ELSEVIER
Journal of Alloys and Compounds 379 (2004) 99–102
Journal of ALLOYS AND COMPOUNDS
www.elsevier.com/locate/jallcom

Method for preparing Ti-doped $NaAlH_4$ using Ti powder: observation of an unusual reversible dehydrogenation behavior

P. Wang*, C.M. Jensen*

Department of Chemistry, University of Hawaii, Honolulu, HI 96822, USA

Received 13 January 2004; accepted 12 February 2004

Abstract

Titanium powder can be directly used as dopant in the preparation of catalytically enhanced Ti-doped $NaAlH_4$ upon mechanical milling under an atmosphere of hydrogen. The hydrogen storage performance of $NaAlH_4$ that was doped through this method was found to be highly dependent on the milling time. A sample mechanically milled under hydrogen for 10 h was initially observed to discharge >3.3 wt.% of hydrogen within 1 h at 150 °C. Rehydrogenation was accomplished at 120 °C under about 12 MPa H_2 within 10 h. The hydrogen capacity of this material was found to gradually decrease to 2.8 wt.% after eight cycles. The dehydriding kinetics and cycling properties of $NaAlH_4$ that is doped through this novel method is clearly distinct from the material that is obtained through the utilization of Ti(III) or Ti(IV) dopant precursors and milling under argon. This suggests that the nature of active Ti-species may differ in these two varieties of doped $NaAlH_4$.

Keywords: Alanate; Hydrogen storage; Kinetics; Titanium powder

1. Introduction

In 1997, Bogdanovic and Schwickardi reported that the elimination of hydrogen from solid $NaAlH_4$ could be markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal based precursors [1]. This was a revolutionary finding in the area of metal hydrides as hydrogen cycling at moderate temperatures was unprecedented for saline hydrides. Following this breakthrough, there have been intensifying efforts aimed at the utilization of $NaAlH_4$ and related hydrides with high gravimetric hydrogen as practical hydrogen storage materials [2–24]. We subsequently discovered an improved doping method that greatly promotes the kinetics of the reversible dehydrogenation of $NaAlH_4$ and stabilizes its hydrogen cycling capacity [2–4]. Further efforts on the development of Ti-doped $NaAlH_4$ have given rise to hydrogen storage materials that stand as the current state-of-the-art [5–11]. However, despite this progress, the reversible hydrogen cycling capacities of only 3–4 wt.% have been achieved under practical conditions. This is far from the 5.6 wt.% hydrogen that is theoretically available according to Eq. (1)

$$NaAlH_4 \rightarrow NaH + Al + \tfrac{3}{2}H_2 \qquad (1)$$

The doping process results in the formation of by-products in the kinetically enhanced hydride. For example, doping with $TiCl_3$ results in the formation of NaCl [9,10]. The by-products are present as segregated crystallites that are dispersed throughout the substituted hydride [9,10]. Although they do not seem to interfere with the dehydriding or hydriding processes, they constitute “dead weight” that becomes increasingly problematic as the doping level of the hydride is raised. Thus despite inducing improved kinetic and thermodynamic properties, current methods for doping the hydride results in the lowering of the gravimetric hydrogen capacity to an unacceptable level.

Clearly, elimination of the doping side-products would greatly improve the hydrogen capacity of these materials. In this regard, it was recently reported that active Ti-dopant was introduced into $NaAlH_4$ upon ball-milling with the Ti(0) precursor, $Ti_{13}\cdot 6THF$ [13,14]. We have now developed a method whereby off-the-shelf titanium powder can be utilized directly for the introduction of Ti dopants into the $NaAlH_4$ host. We herein report the details of this method of

---

* Corresponding authors. Tel.: +1-808-956-2769;
fax: +1-808-956-5908.
E-mail addresses: jensen@gold.chem.hawaii.edu (C.M. Jensen), pwang@hawaii.edu (P. Wang).

0925-8388/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.02.006

preparation of Ti-doped $NaAlH_4$ and the hydrogen storage behavior of this material.

2. Experimental

Titanium powder (99.98%, ~325 mesh) and raw $NaAlH_4$ were purchased from Aldrich Chemical Co. and Albemarle Corp., respectively. The purification of $NaAlH_4$ was accomplished under an atmosphere of nitrogen using standard Schlenk technique. Aluminum powder was removed from the raw hydride via Soxlet extraction with dry, oxygen-free tetrahydrofuran (THF). Final purification was accomplished through recrystallization from THF/pentane.

