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Synthesis of NaAlH₄-based hydrogen storage material using milling under low pressure hydrogen atmosphere

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Abstract

The present study highlights the advantages of milling NaH/Al under moderate hydrogen pressure as a favourable production step for NaAlH₄-based hydrogen storage materials. Firstly, it is demonstrated that NaAlH₄ can be obtained by applying a moderate hydrogen pressure (6-12 bars) during milling of NaH and Al with and without the presence of an inexpensive catalyst (TiCl₄). The yield of NaAlH₄ depends critically on process parameters, such as hydrogen pressure and milling time. A fully converted product is capable of reversible hydrogen storage without any activation procedure. Under optimized conditions, a capacity of 4.2 wt.% was achieved, and kinetics in the first desorption are comparable to NaAlH₄ doped with TiCl₃. Secondly, the synthesis has been optimized towards shorter milling times. By applying a few absorption/desorption cycles to material that was partially converted during milling, almost full reversible storage capacity can be reached. In addition, kinetics is extremely enhanced. For example, such material exhibits an optimum capacity already after two sorption cycles at 100 bar and 125 °C and allows to absorb 80% of the reversible hydrogen content within a few minutes.

Keywords: alanate, hydrogen absorbing materials, mechanochemical processing, X-ray diffraction, kinetics

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Introduction

Hydrogen is the ideal means of storage, transport and conversion of energy for a comprehensive clean-energy mobility concept. 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]. Magnesium hydride also has a high storage capacity by weight, however the temperature for desorption at 1 bar has to be at least 300°C.

Therefore, research has recently focused on alkali alanates as potential storage materials. Bogdanović et al. showed in 1996 that hydrogen can be reversibly stored and released in sodium aluminum hydride, when it is ball milled with a suitable catalyst [2]. Sodium aluminum hydrides with Ti colloids can absorb hydrogen in a few minutes at 100 bar and 100°C and also release hydrogen at 100°C [3]. Under such conditions, 4.5 wt.% out of the theoretical capacity of 5.6 wt.% are reached [3]. These materials, however, are intricately prepared [4, 5]: Na or NaH and Al are diluted in THF, and a hydrogen pressure of 140 bar at 150°C has to be applied. Subsequently, the NaAlH₄ present in solution is filtered, precipitated and dried. Since the solubility of NaAlH₄ is very low, a high amount of solvent is necessary.

Therefore, alternative routes for the production of NaAlH₄ were investigated. Dymova et al. milled AlH₃ with NaH in 1:1 ratio to achieve NaAlH₄ [6]. Indeed, milling in argon atmosphere with and without toluene as milling agent lead to NaAlH₄ in relatively short times [6]. However, AlH₃ itself is produced from alkali alanate, such that this synthesis cannot serve as a feasible production route for NaAlH₄. In addition, Dymova et al. showed that synthesis is possible from Na, Al, and H₂ at high temperature (280°C) and pressure (175 bar), where Na is present in liquid state [7]. However, due to the high temperature and the high pressure this process is technically not favorable.

Fortunately, it could be demonstrated that hydrogenating a composite of NaH and Al is also possible in solid state when adding a titanium-based catalyst [8, 9, 10]. Firstly, these components were mixed, leading to a composite capable of reversible absorption and desorption. The mixing is possible in a glass reactor or in a high-energy ball mill under inert atmosphere. However, full hydrogen capacity is reached only after numerous activation cycles [8]. The highest initial capacity of about 3.5 wt.% was reached, if the mixing is carried out in pentane. However, still a number of cycles are necessary to reach a maximum capacity [9,10]. The best results showed a maximum capacity of only 4.0 wt.% after about 20 cycles [10]. It was also shown that the initial capacity can be increased by milling doped NaH/Al under about 1 bar hydrogen atmosphere instead of inert atmosphere and by using Ti powder instead of Ti based compounds as catalyst [11]. However, sorption kinetics of the material produced in this way is rather slow [11].

