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The influence of ball-milling time on the dehydrogenation properties of the NaAlH₄–MgH₂ composite

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ABSTRACT

The recently developed NaAlH₄–MgH₂ composite shows improved hydrogen-storage properties compared to MgH₂ and NaAlH₄. However, the dehydrogenation reaction rates are still too limited, hampering practical applications. Mechanical ball milling is broadly used to improve the dehydrogenation reaction rates of hydrides. Therefore, the hydrogen-storage properties of the NaAlH₄–MgH₂ (1:1) composite have been investigated as a function of ball-milling time. Expectedly, elongated milling led to a faster dehydrogenation rates. New insights of the structural transformation pathways of the decomposition reaction are provided. A number of Al–Mg alloys, including the only reported Al₁₂Mg₁₇, seem to participate in the dehydrogenation. Thereby, complex alloying process of Al with Mg or MgH₂ has been proposed. Our data indicate the possibility that hydrides Na₃AlH₆ and NaMgH₃, which are the intermediate products of the dehydrogenation, coexist. The study shed a light on the complexity of the decomposition pathways of hydride mixtures in which the key role play alloys.

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Introduction

Nowadays, the growing energy demand and increasing levels of green-house gasses urges the development of alternative energy solutions [1,2]. Amongst many potential solutions a hydrogen-based economy attracts considerable attention. This is based on the so-called ‘green energy’ concept that is

realised as a closed cycle process. At the start of this cycle, hydrogen can directly be produced from water by using sunlight, e.g. by photo-catalysis or indirectly by combining solar cells with electrolysis of water [3]. Subsequently, hydrogen must be stored efficiently for a safe transport. Finally, the green cycle is closed when hydrogen is oxidized together with oxygen to deliver energy and water [4,5]. However,

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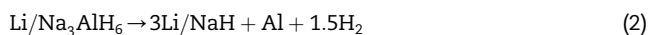
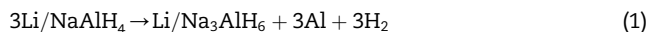
implementation of the hydrogen-based economy suffers of a severe bottleneck. Efficient and safe hydrogen-storage is still very challenging, especially for the automotive industry applications [6].

The most promising methods to store hydrogen are by means of chemisorption and physisorption. In the latter case, most attractive sorbents are used with a large surface area that requires very low temperatures, as low as liquid nitrogen, to storage the hydrogen. These methods reveal good sorption kinetics and often reasonable storage capacities [7]. The chemisorption method is mostly dominated by alkali- and alkaline-earth metal hydrides that often require elevated temperatures for sorption and show high storage capacity. In this group a large number of compounds are composed of light-weight metals like Li and Na.

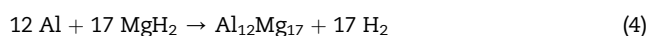
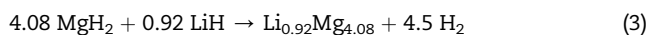
Both metals are able to form so-called alanates, such as LiAlH_4 [8,9] and NaAlH_4 [9]. These alanates have been intensively investigated as prospective complex hydrides with a high theoretical gravimetric storage capacity of 10.6 and 7.5 wt.% for LiAlH_4 and NaAlH_4 , respectively [10].

Thermodynamic destabilization of complex hydrides can be achieved by using an additional hydride that results in the formation of intermediate phases. Attractive hydride composites have been developed, like $\text{LiAlH}_4\text{-MgH}_2$ [11] and $\text{NaAlH}_4\text{-MgH}_2$ [12–14], which have a high storage capacity of 9.4 and 7.6 wt.%, respectively. So far, much emphasis in the hydrogen-storage community was dedicated to the $\text{LiAlH}_4\text{-MgH}_2$ system. Regarding the $\text{NaAlH}_4\text{-MgH}_2$ system only a few limited investigations have been carried out, which leave much space for further improvements of the composite and to get more in-depth knowledge.

