

Preparation of Ti-Doped Sodium Aluminum Hydride from Mechanical Milling of NaH/Al with Off-the-Shelf Ti Powder

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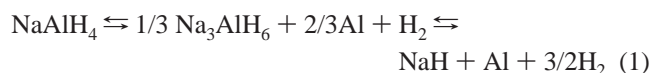
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Ti-doped NaAlH₄ can be directly prepared by mechanical milling a 1:1 mixture of NaH and Al together with a few mole percent of off-the-shelf metallic Ti powder under an argon or hydrogen atmosphere. The hydrogen storage materials that are produced through this process exhibit stable hydrogen capacities through 10 cycles of hydrogenation/dehydrogenation. We have conducted a systematic investigation of this new method for the preparation of Ti-doped NaAlH₄. Consideration of these results, together with those previously obtained for NaAlH₄ that was doped with Ti powder through milling under a hydrogen atmosphere, has provided insight into the nature of active Ti species.

Introduction

Sodium aluminum hydride has been found to undergo reversible elimination of hydrogen at moderate temperatures upon doping with a few mole percent of selected transition metal compounds.^{1,2} This finding has stimulated extensive study of doped NaAlH₄ and other light-metal complex hydrides as viable candidates for onboard hydrogen storage applications.^{3–28} Studies of Ti-doped NaAlH₄ have led to considerable improvement in the kinetic and cycling performance at conditions that are relevant to the practical operation of a PEM fuel cell.^{3–13} However, despite this progress, practical hydrogen storage capacities of only 3–4 wt % have been achieved for Ti-doped NaAlH₄. This is far from the theoretical value of 5.6 wt % for NaAlH₄ undergoing dehydrogenation to NaH and Al as seen in eq 1.



The current state-of-the-art doping technology involves the use of high-valence Ti compounds as dopant precursors. Utilization of these precursors is known to result in the production of nonvolatile byproducts that occupy a significant weight percentage and constitute “dead weight” in the doped materials. For example, it has been well established that the use of TiCl₃ or TiCl₄ as the dopant precursor gives rise to the production of NaCl.^{11,14,27} The incorporation of Na and/or Al in these byproducts also results in a significant reduction in the amount of the parent hydride that is available for hydrogen storage.¹¹ Clearly, the identification of a method for effectively doping NaAlH₄ without generating “dead weight” byproducts would be an important advance in the development of doped NaAlH₄ as practical hydrogen storage media. Limited success toward this goal has been achieved through ball milling NaAlH₄ with Ti13•6THF.^{12,13}

We recently reported a method whereby off-the-shelf Ti powder could be used directly to prepare Ti-doped NaAlH₄ through mechanical milling.²⁸ Unfortunately, the hydride that

was obtained through this direct Ti doping process suffers from serious cycling degradation and dehydriding kinetics that are inferior to doped hydride produced by mechanical milling with Ti(III) or Ti(IV) precursors.^{3–11} These results did, however, suggest that more than one Ti species might be produced by the doping process. Thus, current thinking concerning the nature of active Ti species in the doped hydrides might be oversimplified; it is possible that more than one Ti species contributes to the kinetic enhancement of the dehydrogenation of NaAlH₄.

The practical and economical advantages of introducing dopants into sodium aluminum hydride during its “direct synthesis” from NaH and Al have long been appreciated.^{8,23} As an alternative approach to our direct utilization of Ti powder as dopant precursor, we have explored mechanical milling the mixture of NaH and Al with off-the-shelf Ti powder. The materials obtained through this doping procedure, unlike the material that is prepared through mechanical milling of NaAlH₄ with Ti powder under a hydrogen atmosphere, have been found to undergo a stable hydrogenation/dehydrogenation cycle. We have also observed that variation of the conditions that are employed for milling of the NaH/Al mixtures together with Ti powder leads to significant differences in the hydrogen storage performance.