Recently, it has been shown, that NaAlH₄ can be formed by milling NaH/Al with TiCl₃ under hydrogen atmosphere with an initial pressure of 83 bars [12]. The material exhibits an initial capacity of about 4 wt.% and very fast sorption kinetics without activation. However, the pressure used during milling is too high to be applied in industrial milling equipment. Recent attempts to form NaAlH₄ by milling under hydrogen pressure of less than 8,5 bars failed and led only to partial formation of Na₃AlH₆ [13]. The reason for only partial formation of sodium alanate using moderate pressures remains unclear.

Due to its low thermodynamical stability, higher pressures might be required to form NaAlH₄. For example, thermodynamical studies at low temperature indicate that, at 1 bar hydrogen

pressure, NaAlH_4 is thermodynamically stable only up to 33°C [14]. However, depending on process parameters, much higher temperatures can occur during milling, eliminating the driving force for its formation. This drawback may not be crucial as it could be shown that sodium alanate, only partially converted during milling under hydrogen atmosphere, can be further hydrogenated without activation by applying a subsequent hydrogenation/dehydrogenation cycle reaching about 3.5 wt.% of hydrogen storage capacity [13].

The aim of this work is to develop a simple process route for hydrogen storage materials with optimum storage capacity and kinetics and to obtain a material that does not require a high number of activation cycles. In a first step, NaAlH_4 will be produced by milling of NaH and Al under hydrogen atmosphere at moderate pressures. Then, it will be evaluated, which suitable precursor is to be formed during milling to obtain optimum reversible storage capacity of the material and fast sorption kinetics. In view of a low cost production route, instead of TiCl_3 used in most studies, the less expensive TiCl_4 is used as catalyst in the present study.

Experimental

Milling experiments were conducted using commercial NaH (95%), Sigma Aldrich, Steinheim, Germany and Aluminum (99,5%), Johnson Matthey, Karlsruhe, Germany, as initial materials. The materials were mixed with a spatula and milled in a planetary ball mill, type Pulverisette 5, Fritsch, Germany, in stainless steel vials using 10-mm stainless steel balls. Milling was performed at a rotational speed of 350 rpm and a ball-to-powder-ratio (BPR) of 50:1 and, additionally, at a rotational speed of 230 rpm and a BPR of 10:1.

The heat produced during milling leads to elevated temperatures in the interior of the milling vial. To keep the temperature during milling low, the mill was cooled by fans. The temperature inside the vials was estimated by milling without powder for different milling times and subsequent measurement of the temperature by a thermocouple. The values were confirmed by measuring the pressure before and after different intervals of milling without powder.

All handling including milling was carried out in a glove box with purified Argon atmosphere. Milling was performed with or without the addition of 2 or 5 mol.-% TiCl_4 (Fluka, Buchs, Switzerland) as catalyst. Since TiCl_4 is very volatile in dry Argon atmosphere, it was added with a pipette and the milling vessel was immediately closed. Subsequently, hydrogen was introduced by a device, that allows charging the milling vessel through a non-return valve with a defined initial hydrogen pressure and, additionally, allows measuring the pressure after milling. Thus it was confirmed that the pressure in the vial never decreased to less than 80% of the initial value.

The product was characterized by x-ray diffraction (XRD) using a diffractometer (Siemens D5000) with Cu-K_α radiation and a secondary monochromator. To prevent the reaction with air, the specimen was encapsulated with a polyimide film (capton foil) during XRD. The data were collected in the range between 28° and 50° in steps of 0.02° .

The sorption kinetics were 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.

Results and Discussion

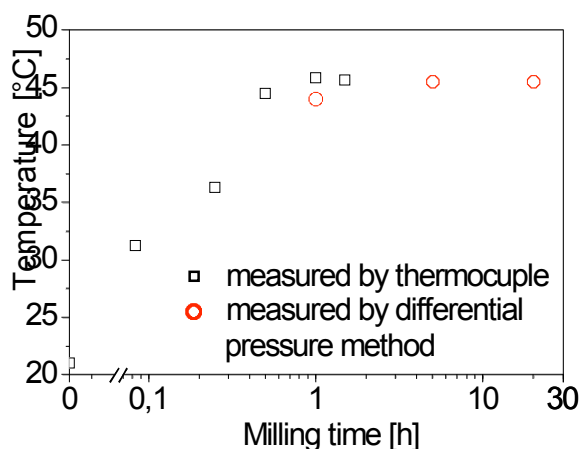


Fig 1: Temperature in the milling vials without powder as a function of milling time at a rotational speed of 350 rpm in the fan-cooled planetary ball mill

