Improved hydrogen sorption of sodium alanate by optimized processing

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Abstract

This work demonstrates that fast sorption kinetics in complex hydrides can be achieved by a simple synthesis method using cost-efficient initial components, if microstructure and powder morphology are optimized. NaH/Al precursors with $TiCl_4$ catalyst were synthesised under varying conditions in argon atmosphere and cycled. The influence of powder morphology and microstructure resulting from different process conditions were studied in detail. It is shown that a homogeneous mixing of the phases and a high surface area of the material is essential for fast kinetics and high reversible capacity. The optimized process can be easily scaled up to a cost-efficient production process for large amounts of storage material and can also be applied for other complex hydrides.
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1. Introduction

Hydrogen is the ideal means of storage, transport and conversion of energy for a comprehensive clean-energy concept for mobile applications. Regarding the use of hydrogen as fuel for the zero-emission vehicle, one of the main problems is the storage of hydrogen. Metal hydrides offer a safe alternative to storage in compressed or liquid form. In addition, metal hydrides have the highest storage capacity by volume [1]. In recent years, research has focused on light weight complex hydrides, in particular on alkali alanates as potential storage materials. Bogdanović and Schwickardi showed in 1996 that hydrogen can be reversibly stored and released in sodium alanate, if doped with a suitable catalyst [2]. $NaAlH_4$ decomposes in a two stage reaction within the technically favorable temperature range up to about 125 °C:

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

$$Na_3AlH_6 \rightarrow 3NaH + Al + 1.5H_2 \qquad (2)$$
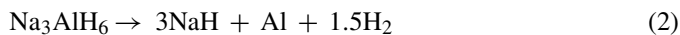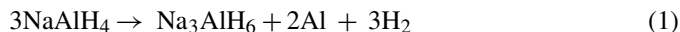
Hydrogenation kinetics critically depends on the catalyst as well as on the synthesis method of the storage material. Bogdanović et al. initially added $Ti(OBu)_4$ and $TiCl_3$ to a solution of purified $NaAlH_4$. The solvent was subsequently evaporated [2]. However, it was shown that by dry mixing of $NaAlH_4$ and $Ti(OBu)_4$ a comparable or even better effect can be achieved [3,4]. Anton found that among various transition and rare earth metals, Ti either in the form of chloride or fluoride was most effective [5]. Recently, it was reported that $ScCl_3$ has an even higher effect on kinetics than $TiCl_3$ [6,7], however, the extremely high price of scandium renders it unsuitable for any industrial use. Equally highly fast kinetics can be achieved by short ball milling of the pure $NaAlH_4$ together with Ti nanoclusters [8]. However, Ti nanoclusters are also quite expensive and therefore not suitable for large scale production. More recently, high kinetics was also observed on material produced from NaH and Al with cheaper catalysts, such as $TiCl_3$ and $TiCl_4$. If the components are milled under high hydrogen pressure of initially 83 bar, the material exhibits an initial capacity of about 4 wt.% and reabsorbs about 3.5 wt.% in about 20 min at about 100 bar and 125 °C [9]. Alternatively, absorption in a few minutes is possible by partially hydrogenating NaH/Al during milling at low hydrogen pressure (12 bar), and further activation of the material by hydrogenating under 100 bar [10].

In addition to the hydrogenation kinetics, the degree of hydrogenation also depends critically on the powder preparation. The highest reversible capacity was demonstrated on sodium alanate with 2 mol% of Ti-based catalysts and reached about 4.5 wt.% out of the theoretical capacity of 5.6 wt.% for pure $NaAlH_4$ [11]. However, Srinivasan et al. found an initial capacity of only about 1.5 wt.% after dry ball milling of NaH and Al with $Ti(OBu)_4$

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[12]. On the other hand, they could show that a significantly higher initial capacity of 3.5 wt.% is achieved, if the components are ball milled in a pentane suspension [12]. Such material showed a relatively good cycling stability over the maximum measuring range of 100 cycles, whereby the capacity increased continuously to 4.3 wt.% in the first 30 cycles. In the following cycles a slight decrease in capacity was measured, which was found to be caused by slightly decreasing kinetics. Bogdanović et al. used a glass reactor and glass balls to mix the components in pentane, resulting in a comparable hydrogenation behaviour [13]. Wang et al. showed that the degree of hydrogenation of doped NaH/Al increased with milling time, and also by milling under about 1 bar hydrogen atmosphere instead of inert atmosphere [14,15].

The reason for the strong dependence of hydrogenation behaviour on process conditions has not been clarified yet. The aim of this work is, therefore, to investigate the influence of different process parameters on the characteristics of the powder, such as microstructure and morphology, and on its hydrogenation properties to provide a basis for the development of a simple process route for complex hydrides exhibiting optimum storage capacity and kinetics. In view of upscaling and cost-efficiency, $TiCl_4$ was used as catalyst and NaH and Al were used as low cost raw materials.

