Kinetic studies of the decomposition of NaAlH$_4$ doped with a Ti-based catalyst

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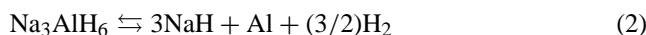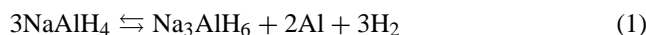[a] *Institute of Nanotechnology, Karlsruhe Research Centre, D-76021 Karlsruhe, Germany*

Abstract

The decomposition kinetics of sodium alanate (NaAlH$_4$) and sodium aluminium hexahydride (Na$_3$AlH$_6$) 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$_3$AlH$_6$ exhibits faster kinetics than Na$_3$AlH$_6$ obtained from the decomposition of NaAlH$_4$, but decomposes more slowly than the first step of NaAlH$_4$.
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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:

$$3NaAlH_4 \leftrightarrows Na_3AlH_6 + 2Al + 3H_2 \tag{1}$$

$$Na_3AlH_6 \leftrightarrows 3NaH + Al + (3/2)H_2 \tag{2}$$

$$3NaH \leftrightarrows 3Na + (3/2)H_2 \tag{3}$$

For technical applications, only the first two steps (release of 5.6 wt.% H$_2$) 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$_4$ shows good kinetic properties when catalysed with titanium-based materials like TiCl$_3$ [2–6]. Recently, it was demonstrated [7,8] that decomposition and absorption kinetics can be further improved using a Ti cluster Ti$_{13}$ · 6THF as catalyst.

Several kinetic studies on the decomposition of NaAlH$_4$ either doped with TiCl$_3$ [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$_4$ and Na$_3$AlH$_6$ doped with Ti$_{13}$ · 6THF and, for comparison, NaAlH$_4$ doped with TiCl$_3$. Due to rather high reaction rates in NaAlH$_4$ doped with Ti$_{13}$ · 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$_4$ 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

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f in the following way [12]:

$$\frac{\mathrm{d}f}{\mathrm{d}t} = y(f)k(T) \tag{4}$$

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

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

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,

$$\int_0^{f_0} \frac{\mathrm{d}f}{y(f)} = \frac{k_0}{\beta} \int_0^{T_0} \exp\left(-\frac{E_A}{RT}\right) \mathrm{d}T \tag{6}$$

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

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

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 $\mathrm{d}f/\mathrm{d}t$ of the reacted fraction per time. Eq. (7) then changes to

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

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:

- $NaAlH_4$ doped with varying concentrations of Ti (1.8, 2.8, and 5 mol%) from $Ti_{13} \cdot 6THF$.
- $NaAlH_4$ doped with 1.8 mol% $TiCl_3$ (Sigma–Aldrich, 99.999% purity).
- Na_3AlH_6 synthesised by mechanical alloying of NaH and $NaAlH_4$ (according to Ref. [16]) doped with 1.8 mol% Ti from $Ti_{13} \cdot 6THF$, named Na_3AlH_6 (MA).
- Na_3AlH_6 synthesised by mechanical alloying of NaH and $NaAlH_4$ doped with 1.8 mol% from $Ti_{13} \cdot 6THF$ and reloaded to $NaAlH_4$, named $NaAlH_4$ (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 $NaAlH_4$ doped with 2.8 mol% Ti from $Ti_{13} \cdot 6THF$ at variable heating rates. For all curves, the two-step-like H_2 release according to Eqs. (1) and (2) is clearly visible. Each $NaAlH_4$ 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 ± 0.1 wt.% H_2, 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
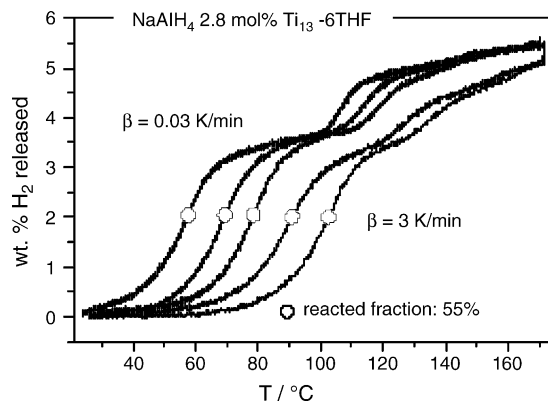

Fig. 1. Decomposition of $NaAlH_4$ doped with 2.8 mol% Ti from $Ti_{13} \cdot 6THF$ with the heating rates 0.03, 0.1, 0.3, 1 and 3 K/min. At a constant reacted fraction $f_0 = 0.55$ (indicated by symbols) the value for the temperature T_0 was taken for the KAS analysis.