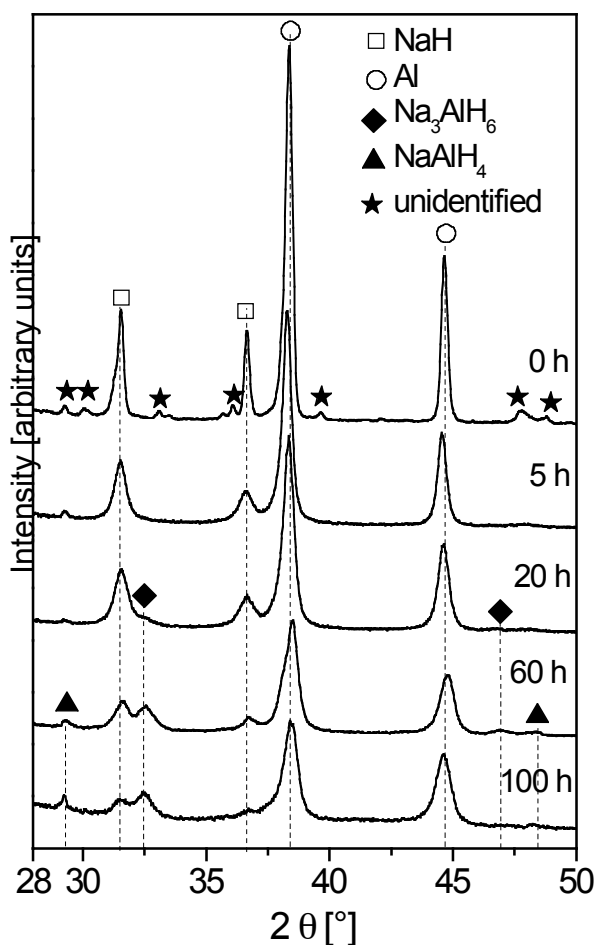


Fig 2: X-ray diffraction patterns of NaH-Al samples after different times of milling at 6 bars hydrogen pressure.

ray diffraction patterns of the initial mixture and milled material both containing 5 mol.% TiCl_4 . As expected, the initial mixture shows NaH and Al and small peaks of NaCl, which

Fig. 1 shows the temperature of the vessels without powder as a function of the milling time. The temperature increases in about half an hour from room temperature to about 45°C and remains constant at this value. At 45°C the equilibrium pressure for NaAlH_4 is about 2 bar [14]. The little higher pressure of 6 bar hydrogen pressure was chosen for the first experiment to guarantee a sufficient driving force for the reaction.

Fig. 2 shows the x-ray diffraction patterns of the 1:1-stoichiometric mixture of NaH and Al. The unmilled mixture shows the characteristic peaks of NaH and Al. After 5 h of milling, NaH and Al are still the dominating phases. The significant broadening of the peaks of both the NaH and the Al phase indicates that the crystallite sizes of both phases have been strongly reduced. However, no phase reaction has occurred yet. After 20 h milling, first traces of Na_3AlH_6 are observed and the phase fraction increases continuously up to the maximum investigated milling time of 100 h. After 60 h of milling, NaAlH_4 is detected additionally. This demonstrates that NaAlH_4 can be formed even without a catalyst by milling under hydrogen atmosphere of 6 bars. The slow conversion, however, indicates that a high yield of NaAlH_4 can probably not be reached in reasonable milling times.

