

# Kinetic studies of the decomposition of NaAlH<sub>4</sub> doped with a Ti-based catalyst

O. Kircher\*, M. Fichtner<sup>a</sup>

<sup>a</sup> Institute of Nanotechnology, Karlsruhe Research Centre, D-76021 Karlsruhe, Germany

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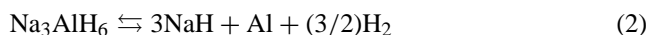
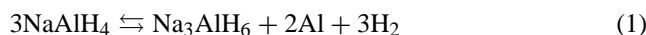
## Abstract

The decomposition kinetics of sodium alanate (NaAlH<sub>4</sub>) and sodium aluminium hexahydride (Na<sub>3</sub>AlH<sub>6</sub>) doped with different concentrations of a Ti cluster have been investigated. By applying variable heating rates, hydrogen was released at different speeds and activation energies were determined for both accessible reaction steps. Isothermal decomposition measurements showed that mechanically alloyed Na<sub>3</sub>AlH<sub>6</sub> exhibits faster kinetics than Na<sub>3</sub>AlH<sub>6</sub> obtained from the decomposition of NaAlH<sub>4</sub>, but decomposes more slowly than the first step of NaAlH<sub>4</sub>. © 2005 Published by Elsevier B.V.

**Keywords:** Metal hydrides; Alanates; Hydrogen absorbing materials; Kinetics; Phase transformations

## 1. Introduction

Among available hydrogen storage materials complex aluminium hydrides (alanates) offer good perspectives for mobile applications due to their high hydrogen content and low decomposition temperatures. Sodium alanate contains 7.5 wt.% hydrogen, which can be released in three steps according to the following reactions:



For technical applications, only the first two steps (release of 5.6 wt.% H<sub>2</sub>) are considered due to the high decomposition temperature of NaH (>400 °C). The release and uptake of hydrogen by the pure material are characterized by very slow kinetics, thus making high working pressures and temperatures unavoidable. Motivated by the work of Bogdanovic and Schwickardi [1], it was found by several groups that NaAlH<sub>4</sub> shows good kinetic properties when catalysed with titanium-based materials like TiCl<sub>3</sub> [2–6]. Recently, it was demon-

strated [7,8] that decomposition and absorption kinetics can be further improved using a Ti cluster Ti<sub>13</sub> · 6THF as catalyst.

Several kinetic studies on the decomposition of NaAlH<sub>4</sub> either doped with TiCl<sub>3</sub> [9,10] or Ti alkoxides [11] can be found in the literature. In these studies activation energies either were determined by heating the sample quickly to the final decomposition temperature [11] or by stepwise increasing the temperature [9,10] and determining the corresponding rate constants. The present study aims at a detailed kinetic study of NaAlH<sub>4</sub> and Na<sub>3</sub>AlH<sub>6</sub> doped with Ti<sub>13</sub> · 6THF and, for comparison, NaAlH<sub>4</sub> doped with TiCl<sub>3</sub>. Due to rather high reaction rates in NaAlH<sub>4</sub> doped with Ti<sub>13</sub> · 6THF, isothermal conditions are hard to fulfil. Thus, instead of stepwise increasing the temperature constant heating rates from room temperature close to the melting point of NaAlH<sub>4</sub> have been applied to monitor the reacted fraction in a precise way without ever interrupting the reaction.

## 2. Kinetics of phase transformations

It is generally accepted in literature that thermally activated reactions can be described by a reaction rate  $df/dt$ , which depends on the temperature  $T$  and the reacted fraction

\* Corresponding author.

E-mail address: Oliver.Kircher@web.de (O. Kircher).

$f$  in the following way [12]:

$$\frac{df}{dt} = y(f)k(T) \quad (4)$$

The temperature dependence is generally assumed to follow an Arrhenius law:

$$k = k_0 \exp\left(-\frac{E_A}{RT}\right) \quad (5)$$

where  $E_A$  is an activation barrier,  $R$  the gas constant, and  $k_0$  is a constant pre-exponential factor. In an ideal isothermal experiment,  $k(T)$  is a constant and the function  $y(f)$  can be determined easily. By measuring  $k$  at different temperatures,  $E_A$  can be determined in a straightforward manner in these experiments. If a reaction has a high reaction enthalpy and shows good kinetics in the temperature range to be investigated, however, strict isothermal conditions are not always easy to fulfil. In these cases, the activation energy can be determined by constant heating rate experiments.