Experimental Section

The starting materials, NaH (95%, ~200 mesh), Al powder (99.95+%, ~200 mesh), and Ti powder (99.98%, ~325 mesh), were all purchased from Aldrich Co. The mixture of NaH + Al + Ti in a mole ratio of 1:1:0.04 was mechanically milled using a Fritsch 6 Planetary mill at 400 rpm in a stainless steel bowl together with eight 7-mm diameter steel balls. The milling was performed under a hydrogen or argon atmosphere, with initial pressures of about 0.8 and 0.1 MPa, respectively. The ball-to-powder ratio varied between 30:1 and 40:1.

Hydrogen absorption/desorption behavior was monitored with a carefully calibrated Sievert's-type apparatus (LESCA Co., Japan). Precise pressure measurement and temperature controlling were accomplished by using a high-precision pressure transducer and a silicon oil bath, respectively. A typical cyclic experiment entailed absorption at 120 °C and desorption at 150

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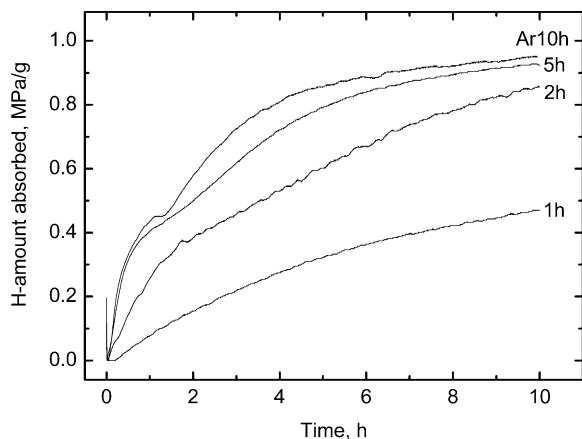


Figure 1. First hydrogenation profiles at 120 °C of NaH + Al + 4 mol % Ti mechanically milled under an Ar atmosphere for different periods.

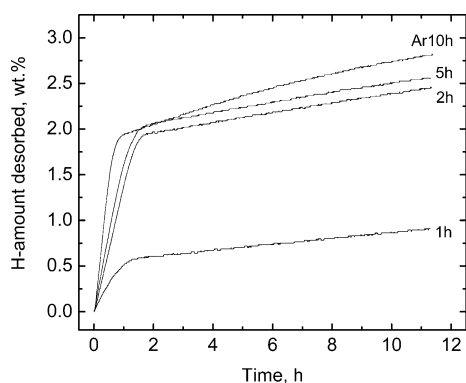


Figure 2. First dehydrogenation profiles at 150 °C of NaH + Al + 4 mol % Ti mechanically milled under an Ar atmosphere for different periods.

°C. The initial pressure conditions were ~ 12 MPa and < 1 Torr, respectively. To allow a practical evaluation of the hydrogen storage performance, the weight of metallic Ti was taken into account in the determination of H capacity.

Results and Discussion

We had previously found that a reactive H_2 atmosphere was required to achieve effective Ti doping of $NaAlH_4$ using Ti powder.²⁸ Thus, it was surprising to find that effective Ti doping could be achieved upon mechanical milling of 1:1 mixtures of NaH and Al with prescribed amounts of Ti powder under an argon atmosphere. The reversible hydriding/dehydriding behaviors of thus-prepared materials were found to be highly dependent on the milling time. This is inconsistent with the findings of our earlier study of the doping of $NaAlH_4$ with off-the-shelf Ti powder.²⁸ Kinetic studies were carried out on samples that were mechanically milled under an argon atmosphere for different lengths of time. All of the samples were hydrogenated under identical conditions (including time and initial hydrogen pressure) before being subjected to dehydrogenation. We experienced difficulties in precisely determining the amount of absorbed hydrogen during the high-pressure hydrogenation process; thus, the change in hydrogen pressure was directly used to characterize the hydrogenation kinetics. Representative initial hydrogenation and dehydrogenation profiles are presented in Figures 1 and 2, respectively. The rate of both hydrogenation and dehydrogenation increased with increased milling time. Remarkably, the marked difference in

