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Reversible hydrogen storage in Ti–Zr-codoped $NaAlH_4$ under realistic operation conditions: Part 2☆

Thomas Schmidt*, Lars Röntzsch, Thomas Weißgärber, Bernd Kieback

Fraunhofer Institute for Manufacturing Engineering and Advanced Materials IFAM, Winterbergstr. 28, 01277 Dresden, Germany

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ABSTRACT

Recently, we have demonstrated that the dehydrogenation of $NaAlH_4$ can be carried out with sufficient kinetics even at a hydrogen back pressure of 4 bar, which is needed for a proton exchange membrane (PEM) fuel cell [10]. In this contribution the influence of hydrogen back pressure in the range of 0.2 up to 5 bar and catalyst concentration in the range between 1 and 5 wt.% overall catalyst concentration on the dehydrogenation of Zr–Ti codoped $NaAlH_4$ is investigated in detail. The influence of the hydrogen back-pressure is significant in the 2nd dehydrogenation step. The catalyst concentration influences both kinetics and storage capacity. Rate constants as a function of the temperature and hydrogen back-pressure and activation energies of the dehydrogenation of $NaAlH_4$ to Na_3AlH_6 at 1 bar and 4 bar hydrogen pressure are calculated from isothermal dehydrogenation experiments.

1. Introduction

Complex metal hydrides are promising materials for energy storage applications [1]. Despite the intensive investigations on these materials most of them have a lack of reversibility under reasonable temperature and hydrogen pressure [2]. Promising strategies to address these issues are catalytic additives and nanostructuring. Yet, transition metal-doped $NaAlH_4$ is actually the only complex metal hydride with almost complete reversibility under technically relevant conditions (temperature < 150 °C, hydrogenation pressure < 100 bar). Among a variety of catalytically active compounds Ti, Zr and Ce halides or nanoparticles have found to be most active [3–5]. However, combining Ti and Zr catalysts or catalyst precursors even enhance the kinetics of the hydrogen storage material compared to solely Zr- or Ti-doped $NaAlH_4$ [6–8].

Hydrogen desorption is commonly studied at a hydrogen partial pressure of 1 bar or less. However, for on-board use in combination with PEM fuel cells a hydrogen pressure of a few bar is desired [9]. With Zr and $TiCl_4$ as inexpensive and highly active catalytic additives we could show that at a hydrogen back pressure of 4 bar during dehydrogenation about 4 wt.% hydrogen can be released. Under this condition, dehydrogenation rates of up to 6.5 wt.%-H_2 h^{-1} (1st step reaction) and 1.5 wt.%-H_2 h^{-1} (2nd step reaction) were achieved at 150 °C. Furthermore, a reversible hydrogen storage density of more than 4 wt.%-H_2 was realized under isothermal conditions at 125 °C [10].

Here we present extended investigations on the effect of hydrogen pressure on the dehydrogenation kinetics of Zr–Ti codoped $NaAlH_4$.

2. Experimental

2.1. Powder preparation

All samples were prepared and handled in a glovebox (MBraun) under Ar to prevent unwanted oxidation. Zr powder (Chemetall, 97.8%) with a particle size of 2–3 μm and $TiCl_4$ (Aldrich, >99% purity) as inexpensive Ti precursor, which was added with a syringe under Argon, were ball-milled, respectively, together with $NaAlH_4$ (Aldrich, technical grade, 90% purity) under argon for 24 h in a Fritsch P6 at 600 rpm and a ball-to-powder mass ratio of 20:1. To prepare codoped $NaAlH_4$, samples with equal concentrations of Ti- and Zr-doped powders (2.5 mol% each, altogether 5 mol% of the overall composition) were ball-milled for 2 h at 400 rpm. To prepare the samples with each 0.5 mol% and 1 mol% Zr and Ti the formerly produced sample was milled together with the respective amount of $NaAlH_4$ for 4 h at 600 rpm.