Different methods have been proposed [12], most of them requiring the determination of a temperature  $T_0$  after a certain proportion of the reaction  $f_0$  has already taken place. By combining Eqs. (4) and (5), separating the variables, and integrating from 0 to  $f_0$ ,

$$\int_0^{f_0} \frac{df}{y(f)} = \frac{k_0}{\beta} \int_0^{T_0} \exp\left(-\frac{E_A}{RT}\right) dT \quad (6)$$

is obtained, where  $\beta = dT/dt$  is the heating rate. For  $E_A \gg RT$ , which is fulfilled for most solid-state reactions (Eq. (6)) can be solved to

$$\ln\left(\frac{\beta}{T_0^2}\right) = -\frac{E_A}{RT_0} + C \quad (7)$$

from which the activation energy can be determined. This method is known as Kissinger–Akahira–Sunose (KAS) method [13]. As an alternative, a certain stage of reaction may be defined at the maximum rate  $df/dt$  of the reacted fraction per time. Eq. (7) then changes to

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = -\frac{E_A}{RT_{\max}} + C \quad (8)$$

where  $T_{\max}$  now denotes the temperature at the maximum reaction rate. This method, known as the Kissinger method [14], in most cases yields a good approximation of Eq. (7). Especially when there are two consecutive reactions, it is sometimes hard to decide to what extent the first step has finished and the second has already started, i.e. it is difficult to exactly determine  $f_0$  for each step.

### 3. Experimental

All sample preparations were done as described in Refs. [7,17]. The synthesis of the Ti cluster  $Ti_{13} \cdot 6THF$  is described in Refs. [7,15].

The following samples were investigated:

- NaAlH<sub>4</sub> doped with varying concentrations of Ti (1.8, 2.8, and 5 mol%) from  $Ti_{13} \cdot 6THF$ .
- NaAlH<sub>4</sub> doped with 1.8 mol%  $TiCl_3$  (Sigma–Aldrich, 99.999% purity).
- Na<sub>3</sub>AlH<sub>6</sub> synthesised by mechanical alloying of NaH and NaAlH<sub>4</sub> (according to Ref. [16]) doped with 1.8 mol% Ti from  $Ti_{13} \cdot 6THF$ , named Na<sub>3</sub>AlH<sub>6</sub> (MA).
- Na<sub>3</sub>AlH<sub>6</sub> synthesised by mechanical alloying of NaH and NaAlH<sub>4</sub> doped with 1.8 mol% from  $Ti_{13} \cdot 6THF$  and reloaded to NaAlH<sub>4</sub>, named NaAlH<sub>4</sub> (MA).

All samples were ball milled for 30 min in a Fritsch P6 planetary mixer/mill using a vial and balls out of silicon nitride. The ball to powder weight ratio was about 20:1. Kinetic measurements were carried out in a carefully calibrated modified Sieverts apparatus, as described in Refs. [7,17]. The design of the reactor is given in detail in Ref. [17]. Heating rates in the reactor were verified experimentally and for further analysis, the measured heating rates were considered.

### 4. Results and discussion

Fig. 1 shows the first decomposition of NaAlH<sub>4</sub> doped with 2.8 mol% Ti from  $Ti_{13} \cdot 6THF$  at variable heating rates. For all curves, the two-step-like H<sub>2</sub> release according to Eqs. (1) and (2) is clearly visible. Each NaAlH<sub>4</sub> sample was heated up to 172 °C well below its melting point of 178 °C to prevent the solid-to-liquid phase transition from influencing the reaction kinetics. All samples released  $5.5 \pm 0.1$  wt.% H<sub>2</sub>, which is in good agreement with theory.