Mixtures of $NaAlH_4$ and titanium powder were mechanically milled by using a Fritsch 6 Planetary mill at 400 rpm in a stainless steel bowl and grinding balls. The milling was performed under hydrogen or argon atmosphere, with an initial pressure of 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 silicon oil bath, respectively. A typical cyclic experiment entailed desorption at 150 °C and absorption at 120 °C with an initial pressure condition of <1 Torr and ~12 MPa, respectively. The weight of elemental Ti was taken into account in the determination of H-capacity.

3. Results

We have found that a pronounced enhancement of the dehydrogenation kinetics of $NaAlH_4$ can be achieved upon mechanical milling the hydride with Ti powder under hydrogen atmosphere. As seen in Fig. 1, over 3.3 wt.% of hydrogen was discharged in about 2 h at 150 °C from a sample of $NaAlH_4$ that was ball-milled with 7 mol% Ti powder under hydrogen for 5 h. The achieved kinetics enhancement is markedly superior to that of $NaAlH_4$ milled under Ar atmosphere. For comparison, $NaAlH_4$ that was ball-milled under hydrogen for 5 h without Ti powder was also examined. As seen in Fig. 1, hydrogen must play a critical role in the generation of the active titanium species from Ti powder.

It is also noteworthy that the dehydrogenation kinetics of $NaAlH_4$ that is doped through this novel method are significantly slower than those arising upon doping the hydride with Ti(III) or Ti(IV) dopant precursors [2–11]. The differing kinetic behaviors can be seen in Fig. 2 which compares the first dehydriding profiles between a sample of $NaAlH_4$ that was doped with TiF_3 by standard milling procedure [2–11] and a sample prepared by the present method.

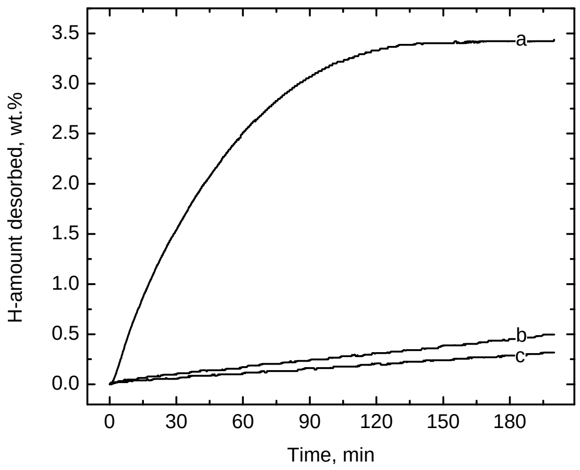

Fig. 1. First H-desorption profiles of different samples at 150 °C. (a) $NaAlH_4$ + 7 mol% Ti mechanically milled under H_2 atmosphere for 5 h; (b) $NaAlH_4$ + 7 mol% Ti mechanically milled under Ar atmosphere for 5 h; (c) $NaAlH_4$ mechanically milled under H_2 atmosphere for 5 h.

In contrast to the standard procedure for preparing Ti-doped $NaAlH_4$ through mechanical milling with Ti(III) or Ti(IV) precursors [2–11], prolonged milling time is required to obtain the maximum kinetic enhancement for the hydride mechanically doped with Ti powder. As seen in Fig. 3, increasing the milling time from 1 to 10 h clearly improves the dehydrogenation kinetics observed at 150 °C. It is notable that the sample milled for 10 h was observed to evolve ~3.3 wt.% hydrogen in about 1 h. This value approaches the theoretical amount of hydrogen that can be obtained from $NaAlH_4$ containing 7 mol% Ti in the dehydrogenation reaction seen in Eq. (2)

$$NaAlH_4 \rightarrow \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2 \qquad (2)$$

However, this material undergoes the subsequent decomposition of Na_3AlH_6 to NaH only at a very low rate, even at 150 °C.

The hydrogen recharging of this material was accomplished at 120 °C under about 12 MPa H_2 within 8–10 h.

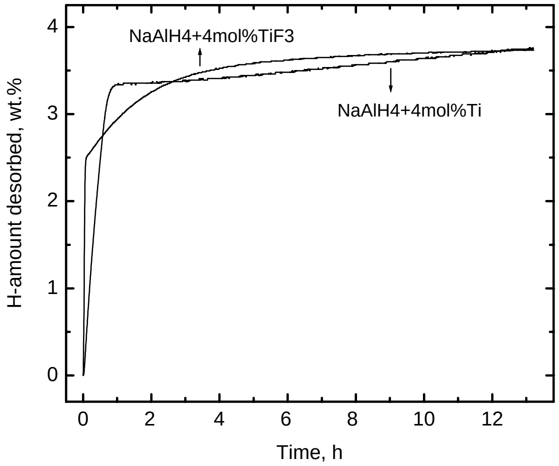

Fig. 2. Comparison of the first H-desorption profile at 150 °C between $NaAlH_4$ + 4 mol% Ti milled under H_2 atmosphere for 10 h and $NaAlH_4$ + 4 mol% TiF_3 milled under N_2 for 0.5 h.

