Contents lists available at ScienceDirect



Letter

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jallcom

Reversible hydrogen storage in Ti–Zr-codoped NaAlH₄ under realistic operation conditions

Thomas Schmidt*, Lars Röntzsch

Fraunhofer Institute for Manufacturing Engineering and Applied Materials Research, Winterbergstr. 28, 01277 Dresden, Germany

ARTICLE INFO

ABSTRACT

Article history: Received 11 February 2010 Accepted 23 February 2010 Available online 3 March 2010

Keywords: Hydrogen storage Alanate Sodium aluminum hydride Codoping Ti Zr Realistic operation conditions PEM fuel cell Ti–Zr-codoped NaAlH₄ exhibits improved hydrogen desorption and reabsorption properties compared with sole Ti- or Zr-doped alanate. This contribution aims on reversible hydrogen storage in such material under realistic operation conditions. Results on isothermal dehydrogenation–rehydrogenation cycles at 125 °C and desorption at 4 bar hydrogen back-pressure are presented, proving NaAlH₄ to be a suitable hydrogen material in combination with proton exchange membrane fuel cells.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of the catalytic effect of Ti halide precursors [1], NaAlH₄ has become a promising candidate for the solid-state storage of hydrogen. This finding was followed by several papers dealing with different approaches to improve the activity of Ti catalysts [2]. Several Ti-containing compounds, such as organic precursors [3], TiH₂ [4] and Ti nanoparticles [5] have been proven to catalyze hydrogen desorption of NaAlH₄ efficiently. In this respect, recent findings indicate that Ti(0) is the actual catalyst [6,7].

Zr is in the same group in the periodic table as Ti, thus, a similar catalytic effect can be anticipated. However, there are only few publications dealing with Zr catalysts for dehydrogenation and rehydrogenation of NaAlH₄. From a systematic screening of a multitude of transition metal chlorides for dehydrogenation of NaAlH₄ it turned out that ZrCl₄ is less efficient than different Ti chlorides but much more efficient than all other catalyst precursors tested [8]. In addition, organometallic Zr additives were successfully used for the dehydrogenation of NaAlH₄. Furthermore, it was demonstrated that the combination of Zr and Ti catalyst precursors helps to improve the desorption kinetics [9]. X-ray diffraction studies were carried out in order to investigate the influence of the dopants Ti and Zr on the lattice parameters of NaAlH₄ [10]. A synergistic effect was observed both for desorption and reabsorption of hydrogen by different authors [11,12].

Doped NaAlH₄ has several promising properties as reversible hydrogen storage material for technical use, such as cycle stability, rather low absorption and desorption temperatures from 100 to 150 °C [2] and the possibility of its direct synthesis starting from NaH and Al via reactive milling [13]. More importantly, the dehydrogenation of NaAlH₄ exploiting the exhaust heat of a high-temperature proton exchange membrane (HT-PEM) fuel cell, working at 1.2 bar has been tested [14]. However, for practical applications a fuel cell back-pressure of several bar is required in order to reach a sufficient performance, in particular for mobile applications [17].

In this contribution, dehydrogenation of doped NaAlH₄ is presented for the first time at a constant *hydrogen back-pressure of 4 bar* and a temperature of 150 °C in order to mimic realistic operation conditions in combination with a HT-PEM fuel cell. For this purpose, NaAlH₄ was ball-milled with Zr, TiCl₄ and both in combination (codoping). In addition, dehydrogenation and rehydrogenation of hydrogen storage material were studied under *isothermal conditions*, being favourable for technical processes.

2. Experimental

2.1. Powder preparation

All samples were prepared and handled in a glovebox (MBraun) under Ar to prevent unwanted oxidation. For Zr-doping, 5 mol% Zr powder (Chemetall, 97.8% purity) with a particle size of 2–3 μ m was intermixed with NaAlH₄ powder (Aldrich,

^{*} Corresponding author. Tel.: +49 351 2537413; fax: +49 351 2554496. *E-mail address:* thomas.schmidt@ifam-dd.fraunhofer.de (T. Schmidt).

^{0925-8388/\$ -} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.02.162



Fig. 1. Hydrogen reabsorption and desorption kinetics of NaAlH₄, doped with Zr, TiCl₄ and Zr+TiCl₄.

technical grade, 90% purity). For Ti-doping, 5 mol% TiCl₄ (Aldrich, >99% purity) as inexpensive and liquid Ti precursor was added to the NaAlH₄ powder using a syringe. Both combinations were individually ball-milled under Ar for 24 h in a Fritsch P6 with 600 rpm and a ball-to-powder ratio of 20:1. To prepare codoped NaAlH₄, samples with equal concentrations of Ti and Zr were ball-milled for 2 h with 400 rpm, thus, the catalyst concentration amounts to 2.5 mol% for each Ti and Zr. To prepare the sample with each 1 mol% Ti and Zr the formerly produced sample was ball-milled together with the respective amount of pure NaAlH₄ for 4 h at 600 rpm.