According to Section 2, the following parameters were determined for both steps:

- the temperature  $T_0$  after reaction of a certain fraction  $f_0$  [18] according to the KAS method (shown for the first step in Fig. 1 with symbols) and

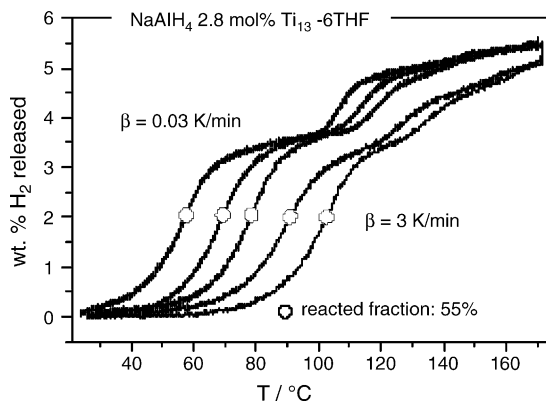


Fig. 1. Decomposition of NaAlH<sub>4</sub> doped with 2.8 mol% Ti from  $Ti_{13} \cdot 6THF$  with the heating rates 0.03, 0.1, 0.3, 1 and 3 K/min. At a constant reacted fraction  $f_0 = 0.55$  (indicated by symbols) the value for the temperature  $T_0$  was taken for the KAS analysis.

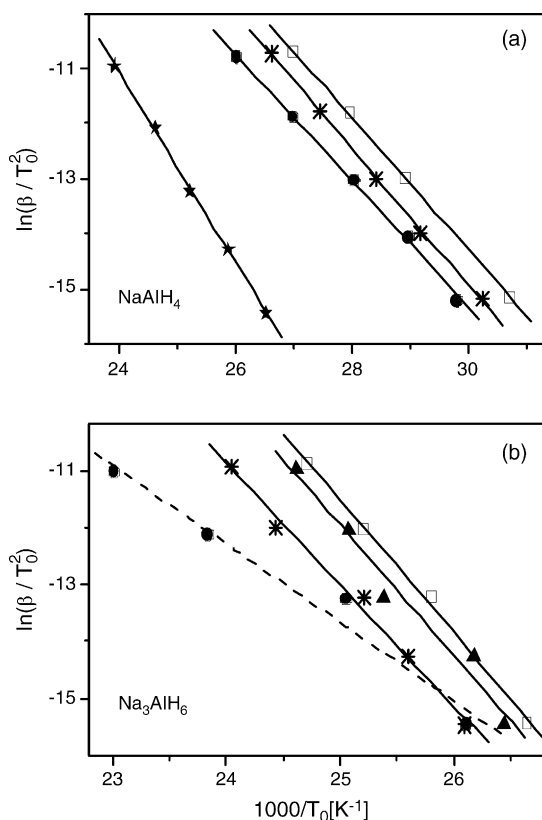


Fig. 2. Activation plots using the KAS method for  $\text{NaAlH}_4$  doped with 1.8 mol% (●), 2.8 mol% (\*) and 5 mol% (□) Ti from  $\text{Ti}_{13} \cdot 6\text{THF}$  for the first (a) and the second decomposition step (b). In (a) data for a sample doped with 1.8 mol% Ti from  $\text{TiCl}_3$  (★) and in (b) data for a mechanically alloyed  $\text{Na}_3\text{AlH}_6$  sample doped with 1.8 mol% Ti from  $\text{Ti}_{13} \cdot 6\text{THF}$  (▲) are also shown. Lines represent fits according to Eq. (7). Fit results are summarized in Table 1.

- the temperature  $T_{\text{max}}$  where the reaction rate reaches a maximum value, according to the Kissinger method.

Plotting  $\ln \beta / T_0^2$  or  $\ln \beta / T_{\text{max}}^2$  versus  $T$  results in a straight line, from the slope of which the activation energy  $E_A$  of the particular reaction step can be determined. In Fig. 2(a), this is done exemplary for the first step using the KAS method for several samples with varying concentrations of  $\text{Ti}_{13} \cdot 6\text{THF}$ . It can be seen that a shift to smaller  $T_0$  values occurs with increasing cluster concentration, thus indicating a faster decomposition. Nevertheless, the slope and, hence,  $E_A$  turns

out to be identical for all samples, namely,  $99.5 \pm 4 \text{ kJ/mol}$ . Table 1 summarises the results for all samples. A sample doped with 1.8 mol%  $\text{TiCl}_3$  is also shown for comparison. For the first step, the  $E_A$  results were not found to be dependent on the method of analysis, i.e. the analysis of  $T_{\text{max}}$  using the Kissinger method led to the same results.