2. Experimental

Milling experiments were conducted using commercial NaH (95%, Sigma–Aldrich Chemie GmbH, Steinheim, Germany), aluminum (99.5%, Johnson Matthey GmbH & CoKG, Karlsruhe, Germany) and 2 mol% $TiCl_4$ (Fluka Chemie GmbH, Buchs, Switzerland) as catalyst. All handling including milling was carried out in a glove box with purified argon atmosphere. Prior to milling, NaH and aluminum were mixed with a spatula in a molar ratio of 1.08–1 according to the reaction:

$$1.08NaH + Al + 0.02TiCl_4 \rightarrow NaH + Al + 0.08NaCl + 0.02Ti$$
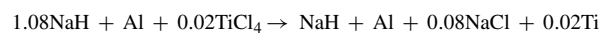
which is expected to occur during milling. Since $TiCl_4$ is very volatile in dry argon atmosphere, it was added with a pipette after mixing, and the milling vessel was immediately closed thereafter. Milling was carried out in a planetary ball mill, type Pulverisette 5, Fritsch GmbH, Germany, in stainless steel vials using 10-mm stainless steel balls at a rotational speed of 350 rpm and a ball-to-powder ratio (BPR) of 10:1. For wet milling, 50 ml of pentane (*n*-pentane) was added 10 min after the addition of the catalyst. The wet milled samples were dried in vacuum after milling.

The sorption kinetics is characterized by a volumetric method in a Sievert's type apparatus (HERA, Quebec, Canada). The powder samples of about 125 mg were filled in a sample holder under purified argon.

Crystallite sizes were estimated for comparative purposes by using the Scherrer method. For this purpose, milled and hydrogenated samples were characterized by X-ray diffraction (XRD) using a diffractometer (Siemens D5000) with Cu Kα radiation and a secondary monochromator. To prevent reaction with air, the specimen was encapsulated using a polyimide film (capton foil). The data were collected in the range between 28° and 50° in steps of 0.02°. The peak width in form of the full-width-at-half-maximum (FWHM) for Cu Kα1 was extracted by using the Pseudo-Voigt peak fit function in the software TOPAS 2, Bruker AXS GmbH, Karlsruhe, Germany. The instrumental broadening was determined using a silicon oxide standard and subtracted from the instrumental breadth. The resulting value was used in the Scherrer equation to determine the crystallite size. Although this method does not take into account the peak broadening due to internal strains, and thus underestimates crystallite sizes, it was chosen because of the small number of high intensity peaks without contributions from other phases. Therefore, only the 2 0 0 reflection for fcc NaH, the 1 1 1 reflection for fcc-Aluminum

and the 1 1 2 reflection for body-centered tetragonal $NaAlH_4$ were taken into account.

Scanning electron microscopy (SEM, Zeiss DSM 962) was used to characterize the powder morphology and microstructure. Due to the high affinity of the samples to oxygen, the sample preparation and the transfer from the inert gas box to the vacuum chamber of the SEM was carried out under argon. The powder samples were distributed on a conductive adhesive strip and subsequently placed in a plastic box, which was closed within inert gas box. The argon containing plastic box was carried to the SEM. The transfer of the samples from the box to the SEM vaccum chamber was carried out within a few seconds while directing a continuous flow of argon towards the sample.

3. Results and discussion

In order to evaluate the potential of NaH/Al mixtures using $TiCl_4$ as catalyst, cycling experiments were performed at optimum absorption conditions and desorption into vacuum. Such optimum absorption conditions are 100 bar and 125 °C [9]. As an example, Fig. 1 shows the sorption behaviour of a NaH/Al mixture milled for 1 h with $TiCl_4$. The 1st absorption proceeds rather slowly, resulting in a total hydrogen uptake of about 2.5 wt.% after 3 h and 3.5 wt.% after 18 h. The following desorption/absorption cycles show much faster kinetics than the initial absorption. Absorption of 3 wt.% of hydrogen is completed in about 5 min and a total desorption could be reached in about 3 h. This indicates that a strong activation of the material takes place during the 1st absorption. Although the absorption kinetics after activation is close to the targets for automobile application of 3–5 min, the capacity is far below the theoretical value of 5.1 wt.% (including the weight of NaCl and the catalyst) and still significantly below 4.5 wt.%, which was reached by different preparation methods in other investigations [11]. Since the amount absorbed in the 1st activation seems to determine the reversible capacity in the following cycles, the following investigations concentrate on the influence of process conditions on the initial absorption.

Fig. 2a shows the 1st absorption of samples dry milled for different times. The curves show that a longer process time has a positive effect on the sorption rate, and the amount of hydrogen absorbed increases up to 5 h of milling time. The first hydro-
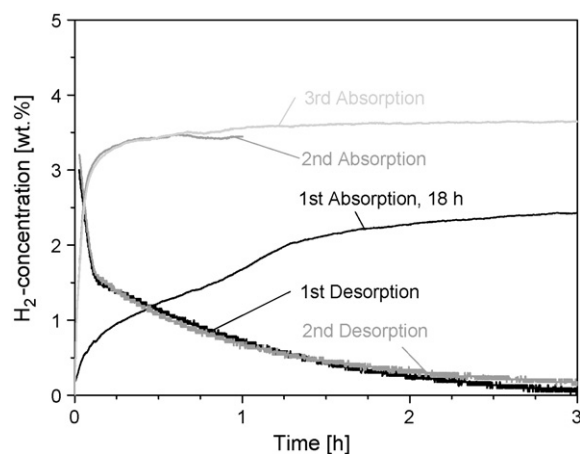

Fig. 1. Absorption and desorption cycles at 100 bar hydrogen and vacuum, respectively, at 125 °C of dry milled NaH–Al composites with 2 mol% $TiCl_4$ (1 h milling time).