Sorption kinetics of sodium alanate can be improved by a suitable catalyst, which should be homogeneously and finely dispersed in the material. Therefore, it is reasonable to add the catalyst before milling. Fig. 3 shows x-

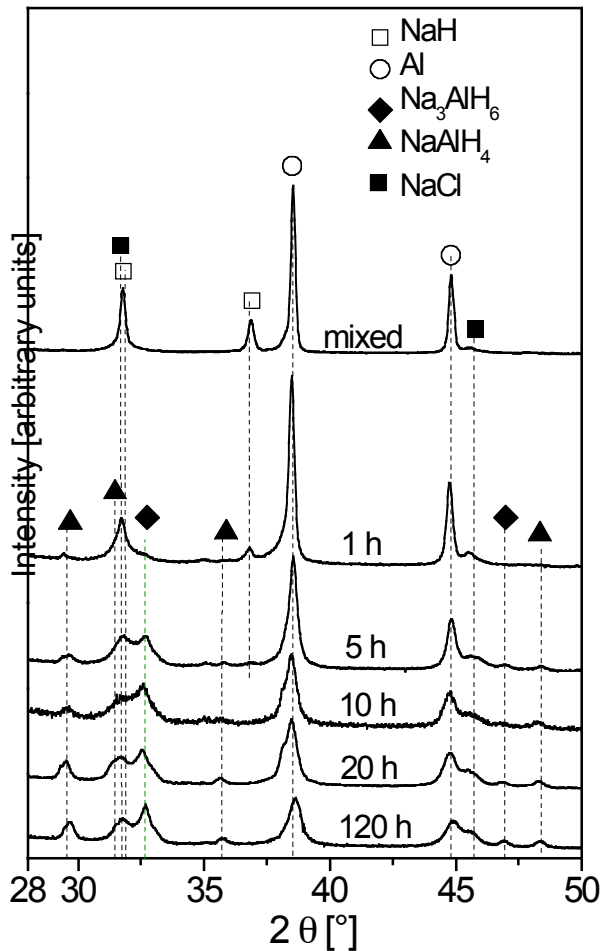


Fig 3: X-ray diffraction patterns of NaH-Al+5mol.%TiCl₄ after different times of milling at 6 bars hydrogen pressure.

produced by the exothermic formation of alane phase. Thus, the powder might temporarily exceed the temperature range, in which NaAlH₄ is stable at the surrounding hydrogen pressure, leading only to a partial conversion. To prove the assumption that local temperatures impede a complete conversion, an experiment with increased pressure (12 bar) was conducted. The phase evolution is shown in Fig. 4: The conversion is faster and the amount of NaAlH₄ formed is significantly higher, if 12 bars are used instead of 6 bars. However, after 60 h, Al and minor amounts of Na₃AlH₆ are still present, and no further conversion is achieved. This may originate from some temperature peaks that still impede a full conversion. In addition, a stoichiometric mixture of NaH and Al was used as initial material. As part of the NaH reacts with TiCl₄ to NaCl, a surplus of Al remains in the final product, thus decreasing the capacity of the material.

indicates that TiCl₄ reacted with a small amount of NaH. Already after one hour of milling, a first small peak of Na₃AlH₆ and one of NaAlH₄ is detectable. After five hours of milling, the peaks of Al have significantly broadened, as it was also observed during milling without catalyst. However, due to the presence of a catalyst significant amounts of Na₃AlH₆ have already formed, proving that the catalyst leads to a much faster formation of Na₃AlH₆. The formation of NaAlH₄, however, is still very slow and after 20 h no significant further conversion is observed.

Although a maximum temperature of 45°C was measured at the bottom of the milling vials, locally higher temperatures may occur. Particularly, in powder particles which are trapped between the grinding balls and the wall of the vial during a collision, the temperature can increase significantly due to the heat released by deformation of powder particles and the friction of particles against each other. Additionally, heat is