2.2. Analysis

The crystal X-ray diffraction analysis (XRD) was carried out in a D5000 Siemens using Co K α radiation in the scanning range of the diffraction angle $40^\circ \le 2\Theta \le 100^\circ$. The samples were covered with a capton foil to avoid sample contamination with moisture and oxygen.

The morphology of the specimens has been analyzed using an EVO 50 ZEISS scanning electron microscope (SEM).

2.3. Kinetics

The rehydrogenation/dehydrogenation kinetics and cycle stability of the samples were studied using a magnetic suspension balance (Rubotherm). Therefore, hydrogen desorption and reabsorption can be investigated at constant hydrogen pressures in the range from 10^{-5} to 200 bar (flow-through mode), i.e. covering the operating pressure range of most PEM fuel cell systems.

3. Results and discussion

The doped NaAlH₄ samples were activated by a first desorption step. Thereafter, the hydrogenation and dehydrogenation properties of the hydrogen storage material were investigated in dependence of the catalyst under isothermal conditions, being favourable for technical processes. The catalytic effect of Zr was compared with TiCl₄ as benchmark catalyst precursor. The effect of codoping NaAlH₄ with both Zr and Ti on the kinetics of hydrogen sorption and the influence of the catalyst concentration was investigated (cf. Fig. 1).

In accordance with the thermodynamic data of the reaction equilibria between NaAlH₄, Na₃AlH₆ and NaH [15,16], two steps can be observed during both absorption and desorption (Scheme 1). At a constant temperature of 125 °C rehydrogenation of Na₃AlH₆

$$3 \operatorname{NaAlH_4} \longrightarrow \operatorname{Na_3AlH_6} + 2 \operatorname{Al} + 3 \operatorname{H_2} \quad (1)$$

 $Na_{3}AlH_{6} \longrightarrow 3 NaH + Al + 3/2 H_{2}$ (2)

Scheme 1. Decomposition reactions of NaAlH₄ to NaH.



Fig. 2. X-ray diffraction patterns of NaAlH $_4$ + 2.5 mol% Zr + 2.5 mol% TiCl $_4$ prior to and after cyclization.

to NaAlH₄ (reverse reaction of (1)) starts at a pressure of >70 bar. Dehydrogenation of Na_3AlH_6 to NaH (2) is restricted to maximum pressures of a few bar. Detailed kinetic and thermodynamic investigations will be presented elsewhere.

For both hydrogen absorption and desorption, the Zr–Ticodoped system achieved faster kinetics than the storage material with pure Zr or Ti as catalyst. This in qualitative agreement with the findings in Ref. [12], whereas we achieved faster kinetics (especially for hydrogenation) with lower catalyst loading under milder conditions (lower hydrogenation pressure and lower dehydrogena-



Fig. 3. SEM micrographs (BSE mode) of NaAlH₄ + 2.5 mol% Zr + 2.5 mol% TiCl₄ prior to (a) and after (b) cyclization.



Fig. 4. Dehydrogenation of NaAlH₄ at 4 bar in dependence of the catalytic system in comparison with the dehydrogenation of Zr-TiCl₄-codoped NaAlH₄ at 1 bar.

tion temperature, respectively). The codoped NaAlH₄ reversibly stored about 4 wt% hydrogen at a constant temperature of $125 \,^{\circ}$ C with a total catalyst amount of only 2 mol%. Values of >4 wt% reversible hydrogen release were achieved after 5 h of dehydrogenation, and hydrogen uptake of 4 wt% after 1 h was demonstrated for this sample. Within the investigated range the catalyst concentration in the codoped system has only a minor effect on the sorption kinetics of NaAlH₄. However, the storage system with 2 mol% catalyst stored 0.4 wt% hydrogen more than the sample with 5 mol%.

The reversibility was confirmed by XRD analysis (cf. Fig. 2). In the representative XRD pattern of codoped NaAlH₄ prior to dehydrogenation and after three cycles of dehydrogenation and rehydrogenation Ti could not be detected directly, probably due to an overlap with the Al peaks of the finely dispersed catalyst. However, NaCl was found which is formed during the reduction of TiCl₄. As expected from Fig. 1, Na₃AlH₆ has not been detected, thus, indicating a low concentration. The XRD patterns of the other samples we investigated provide similar results and are therefore not presented.

