}_4)_2$ can be localized on the XRD pattern. Nevertheless, the contribution of both low and high temperature modifications can be detected after the exothermic peak at 150 °C (Fig. 2b). These results suggest that first, an amorphization reaction of $\alpha\text{-Mg}(\text{BH}_4)_2$ as well as a partial polymorphic transformation into the $\beta\text{-Mg}(\text{BH}_4)_2$ and grain refinement take place during milling and second, the exothermic peak in the DSC profile originates from the recrystallization of amorphous $\text{Mg}(\text{BH}_4)_2$. Moreover, the recrystallization of the amorphous phase leads to the formation of $\alpha\text{-Mg}(\text{BH}_4)_2$ which is known to be (thermally) non-

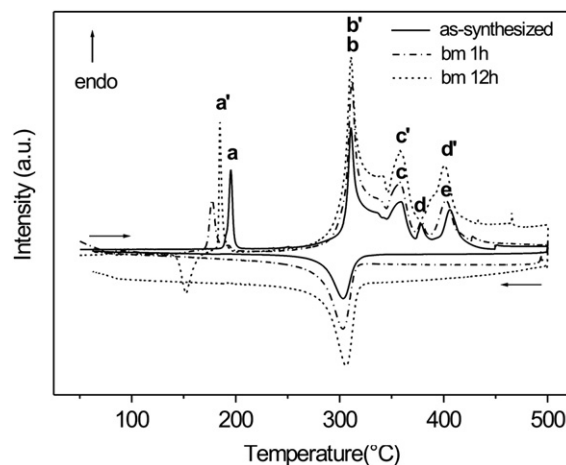


Fig. 1 – HP-DSC profiles of $\text{Mg}(\text{BH}_4)_2$ under 5 bar H_2 and at a heating rate of 5 °C min^{-1} : as-synthesized, after ball milling for 1 h and after ball milling for 12 h.

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