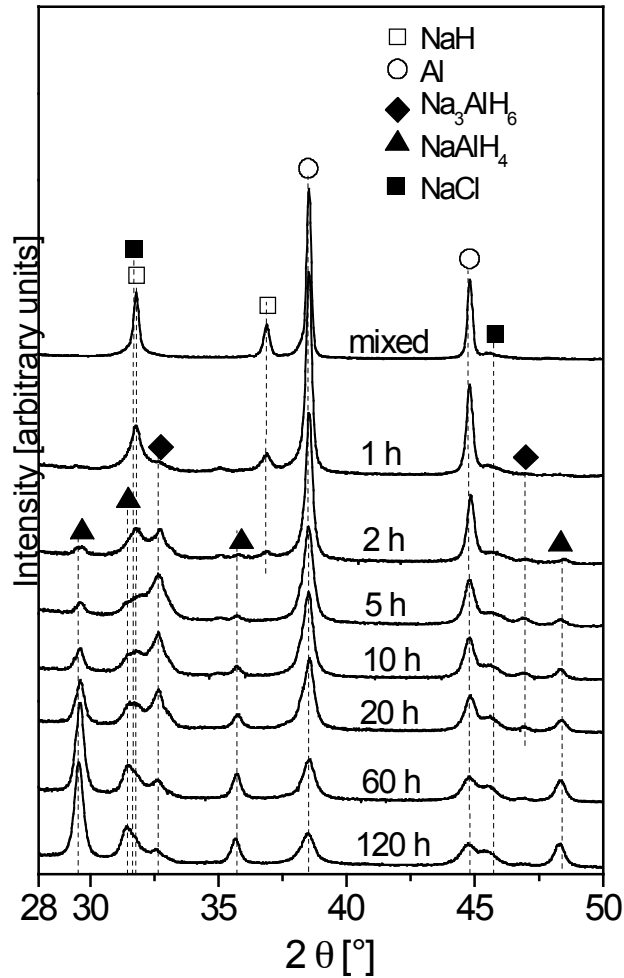
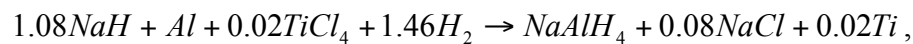


Fig 4: X-ray diffraction patterns of NaH-Al+5mol.%TiCl₄ after different times of milling at 12 bars hydrogen pressure.

Therefore, to optimize conversion of the storage material, a further experiment was performed with significantly less milling intensity to prevent high temperatures. The milling intensity was decreased by using a lower ball to powder ratio (10:1 instead of 50:1) and less rotational speed (230 rpm instead of 350 rpm). Additionally, the amount of catalyst was reduced to 2mol.%TiCl₄ to decrease the amount of NaCl in the product. Moreover, to eliminate the excessive aluminium, the ratio of NaH to Al was adjusted to 1.08:1 according to the reaction



assuming, in a first approach, that Ti is present as pure metal after milling.

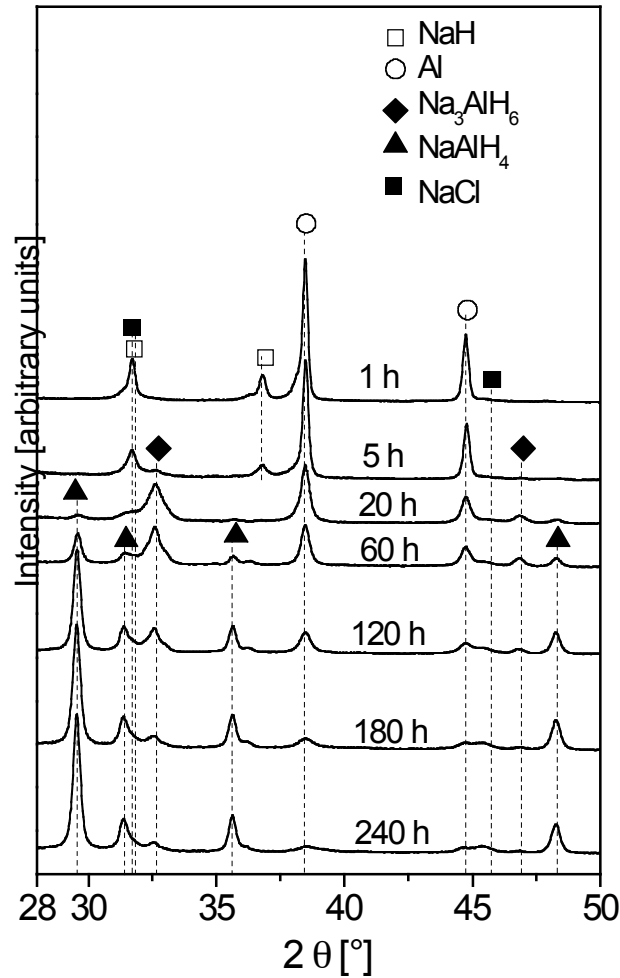
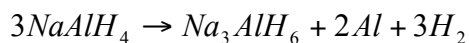


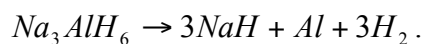
Fig 5: X-ray diffraction patterns of NaH-Al+2mol.%TiCl₄ after different times of milling with low milling intensity at

In Fig. 5, the x-ray diffraction patterns of this mixture are shown after different milling times. Due to the lower content of catalyst and the lower milling intensity, the conversion rate is quite slow. However, after 240 h of milling the conversion is almost complete.