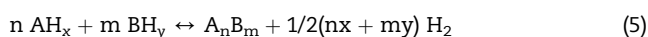
The process of the thermodynamic destabilization of $\text{LiAlH}_4\text{-MgH}_2$ and $\text{NaAlH}_4\text{-MgH}_2$ involves complex multi-step reactions. Firstly, LiAlH_4 and NaAlH_4 are expected to form intermediate complex hydrides (Li_3AlH_6 or Na_3AlH_6) during the decomposition. Furthermore, hydrogen gas, Al and metal hydrides (LiH or NaH) are formed, according to a two-step reaction [11–14].



The studies in which various molar ratios of $\text{LiAlH}_4\text{:MgH}_2$ (1:1, 1:2 and 1:4) were used, revealed that the dehydrogenation pathway follows always the reactions (1) and (2) [15]. It has been described that $\text{Li}_{0.92}\text{Mg}_{4.08}$ and $\text{Al}_{12}\text{Mg}_{17}$ alloys are formed as well [11,16], according to the following reactions



Reaction (3) has been described in more general terms in Ref. [17].



It is believed that the above alloys play a dominant role in the thermodynamic destabilization of the $\text{LiAlH}_4\text{-MgH}_2$ composites [11,15–17].

The investigation of $\text{NaAlH}_4\text{-MgH}_2$ [14] revealed two possible reaction schemes (1:4 and 1:2 vs. 1:1), unlike $\text{LiAlH}_4\text{-MgH}_2$ (1:1, 1:2 and 1:4) [11]. The $\text{NaAlH}_4\text{-MgH}_2$ (1:1) composition [13,14] is expected to form the dehydrogenation product Na_3AlH_6 and follow the anticipated reactions (1), (2) and (4) [11,13,14]. Further decomposition of NaH and residual MgH_2 leads to hydrogen gas and respective metals without the formation of a Na–Mg alloy.

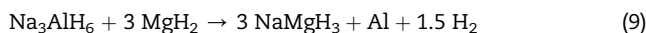
The $\text{NaAlH}_4\text{-MgH}_2$ (1:4 and 1:2) composites are proposed to dehydrogenate via intermediate products such as $\text{Al}_{12}\text{Mg}_{17}$ (reaction (4)) and NaMgH_3 [12–14], without the formation of Na_3AlH_6 . It is expected that the formation of the $\text{Al}_{12}\text{Mg}_{17}$ alloy during dehydrogenation improves the thermodynamic properties of the $\text{NaAlH}_4\text{-MgH}_2$ system [12,14]. NaMgH_3 is formed according to



It is not clear yet why the reaction (6) was not observed in the $\text{NaAlH}_4\text{-MgH}_2$ composites with the molar ratio of 1:1 [13,14] but only in the mixtures with excess MgH_2 [12,14]. Furthermore, the decomposition of the excess MgH_2 into Mg and hydrogen as well as reaction (4) take place. At a later stage of the dehydrogenation process, NaH and NaMgH_3 decompose according to



Recently, it has been reported that during the dehydrogenation of the $\text{Na}_3\text{AlH}_6\text{-MgH}_2$ mixture, NaMgH_3 can also be formed [18].



The decomposition reactions of the $\text{NaAlH}_4\text{-MgH}_2$ and $\text{Na}_3\text{AlH}_6\text{-MgH}_2$ composites as presented above indicate the possibility of a coexistence of the intermediate hydrides Na_3AlH_6 and NaMgH_3 since both can be formed from the same hydride mixtures. So far, it was suggested that the reported $\text{NaAlH}_4\text{-MgH}_2$ mixture dehydrogenates exclusively via one intermediate hydride NaMgH_3 or Na_3AlH_6 which depends on the molar ratio of the primary hydrides. However, the X-ray diffraction (XRD) reflections of these ball-milled samples may show much overlap, since the crystallinity is typically significantly decreased by grinding, which may lead to issues with the data interpretation.

The goals of the present study are twofold. Firstly, to analyse the influence of the high-energy ball-milling on the dehydrogenation properties as a function of time and secondly, to gain more knowledge about the structural transformation pathways of the $\text{NaAlH}_4\text{-MgH}_2$ (1:1) composite.

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