The activation plots obtained for the second reaction step using the KAS method are shown in Fig. 2(b). In analogy to the first reaction step, the slope and, hence,  $E_A$  does not depend on the catalyst content for three of the four samples shown. However,  $\text{NaAlH}_4$  doped with 1.8 mol% Ti from  $\text{Ti}_{13} \cdot 6\text{THF}$  differs significantly from the other samples. This might be explained by the fact that the first reaction step was not finished when the second step started and, thus, influenced the latter at higher heating rates [19]. Indeed, the two-step-like decomposition (as observed for a higher content of  $\text{Ti}_{13} \cdot 6\text{THF}$ , cf. Fig. 1) is less pronounced and hardly observable when high heating rates have been applied. However, when the Kissinger method is taken for analysis, the value of  $E_A$  is in agreement with that of the other samples within the range of experimental error. The values for the second step are also summarised in Table 1.

In their kinetic study, Kiyobayashi et al. [11] found that Ti-doped  $\text{NaAlH}_4$  and directly Ti-doped  $\text{Na}_3\text{AlH}_6$  (taking titanium *n*-butoxide as dopant) show the same activation energy of about 100 kJ/mol for each reaction [20]. Concerning the first reaction step in the Ti cluster doped sample, this coincides with the value found in our experiments. For the second step the results differ, as we found significantly higher values (cf. Table 1). Sandrock et al. ( $\text{TiCl}_3$  as dopant, [9]) also found a higher activation energy for the second step compared to the first one. However, both values (80 kJ/mol for the first and 97.5 kJ/mol for the second step) are smaller than those found in this work. In a recent kinetic study, Luo and Gross ( $\text{TiCl}_3$  as dopant, [10]) also found smaller values for the activation energies and according to their study both values nearly coincide (85.6 kJ/mol for the first and 88.3 kJ/mol for the second step, respectively).

To summarize, the activation energy  $E_A$  of the first step of  $\text{NaAlH}_4$  doped with  $\text{Ti}_{13} \cdot 6\text{THF}$  is in the same range like published data of Ti-doped  $\text{NaAlH}_4$ , even though different Ti-catalyst precursors have been used. However,  $E_A$  of the second step of  $\text{NaAlH}_4$  doped with  $\text{Ti}_{13} \cdot 6\text{THF}$  is significantly higher compared to  $\text{NaAlH}_4$  doped with other Ti precursors.

Table 1

Activation energies  $E_A$  of  $\text{NaAlH}_4/\text{Na}_3\text{AlH}_6$  doped with different concentrations of Ti from  $\text{Ti}_{13} \cdot 6\text{THF}$  and 1.8 mol%  $\text{TiCl}_3$ . Both results using the Kissinger and the KAS method are presented (cf. Section 3)

Sample	$E_A$ first step (Kissinger method) (kJ/mol)	$E_A$ first step (KAS method) (kJ/mol)	$E_A$ second step (Kissinger method) (kJ/mol)	$E_A$ second step (KAS method) (kJ/mol)
1.8 mol% Ti/ $\text{Ti}_{13} \cdot 6\text{THF}$	$96.2 \pm 1.5$	$95.5 \pm 2.5$	$197.2 \pm 6$	$120 \pm 14.5$
2.8 mol% Ti/ $\text{Ti}_{13} \cdot 6\text{THF}$	$103 \pm 2.5$	$103.1 \pm 2$	$195.9 \pm 10$	$177 \pm 9.5$
5 mol% Ti/ $\text{Ti}_{13} \cdot 6\text{THF}$	$103.1 \pm 2$	$99.6 \pm 1.5$	$235 \pm 19.5$	$193.8 \pm 9.5$
1.8 mol% Ti/ $\text{Ti}_{13} \cdot 6\text{THF}$ (MA)	–	–	182.6	$190.3 \pm 18.5$
1.8 mol% Ti/ $\text{TiCl}_3$	$139.5 \pm 12.5$	$143.6 \pm 2.5$	–	–