In Fig. 6, the first desorption of the samples produced by milling with low milling intensity is plotted. Desorption was performed at 125 °C into vacuum (fixed volume). The change in desorption rate, occurring after 1 h, can be attributed to the transition from the first decomposition reaction,



to the second decomposition reaction,



As expected, the amount of hydrogen released in the first step of desorption continuously increases with the milling time. Since the second decomposition reaction is very slow, desorption was accelerated by increasing the temperature to 150°C for the 240 h milled

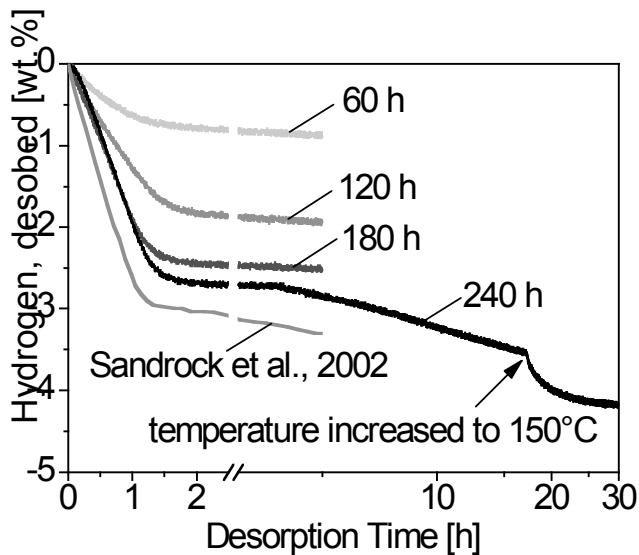


Fig 6: First desorption at 125°C into vacuum of NaH-Al+2mol.%TiCl₄ after different times of milling at 12 bars hydrogen pressure in comparison with 2nd desorption of NaAlH₄ with 2mol.%TiCl₃ [16].