SEM measurements prior to and after cyclization (cf. Fig. 3) of the codoped sample show the particle fragmentation that can explain the increasing activity after the first cycle, which we observed for all samples. This effect is consistent to the observations in Ref. [9].

Since for many fuel cell applications a hydrogen pressure of 4 bar is needed during desorption [17], the material systems investigated here were tested under such realistic operation conditions. Fig. 4 exhibits the dehydrogenation kinetics of the NaAlH₄ samples at 4 bar hydrogen pressure with three different catalytic additives and desorption of the codoped system at 1 bar for comparison. The hydrogen desorption at 4 bar starts at higher temperature than in the case of 1 bar hydrogen pressure and proceeds slower. There is a characteristic step in the desorption curves of the systems with TiCl₄ and the Zr–TiCl₄ mixture at 4 bar and temperatures below 150 °C, indicating a temperature range where the desorption reaction nearly stops at the stage of Na₃AlH₆. The codoped system is superior to the other catalysts over the whole temperature range. About 4 wt% hydrogen were desorbed within 5 h.

4. Conclusions

Codoping NaAlH₄ with Zr and TiCl₄ considerably improves the kinetics for hydrogen desorption and reabsorption, compared to sole doping with Zr or TiCl₄. Reversible hydrogen storage of 4 wt% via pressure variation between 1 and 100 bar at a constant temperature of 125 °C with reasonable kinetics was demonstrated. It was shown for the first time that about 4 wt% of hydrogen could be released during dehydrogenation of NaAlH₄ against a hydrogen pressure of 4 bar, which will be needed for PEM fuel cells in automotive applications.

Acknowledgements

The authors would like to acknowledge financial support of the Fraunhofer Attract program. We thank M. Eckardt and V. Pacheco for assistance with XRD measurements and T. Richter and S. Kalinichenka for SEM analysis.

References

- [1] B. Bogdanovic, M. Schwickardi, J. Alloys Compd. 253 (1997) 1-9.
- [2] Review: F. Schüth, B. Bogdanovic, M. Felderhoff, Chem. Commun. (2004) 2249–2258.
- [3] C.M. Jensen, R. Zidan, N. Mariels, A. Hee, C. Hagen, Int. J. Hydrogen Energy 24 (1999) 461–465.
- [4] K.J. Gross, E.H. Majzoub, S.W. Spangler, J. Alloys Compd. 356–3578 (2003) 423–428.
- [5] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schliche, F. Schüth, Adv. Mater. 15 (2003).
- [6] M. Felderhoff, K. Klementiev, W. Grünert, B. Spliethoff, B. Tesche, J.M. Bellosta von Colbe, B. Boddanovic, M. Härtel, A. Pommerin, F. Schüth, C. Weidenthaler, Phys. Chem. Chem. Phys. 6 (2004) 4369–4374.
- [7] J. Graetz, J. Reilly, J.J. Johnson, Appl. Phys. Lett. 85 (2004) 500-502.
- [8] D.L. Anton, J. Alloys Compd. 353–357 (2003) 400–404.
- [9] R.A. Zidan, S. Takara, A.G. Hee, C.M. Jensen, J. Alloys Compd. 285 (1999) 119–122.
 [10] D. Sun, T. Kiyobayashi, H.T. Takeshita, N. Kuriyama, C.M. Jensen, J. Alloys Compd.
- 337 (2002) L8–L11.
- [11] J. Wang, A.D. Ebner, R. Zidan, J.A. Ritter, J. Alloys Compd. 391 (2005) 245-255.
- [12] X. Xiao, L. Chen, X. Wang, S. Li, C. Chen, Q. Wang, Int. J. Hydrogen Energy 33 (2008) 64–73.
- [13] N. Eigen, C. Keller, M. Dornheim, T. Klassen, R. Bormann, Scr. Mater. 56 (2007) 847–851.
- [14] P. Pfeifer, C. Wall, O. Jensen, H. Hahn, M. Fichtner, Int. J. Hydrogen Energy 34 (2009) 3457–3466.
- [15] B. Bogdanovic, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys Compd. 302 (2000) 36–58.
- [16] K.J. Gross, G.J. Thomas, C.M. Jensen, J. Alloys Compd. 33 (2002) 683–690.
- [17] http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_ onboard_hydro_storage.pdf.