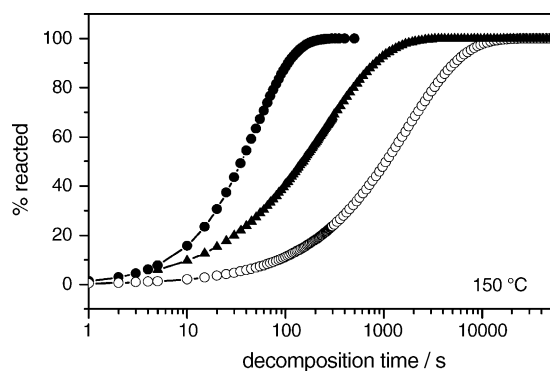


Fig. 3. Isothermal decomposition curves of the first (●) and second step of  $\text{NaAlH}_4[\text{B}]$  and, respectively, of  $\text{Na}_3\text{AlH}_6$  (MA) (○). Non-isothermal measurement conditions were detracted and renormalized to  $150^\circ\text{C}$  according to Eqs. (4) and (5), supposing a JMA equation for  $y(f)$ .

As already outlined in Section 1, different experimental methods were employed in the mentioned studies compared to our work. Apart from the fact that stainless steel tubes have been used, no further details are given in Refs. [9–11] concerning the design of the reactor. To our opinion this could be a crucial point, as it was reported that  $\text{NaAlH}_4$  is not a good heat conductor [21], thus leading to possible temperature gradients in the sample, unless a good heat transfer to the bath is ensured.

In Ref. [11] the decomposition rates of Ti-doped  $\text{NaAlH}_4$  and directly Ti-doped  $\text{Na}_3\text{AlH}_6$  were also found to coincide. However, the  $\text{Na}_3\text{AlH}_6$  produced from the decomposition of doped  $\text{NaAlH}_4$  exhibited a slower reaction rate. To compare these results with Ti cluster-doped samples, isothermal decomposition kinetics of  $\text{Na}_3\text{AlH}_6$  and  $\text{NaAlH}_4$  samples were studied carefully (cf. Section 3). Fig. 3 shows the isothermal decomposition at  $150^\circ\text{C}$  of the first and the second step of  $\text{NaAlH}_4$  and of  $\text{Na}_3\text{AlH}_6$  (MA). All samples were doped with 1.8 mol% Ti from  $\text{Ti}_{13} \cdot 6\text{THF}$ . Non-isothermal conditions during the measurements were renormalized to constant temperature by applying Eqs. (4) and (5), where  $y(f)$  is supposed to follow a Johnson–Mehl–Avrami (JMA) equation  $y(f) = 1 - \exp[-(kt)^n]$ , which provides a good fit to the measured data (not shown) and also was successfully used for fitting the absorption steps in Ti-doped  $\text{NaAlH}_4$  [17]. It can be seen that the decomposition of  $\text{Na}_3\text{AlH}_6$  (MA) is much faster than the second step of  $\text{NaAlH}_4$ . However, the first step of  $\text{NaAlH}_4$  still shows the best kinetics, which is different from the observations in Ref. [11].

## 5. Conclusion

Activation energies  $E_A$  for the decomposition of  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  doped with  $\text{Ti}_{13} \cdot 6\text{THF}$  have been determined

using the Kissinger and the Kissinger–Akahira–Sunose method.  $E_A$  was found to be about 100 kJ/mol for  $\text{NaAlH}_4$  and about 190 kJ/mol for  $\text{Na}_3\text{AlH}_6$ , irrespective of the concentration of the dopant  $\text{Ti}_{13} \cdot 6\text{THF}$ . The high value of the second step differs to observations made for  $\text{NaAlH}_4$  doped with  $\text{TiCl}_3$  [9,10] or Ti alkoxides [11]. However, different methods have been applied to determine these values. Isothermal experiments showed that by adding the catalyst to mechanically alloyed  $\text{Na}_3\text{AlH}_6$ , the decomposition kinetics of  $\text{Na}_3\text{AlH}_6$  could be improved compared to the second decomposition step of  $\text{NaAlH}_4$ . Nevertheless, reaction rates were slower than those of the first step of  $\text{NaAlH}_4$ . These findings are in partial contrast to the observation made by Kiyobayashi et al. for  $\text{NaAlH}_4$  doped with Ti alkoxides [11].

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