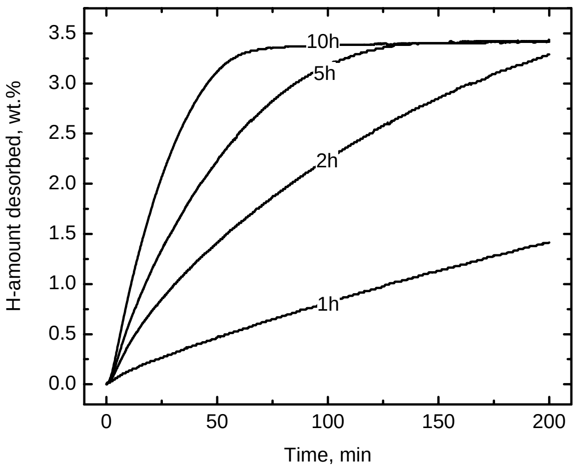

Fig. 3. First 150 °C H-desorption profiles of $NaAlH_4$ + 7 mol% Ti mechanically milled under H_2 atmosphere for different periods.

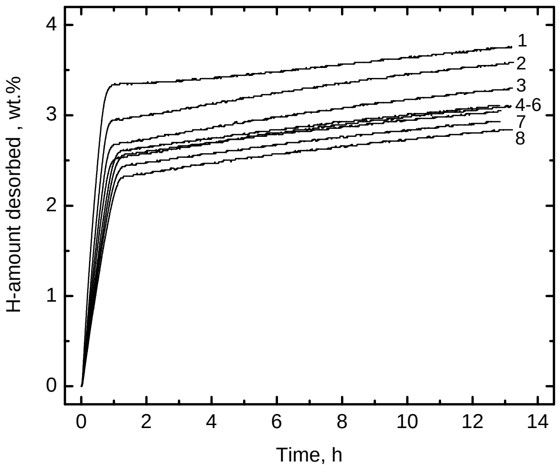

Fig. 4. 150 °C H-desorption profiles of $NaAlH_4$ + 4 mol% Ti (the first eight cycles) milled under H_2 atmosphere for 10 h.

However, the initial hydrogen capacity can not be fully restored. As seen in Fig. 4, the hydrogen capacity gradually decreases with increasing the cycle number and down to 2.8 wt.% after eight cycles. Additionally, the kinetics of the first decomposition step were also observed to gradually decrease.

4. Discussion

The nature of the active Ti-species in Ti-doped $NaAlH_4$ has been a subject of interest, speculation, and controversy. It was initially suggested that the remarkable enhancement of the hydrogen cycling kinetics in Ti-doped $NaAlH_4$ was due to surface-localized catalytic species consisting of titanium metal or a Ti–Al alloy [1,5,8]. Alternatively, we have hypothesized that doping involves the substitution of titanium into the bulk of the hydride [19]. Evidence for both the presence of a Ti–Al alloy in the doped hydride [23] and substitution of Ti into the bulk hydride lattice [19,24] have been reported. However, neither a catalytically active Ti–Al alloy nor evidence for well characterized sites of lattice substitution has yet been obtained. Thus the nature of the active Ti-species in the doped hydride has not been firmly established.

The results obtained in this study suggest other possibilities as to the nature of the active Ti-species in doped $NaAlH_4$. Doping through our alternative method clearly confers reversible dehydrogenation behavior and a pattern of cycling stability that are quite distinct from Ti-doped $NaAlH_4$ arising from milling with Ti(III) and Ti(IV) dopant precursors. This finding raises the additional possibility that more than one Ti-species can contribute to the kinetic enhancement of the dehydrogenation of $NaAlH_4$. This possibility is also suggested by the discontinuity in the relationship between level of Ti doping and the rate of dehydrogenation that is observed at higher (>2 mol%) doping levels [10].

The observations of reduced kinetic enhancement and cycling instability suggest that the Ti-dopant not be as tightly incorporated in the doped hydride that is produced by our alternative method. One possibility is that in this material, Ti-species occupy interstitial rather than lattice positions. By material design, a suitable interstitial position in host lattice could be created that would better accommodate the Ti-species such that improved reversible dehydrogenation performance could be achieved. Following this approach, we have obtained some promising results that will be presented in forthcoming publication.