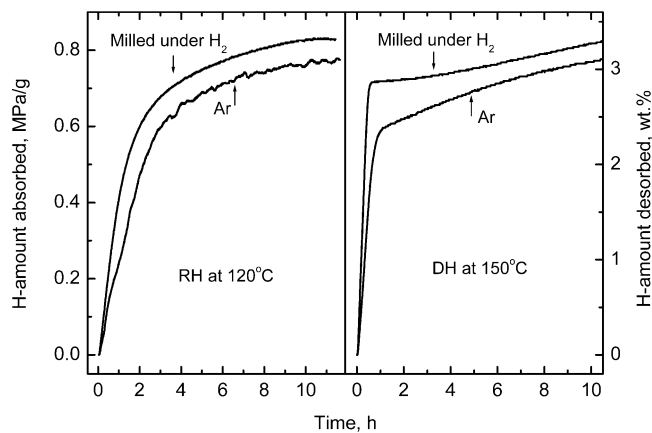


Figure 3. Comparison of the hydrogenation/dehydrogenation profiles in the third cycle between the materials that were prepared by mechanically milling the mixture of NaH + Al + 4 mol % Ti for 10 h under H_2 and Ar atmospheres, respectively. RH, rehydrogenation; DH, dehydrogenation.

kinetic performance arising upon variation of the milling time persisted in the following cycles of hydrogenation/dehydrogenation.

Mechanical milling of NaH/Al mixture with Ti powder under H_2 rather than argon was found to significantly influence the hydrogen storage performance of the doped hydride. Figure 3 compares typical hydrogenation and dehydrogenation profiles of 1:1 mixtures of NaH and Al that were mechanically milled with Ti powder under the differing atmospheres for 10 h. It was observed that the material prepared under a H_2 atmosphere exhibited significant improvements in both the hydrogenation rate and attainable hydrogen capacity vs the material that arises upon milling under an argon atmosphere. Additional, the kinetic behaviors during dehydrogenation were also affected. Similar small, but significant, improvements in hydrogen storage behaviors were also observed in analogous comparison studies of the doped hydrides that were prepared through mechanical milling for 2 and 5 h.

We initially considered the possibility that the mechanical milling of the mixture of NaH and Al with Ti powder under a H_2 atmosphere might result in the direct synthesis of Na_3AlH_6 . To explore this possibility, several samples were intensively milled for long periods. Following only the mechanical milling, none of the samples were found to undergo substantial dehydrogenation at 150 °C, clearly indicating that Na_3AlH_6 was not formed. Apparently, the applied hydrogen pressure was lower than the plateau pressure of Na_3AlH_6 at the local temperatures that were reached during the mechanical milling process.^{6,9}

The hydrogen capacity of the material obtained from the milling of 1:1 NaH and Al with off-the-shelf Ti under a H_2 atmosphere was found to be highly stable. This markedly contrasts with the behavior of the doped hydride obtained through milling $NaAlH_4$ with Ti powder under a H_2 atmosphere, in which a serious cycling degradation on hydrogen capacity was detected.²⁸ Figure 4 compares the cycling dehydrogenation performance between these two materials that were both prepared through mechanical milling under a H_2 atmosphere for 10 h. No signs of degradation of either hydrogen capacity or dehydrogenation kinetics are detectable for the present material after 10 cycles. Unfortunately, the potential for an improved hydrogen capacity upon the elimination of doping byproducts was not realized as only 3.3 wt % hydrogen is available from the material after desorption at 150 °C for 10 h. The low hydrogen cycling capacity is, at least partly, due to the slow kinetics in the second dehydriding step, which is