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

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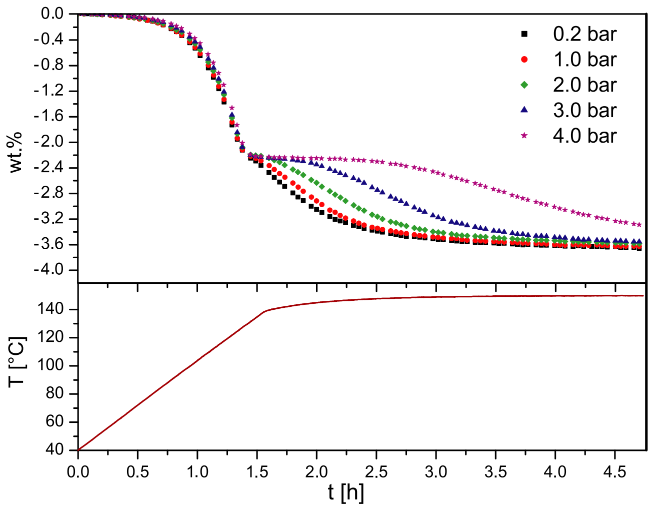

Fig. 1. Dehydrogenation of $NaAlH_4$, codoped with 2. mol% $TiCl_4$ and 2.5 mol% Zr at different hydrogen pressures.

2.2. 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 2×10^{2} bar (flow-through mode), i.e. covering the operating pressure range of most proton exchange membrane fuel cell systems.

In order to investigate the influence of the hydrogen back pressure and catalyst concentration on the hydrogen desorption a constant heating rate of 1 K/min was applied. For reasons of temperature control, the heating rate was dropped drastically when 140 °C was reached in order not to exceed 150 °C during dehydrogenation.

Isothermal dehydrogenation measurements were performed to obtain the rate constants of dehydrogenation. For those experiments the heating ramp was set to maximum in order to reach the respective temperature within a few minutes. For evaluation we chose the data where the offset from the set temperature was less than 0.2 K.

3. Results and discussion

3.1. Pressure dependence of dehydrogenation

As shown in [6] the dehydrogenation of Zr–Ti codoped $NaAlH_4$ against 4 bar hydrogen back pressure can be carried out at 150 °C with reasonable kinetics, although somewhat slower than at 1 bar hydrogen pressure. For further investigation of the influence of the hydrogen pressure we screened the dehydrogenation of $NaAlH_4$ doped with 2.5 mol% Zr and 2.5 mol% $TiCl_4$ at different pressures of hydrogen after running three activation cycles (cf. Fig. 1).

The dehydrogenation of $NaAlH_4$ proceeds in two reaction steps, which can be seen clearly in the dehydrogenation curves:

$$3NaAlH_4 \rightleftarrows Na_3AlH_6 + 2Al + 3H_2 \qquad (1)$$

$$Na_3AlH_6 \rightleftarrows 3NaH + Al + 3/2H_2 \qquad (2)$$

Reaction (1) shows rather little pressure dependence at the advanced heating rate of 1 K/min. Reaction (2) is significantly influenced by the applied hydrogen pressure. The amount of hydrogen desorbed after 4 h was about 3.6 wt.% for pressures from 0.2 to 3 bar. This corresponds to 77% of the maximum capacity for the doped hydrogen storage material. When 4 bar hydrogen pressure was applied it took significantly longer to release this amount of hydrogen (not shown).