5. Conclusion

Mechanical milling of $NaAlH_4$ with off-the-shelf Ti powder under hydrogen atmosphere has been found to produce Ti-doped $NaAlH_4$ that exhibits kinetically enhanced, reversible dehydrogenation behavior. The Ti-doped hydride that was obtained in the present study from the alternative doping procedure has practical hydrogen storage properties that are inferior to the doped hydride that is produced by mechanical milling with Ti(III) or Ti(IV) precursors under an inert atmosphere. However, our findings establish a possibility of developing a high-performance Ti-doped $NaAlH_4$ for hydrogen storage. This process would eliminate the problems that plague the standard method of preparation of the doped hydride: capacity loss due to the generation of inactive by-products; and the evolution of gaseous impurities that are highly detrimental to fuel-cell operation. Furthermore, our results suggest that more than one Ti-species and/or Ti in more than one structural environment can kinetically enhance the dehydrogenation of $NaAlH_4$. In view of the quite limited understanding on the role(s) of Ti-species played in the reversible dehydrogenation of alanates, the researchers developing alanate-based materials for hydrogen storage applications should maintain a wide perspective.

Acknowledgements

The authors are very grateful to Mr. D. Kempton for his assistance in constructing the experimental apparatus. The financial support for this research from the Office of Hydrogen, Fuel Cells, and Infrastructure Technologies of the US Department of Energy is greatfully acknowledged.

References

[1] B. Bogdanovic, M. Schwickardi, J. Alloys Comp. 253–254 (1997) 1.
[2] C.M. Jensen, R. Zidan, N. Mariels, A. Hee, C. Hagen, Int. J. Hydrogen Energy 24 (1999) 461.
[3] R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen, J. Alloys Comp. 285 (1999) 119.
[4] C.M. Jensen, R.A. Zidan, US Patent 6,471,935 (2002).
[5] B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys Comp. 302 (2000) 36.
[6] C.M. Jensen, K.J. Gross, Appl. Phys. A 72 (2001) 213.
[7] B. Bogdanovic, M. Schwickardi, Appl. Phys. A 72 (2001) 221.
[8] K.J. Gross, G.J. Thomas, C.M. Jensen, J. Alloys Comp. 330–332 (2002) 683.
[9] K.J. Gross, G. Sandrock, G.J. Thomas, J. Alloys Comp. 330–332 (2002) 691.
[10] G. Sandrock, K. Gross, G. Thomas, J. Alloys Comp. 339 (2002) 299.
[11] B. Bogdanovic, G. Sandrock, MRS Bull. 27 (2002) 712.
[12] G. Sandrock, K. Gross, G. Thomas, C. Jensen, D. Meeker, S. Takara, J. Alloys Comp. 330/332 (2002) 696.
[13] M. Fichtner, O. Fuhr, O. Kircher, J. Rothe, Nanotechnology 14 (2003) 778.
[14] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, F. Schüth, Adv. Mater. 15 (2003) 1012.
[15] A. Zaluska, L. Zaluski, J.O. Ström-Olsen, J. Alloys Comp. 298 (2000) 125.
[16] K.J. Gross, S. Guthrie, S. Takara, G.J. Thomas, J. Alloys Comp. 297 (2000) 270.
[17] V.P. Balema, K.W. Dennis, V.K. Pecharsky, Chem. Commun. (2000) 1665.
[18] G.J. Thomas, K.J. Gross, N.Y.C. Yang, C. Jensen, J. Alloys Comp. 330–332 (2002) 702.
[19] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, J. Alloys Comp. 337 (2002) L8.
[20] G.P. Meisner, G.G. Tibbetts, F.E. Pinkerton, C.H. Olk, M.P. Balogh, J. Alloys Comp. 337 (2002) 254.
[21] M.P. Balogh, G.G. Tibbetts, F.E. Pinkerton, G.P. Meisner, C.H. Olk, J. Alloys Comp. 350 (2003) 136.
[22] M. Fichtner, O. Fuhr, J. Alloys Comp. 345 (2002) 286.
[23] B. Bogdanovic, M. Felderhoff, M. Germann, M. Härtel, A. Pommerin, F. Schüth, C. Weidenthaler, B. Zibrowius, J. Alloys Comp. 350 (2003) 246.
[24] T. Kiyobayashi, S.S. Srinivasan, D. Sun, C.M. Jensen, J. Phys. Chem. A 107 (2003) 7671.