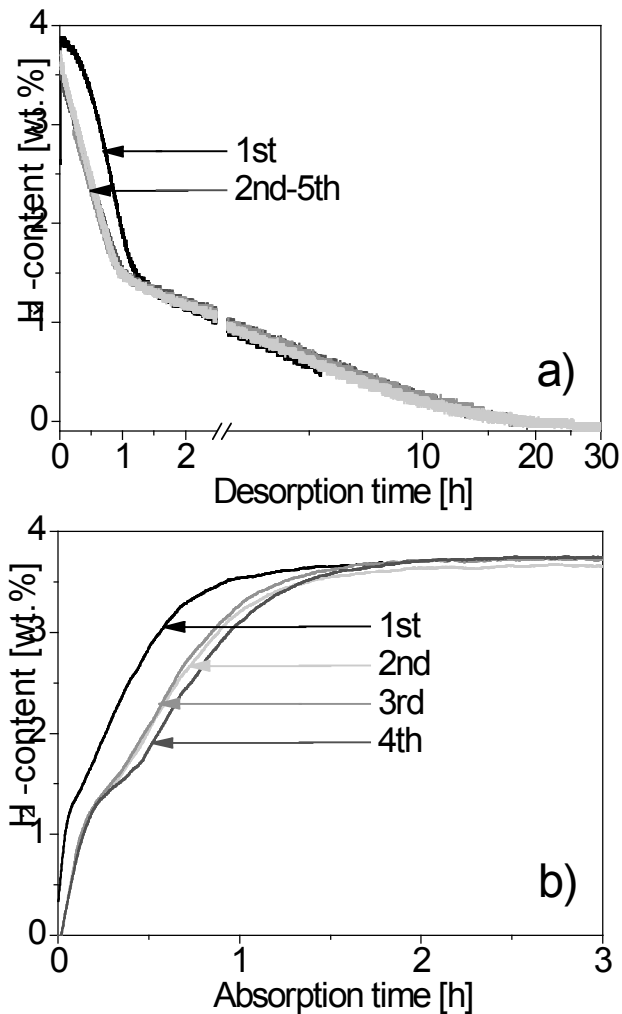


Fig 7: Cycling experiment at 125°C of almost fully converted NaAlH₄, produced by 180 h reactive milling of NaH-Al+2mol.%TiCl₄ in 12 bars hydrogen atmosphere: a) desorption in vacuum, b) absorption at 80 bars. The experiment was started with desorption.

sample. Thus a total capacity of 4.2 wt.% could be measured. Considering the incomplete conversion into NaAlH₄, this value is very favourable when compared to the highest capacity of 4.5 wt.%, which could so far be achieved on TiCl₃ doped NaAlH₄ [15]. Also desorption kinetics seem to be satisfying when compared to the kinetics observed on TiCl₃ doped NaAlH₄ as measured by Sandrock et al [15]: The first decomposition reaction is completed in about 1 h.

In order to clarify, to what extent capacity and kinetics change upon further absorption-desorption cycles, a cycling test was carried out at 125°C, using a sample with 2 mol.% TiCl₄ content, prepared under 12 bar hydrogen atmosphere with low milling intensity. It can be seen in Fig. 7 that the material desorbs about 3.8 wt.% of hydrogen at 125°C. Nearly all hydrogen released in the first desorption, can be re-absorbed at 80 bars of hydrogen pressure. Also in the following cycles, no significant change in the reversible storage capacity is found. However, kinetics slow down slightly from the first to the second cycle in both desorption and absorption, as can be deduced from the sorption slopes in Fig. 7. After the second cycle, kinetics remains unchanged until the end of the experiment: The curves from second to fourth cycle are identical within the accuracy of the experimental method. This shows that the NaAlH₄ based storage material synthesized by reactive milling does not have to be activated by a cycling procedure to achieve a high reversible capacity and optimum kinetics.

In view of an industrial production of hydrogen storage material, the milling times to achieve a full conversion into NaAlH₄ during

milling are by far too high. Therefore, in a second approach, sorption properties of material are investigated, that is only partially converted into NaAlH_4 . Fig. 8 shows the first cycles of hydrogenation/dehydrogenation of a sample milled for 10 h in 6 bars of hydrogen atmosphere. A relatively high catalyst content of 5 mol.% TiCl_4 was used to improve reaction kinetics. Although the first hydrogenation of the sample is very slow, more than 1 wt.% of hydrogen is absorbed additionally to the amount of hydrogen, that was already introduced during reactive milling. The lack of any abrupt change in the absorption rate in this first absorption confirms that Na_3AlH_6 has already been formed during milling. In the second and third absorption, a reversible capacity of about 3.3 and 3.5 wt.% can be detected. This amount compares well with the reversible capacity observed by Sandrock et al., who found 3.0 wt.% H_2 for a sample doped with 6 mol.% TiCl_3 and 3.9 wt.% H_2 for a sample doped with 4 mol.% TiCl_3 . In addition, our results demonstrate that maximum possible capacity is already obtained in the third absorption. From a technical point of view, the activation can be carried out in the tank shell, because the first two activation cycles can be carried out at 100 bar and 125°C only.