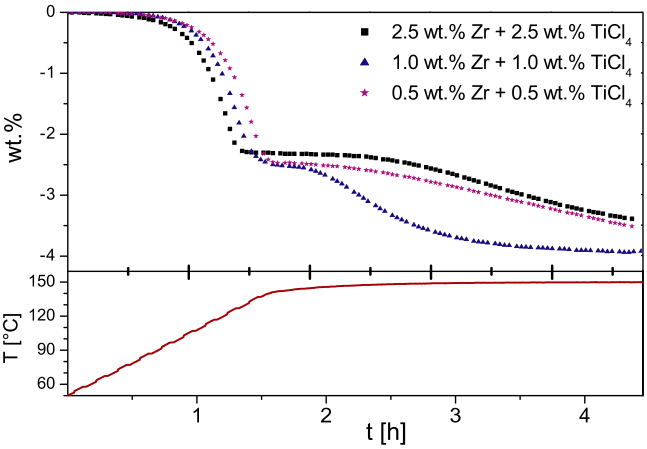

Fig. 2. Influence of the catalyst amount on the dehydrogenation kinetics of $NaAlH_4$, codoped with different amounts of $TiCl_4$ and Zr at 4 bar.

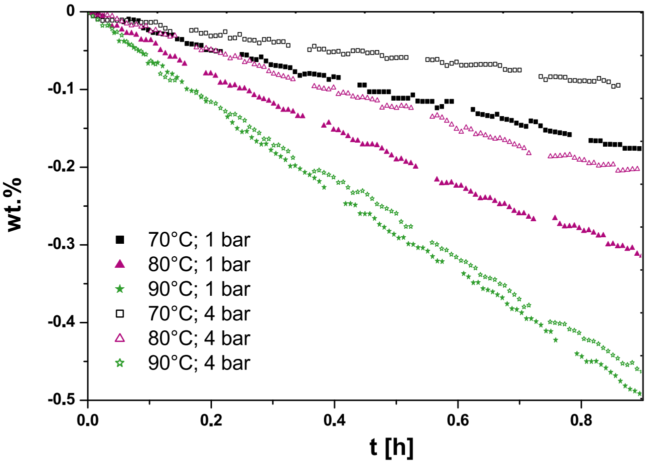

Fig. 3. Dehydrogenation isotherms for 70 °C, 80 °C and 90 °C at 1 bar and 4 bar, respectively, for determination of the reaction order and the correspondent rate constants $k(T, p)$.

3.2. Dependence of the catalyst concentration on the dehydrogenation kinetics

With a reduced catalyst amount the accessible amount of hydrogen within 4 h can be increased to 4 wt.% (cf. Fig. 2). However, in comparison to the samples with 2.5 mol% Zr and 2.5 mol% $TiCl_4$ the

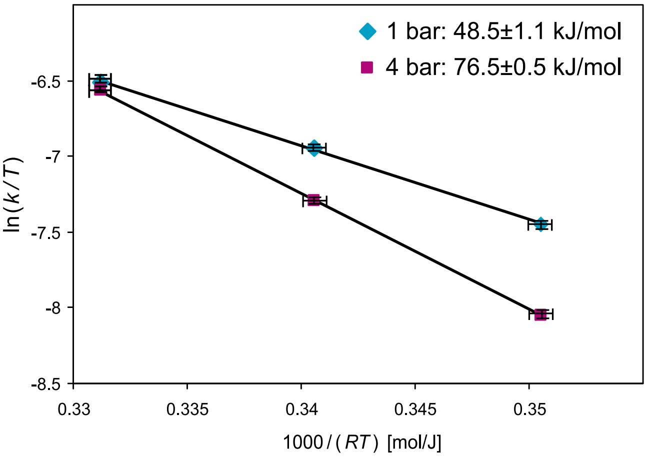

Fig. 4. Arrhenius plots for the determination of the activation enthalpy ΔH_A.

initial kinetics slows down when decreasing the catalyst concentration. Interestingly, after 4 h the highest hydrogen amount was released from the sample with the medium catalyst concentration (blue curve). This can be explained by two counteracting effects. On the one hand the hydrogen storage capacity increases with decreasing catalyst amount. On the other hand a decreasing catalyst amount leads to a worse kinetics. Consequently, when waiting long enough the highest amount of hydrogen is released from the sample with the lowest catalyst amount.