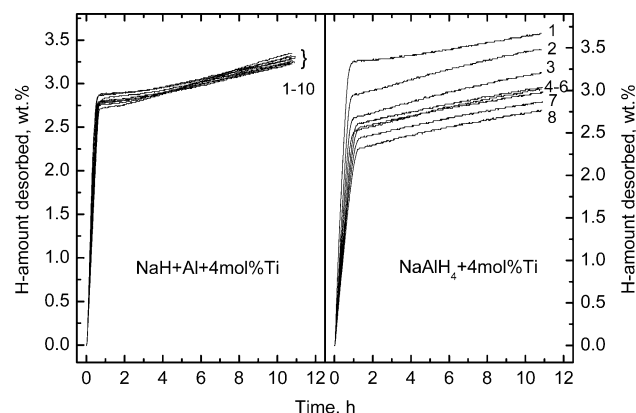


Figure 4. Comparison of the cycling dehydrogenation profiles between $\text{NaH} + \text{Al} + 4 \text{ mol } \%$ Ti and $\text{NaAlH}_4 + 4 \text{ mol } \%$ Ti. Both samples were prepared by mechanical milling under a H_2 atmosphere for 10 h.

significantly inferior to those arising upon doping the hydride with Ti(III) or Ti(IV) dopant precursors.^{3–9,11,14,15} Additionally, the persistent problem of incomplete conversion of Na_3AlH_6 to NaAlH_4 in the rehydrogenation process contributes to the wide gap between the practically attained values and the theoretical values for the available weight percent of hydrogen.²¹ The results of our attempts to resolve the problem of low available hydrogen capacity through a functionally designed, structural modification of doped material (inspired by this study) will be presented in forthcoming publications.

The finding of hydrogen storage performances that are characteristic of the variations in this method of preparation of the Ti-doped hydride has several important implications about the nature of the active Ti species in these materials. Clearly, mechanical milling accomplishes more than merely the high dispersion of the atomic Ti on the surface of the hydride^{1,6,9} as changes in the milling atmosphere and/or the bulk environment (hydrogenated vs dehydrogenated form) exert influences that are as pronounced as those resulting from variation in milling time.²⁸ Furthermore, our findings suggest that these materials do not all contain the same active Ti species; rather, they contain a variety of related active Ti species. Kinetic studies have indicated that the abilities of active Ti species to migrate within the bulk of the hydride and interact with complex Alanate anions are the factors that dictate the kinetics of dehydrogenation and rehydrogenation of the doped hydride.²² Thus, the observed differences in the hydrogen storage performance of these materials can be ascribed to variations in the active Ti species that effect its stability, bulk mobility in the hydride, and/or interaction with the complex Alanate anions.

Conclusions

We have developed a method for the preparation of Ti-doped NaAlH_4 by mechanically milling a 1:1 mixture of NaH and Al with a few mole percent of off-the-shelf Ti powder. This method has practical advantages over the doping of NaAlH_4 with (1) Ti(III) and Ti(IV) precursors that result in the incorporation of dead weight byproducts or (2) $\text{Ti13}\cdot 6\text{THF}$, which is much more expensive and less generally available. Moreover, our results clearly demonstrate that kinetic enhancement of the reversible dehydrogenation of Ti-doped NaAlH_4 can be induced upon milling the hydride with simple Ti powder. Thus, there is no requirement for exotic nanostructured precursors. The doped Alanate that is prepared through our novel method shares several common characteristics with NaAlH_4 that is doped through mechanical milling with off-the-shelf Ti powder under a H_2 atmosphere. However, it has the important practical advantage

that its hydrogen storage capacity does not diminish upon cycling. The kinetic enhancement of the dehydrogenation process observed in the thus-prepared Alanate has been found to be inferior to that arising from doping NaAlH_4 with Ti(III) and Ti(IV) precursors. As a result, the material does not exhibit an improved hydrogen cycling capacity despite not containing any doping byproducts. We have found that this problem is partially alleviated when the mechanical milling is carried out under an atmosphere of H_2 rather than of argon. Thus, it is evident that the presence of hydrogen in the milling process affects the nature of the active Ti species. Further investigation into the nature of this modification may lead to the elucidation of the mechanism of action of the active Ti species in the dehydrogenation of the complex Alanate anions. Thus, further investigation could provide insight into means of improving the hydrogen storage properties of Ti-doped NaAlH_4 .

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