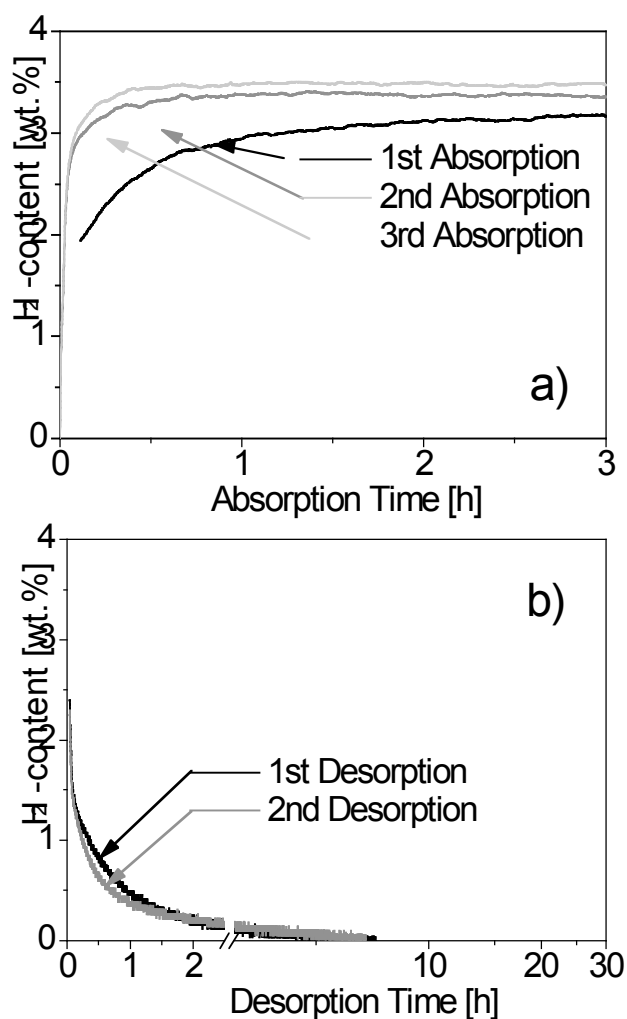


Fig 8: First hydrogenation/dehydrogenation cycles at 125°C of NaH-Al+5mol.%TiCl₄ after 10 h of milling in 6 bars hydrogen atmosphere: a) absorption at 100 bars, b) desorption in vacuum. The experiment was started with absorption.

Fehler! Verweisquelle konnte nicht gefunden werden. also shows that, after the first absorption, desorption and absorption both exhibit extraordinarily fast kinetics: 80% of the maximum reversible hydrogen content is absorbed in about 3 min. Desorption is so fast that, during establishing the vacuum, the sample desorbs already a high amount of hydrogen, leading to incomplete desorption curves. By considering the time of about 2 min. for establishing the vacuum, it can be estimated that the first step of desorption is completed in about 5 min. This shows that for material, produced by partial hydrogenation during reactive milling and subsequent hydrogenating, kinetics is more than an order of magnitude faster than the material that is fully converted into NaAlH_4 during reactive milling. The faster kinetics can be in part explained by the higher catalyst content and the slightly higher pressure. However, it was reported, that increasing the catalyst content from 2 to 6 mol.% TiCl_3 , leads only to about 3 times faster kinetics [15]. Therefore, further studies have to evaluate the microscopic reasons for the fast kinetics.

It is interesting to note, that the obtained sorption kinetics under our optimized conditions are almost comparable to the best material based on NaAlH_4 that was prepared in a complicated

procedure by synthesizing NaAlH₄ at high pressure in solvent, purifying and subsequently doping with Ti-clusters [3, 16]. Therefore, the applied method of reactive milling under moderate hydrogen pressure and subsequent hydrogenation, which does not necessitate the use of any solvent and utilizes TiCl₄ as a cost-effective catalyst, is very promising for an industrial production route for hydrogen storage material based on NaAlH₄ and other related materials.

Conclusions

By reactive milling of NaH and Al under moderate hydrogen pressure, NaAlH₄ can be formed with and without the addition of a TiCl₄ as catalyst. The addition of catalyst speeds up the conversion and leads to a hydrogen storage material with sorption kinetics and a hydrogen storage capacity comparable to conventionally prepared material. Favourably, no activation process is required to obtain good capacity and sorption kinetics. However, complete conversion of NaH and Al into NaAlH₄ during reactive milling is very slow at moderate pressures and consequently requires very long milling times. Therefore, in a subsequent approach, it was demonstrated that a partial conversion into NaAlH₄ is sufficient to obtain a storage material that is capable of reversibly storing hydrogen with nearly optimum capacity after only two cycles of sorption. Moreover, such material exhibits extraordinarily fast kinetics. Consequently, this production method has a high potential for a low cost industrial production process for hydrogen storage materials based on alanates or other related materials.

Acknowledgement

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