3.3. Determination of reaction order, rate constants and activation energy of the first decomposition step of $NaAlH_4$

Isothermal conditions were chosen for the determination of the reaction order. Fig. 3 shows the weight change of $NaAlH_4$, doped with 2.5 mol% Zr and 2.5 mol% $TiCl_4$ at different temperatures and hydrogen pressures. In all cases the rates of reaction are independent on the concentration of $NaAlH_4$ in the investigated reaction time of 1 h, i.e. the order of reaction is zero in that regime. At 70 °C and 80 °C the dehydrogenation at 1 bar hydrogen pressure proceeds much faster than at 4 bar. However, at 90 °C the reaction rate is almost independent on the hydrogen pressure.

For a zero order reaction the rate constant can easily be taken from the slope of the dehydrogenation curve, since it is independent on the concentration of the starting material (3).

$$k(T,p)=\frac{\mathrm{d(wt.\%)}}{\mathrm{d}t} \tag{3}$$

The activation enthalpy ΔH_A is determined according to the Eyring theory [11] via plotting $\ln(k/T)$ vs. $1000/(RT)$ (cf. Fig. 4):

$$\ln\frac{k(T,p)}{T}=-\Delta H_A\cdot\frac{1}{RT}+C \tag{4}$$

The following table summarizes the determined values of k and ΔH_A:

p (bar)	k (70 °C) (wt.% h^{-1})	k (80 °C) wt.% h^{-1})	k (90 °C) wt.% h^{-1})	ΔH_A (kJ mol^{-1})
1	0.20 ± 0.01	0.34 ± 0.01	0.54 ± 0.01	48.5 ± 1.1
4	0.11 ± 0.01	0.24 ± 0.01	0.51 ± 0.01	76.5 ± 0.5

At 70 °C and 80 °C the rate constants are strongly influenced by the hydrogen pressure. A plausible explanation is the higher thermodynamic driving force towards dehydrogenation in case of 1 bar hydrogen pressure compared to 4 bar. At 90 °C, however, the measured k values at 1 bar and 4 bar are almost equal. Here the difference between the applied hydrogen pressure and the equilibrium pressure is much higher as can be taken from the phase diagram [12].

The activation energy appears to be strongly pressure dependent. The pressure increase from 1 bar to 4 bar leads to an increase of the activation energy of 28 kJ/mol. For comparison, other groups have measured barriers for hydrogen desorption of solely Ti-doped $NaAlH_4$ at 1 bar in the range of 80 kJ/mol [13,14]. However, for Zr–Ti-codoped $NaAlH_4$ no values for the activation enthalpy or energy have been found.

Several reasons or a combination of them can explain the large difference between the activation enthalpy measured by us and the values in literature: The values given in Refs. [13,14] are reaction energies, derived from the Arrhenius equation, so the actual activation enthalpies should be slightly lower. The codoping with Zr and Ti catalyst precursors is superior to doping with just one of the mentioned species [6–8,10], which is probably also caused by the drop of the activation barrier. It is further proven that both types of catalyst precursor and the preparation methods have a strong influence on the rate constants which in turn influence the activation enthalpy [13,15].

4. Summary and outlook

Dehydrogenation of Zr–Ti codoped $NaAlH_4$ is slowed down with increasing hydrogen pressure and decreasing catalyst concentration. However, even at 4 bar hydrogen back pressure a sufficient kinetics for technical applications, such as hydrogen delivery for a PEM fuel cell can be achieved. Reducing the catalyst amount can be useful to achieve a higher hydrogen storage capacity but leads to the reduction of the kinetics at lower temperature. The decomposition of $NaAlH_4$ to Na_3AlH_6, Al and H_2 follows a zero order rate law with respect to the concentration of the starting material. The rate constants are both affected by temperature and pressure. The latter has its strongest influence at lower temperature. The activation energy of the decomposition of Zr–Ti codoped $NaAlH_4$ is clearly affected by the applied hydrogen back pressure.

Future investigations will deal with the kinetics of the second dehydrogenation step and the rehydrogenation of the decomposition products. Furthermore, different mixes of catalyst levels and combinations of other active catalysts will be investigated.

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