$TiCl_3$-Enhanced $NaAlH_4$: Impact of Excess Al and Development of the $Al_{1-y}Ti_y$ Phase during Cycling

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$NaAlH_4$ with $TiCl_3$ and Al were mixed by ball-milling and cycled three times. The hydrogen storage properties were monitored during cycling, and the products were characterized by synchrotron X-ray diffraction. Because of the previously described formation of $Al_{1-y}Ti_y$ with $y \approx 0.15$ during cycling that traps Al beyond the amount associated with the formation of NaCl, some Na_3AlH_6 has no free Al to react with to form $NaAlH_4$. This was counteracted in the present work by adding a stoichiometric amount of Al that increases the theoretical storage capacity. Due to limitations in metal diffusion small amounts of Na_3AlH_6 were still detected. When ~7 mol % more Al than the stoichiometric amount was added, the observed storage capacity increased significantly, and the Na_3AlH_6 content was negligible after prolonged rehydrogenation. Cycled $NaAlH_4$ + 10 mol % $TiCl_3$ were desorbed to two different levels, and the diffraction patterns were compared. There is no change in unit-cell dimensions during desorption, and there is no sign of changes in the bulk composition of the $Al_{1-y}Ti_y$ phase during a cycle. Adding pure Ti to a NaH + Al mixture by ball-milling in argon or hydrogen results in formation of TiH_2 that is stable during at least one cycle.

1. Introduction

The development of lightweight hydrogen storage materials with high reversible capacity are essential for the realization of practical hydrogen-powered vehicles. In 1997, Bogdanovic et al.[1] reported that dehydrogenation of solid $NaAlH_4$ is markedly accelerated and rendered reversible under moderate conditions upon mixing the hydride with a few mole percent of selected transition metal complexes. Hydrogen cycling capacities of 3−4 wt % have now been achieved for Ti-enhanced $NaAlH_4$ at 120−160°C with relatively good kinetics.[2−5]

$NaAlH_4$ decomposes in two steps to NaH + Al as shown in eqs 1 and 2, releasing in total 5.6 wt % hydrogen. Dehydrogenation of NaH occurs at too high temperature to be of practical importance.

$$NaAlH_4 = {}^1/_3Na_3AlH_6 + {}^2/_3Al + H_2 \quad (1)$$

$${}^1/_3Na_3AlH_6 = NaH + {}^1/_3Al + {}^1/_2H_2 \quad (2)$$

Ti can be introduced into the hydride either by mixing $NaAlH_4$ with the Ti-based additive (often titanium halides) in a dispersion[1] or by ball-milling.[6] Ball-milling is a simpler technique and results in samples with at least as good kinetics as the samples prepared in a dispersion. For samples prepared by ball-milling recent X-ray absorption studies of $NaAlH_4$ with Ti additives indicate zerovalent Ti^0, at least after cycling.[7−9] Thorough powder X-ray diffraction (PXD) studies of fresh and cycled $NaAlH_4$ samples with different additives[10,11] as well as a neutron diffraction study[10] do not indicate any significant bulk solid solution of Ti in Na or Al sites of crystalline $NaAlH_4$ from precise determination of the unit-cell dimensions. No crystalline Ti-containing phases were detected in samples that were ball-milled but not cycled.[10,11] However, after being cycled at least part of the Ti is forming a phase with Al with a lower Ti content than Al_3Ti.[10] The content of this Ti−Al phase has been reported to increase with increasing amount of Ti additive.[12] Ti−Al alloys have been prepared by ball-milling of the elements,[13−19] including a metastable $Al_{1-y}Ti_y$ phase with $y < 0.25$.[13] Recently it was found that $Al_{1-y}Ti_y$ formed during cycling of $NaAlH_4$ with various Ti additives has a composition of $y \approx 0.15$.[20]

An important consequence of an irreversible formation of $Al_{0.85}Ti_{0.15}$ is that more Al is bound in this phase than released from a complete redox reaction between $NaAlH_4$ and $TiCl_3$; hence the Al content is the limiting factor for rehydrogenation of Na_3AlH_6. In this study, excess Al was added in an attempt to compensate for this and to investigate the completeness of the rehydrogenation. Samples with additional Al, i.e., with even more Al than trapped in $Al_{0.85}Ti_{0.15}$ such that free Al should be present in the sample after complete rehydrogenation, were also investigated with the same purpose. To gain more information about the effect of $Al_{0.85}Ti_{0.15}$ on the kinetics, a Ti-rich sample was stepwise desorbed and studied by PXD.

2. Experimental Section

All reactions and operations were performed under argon in a glovebox or using standard Schlenk techniques with oxygen and water-free solvents. $NaAlH_4$ was purchased from Albemarle Corp. and recrystallized with tetrahydrofuran/pentane before use. $TiCl_3$ was purchased from Aldrich Chemicals Inc. and used without further purification. $TiCl_3$ was added to $NaAlH_4$ by ball-milling 30 and 60 min, respectively, in a Fritsch Pulverizette 7 at 350 rpm. The ball-to-sample mass ratio was approximately 20:1.

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The cycled samples, with $TiCl_3$, were dehydrogenated at 160 °C against 1 bar pressure and rehydrogenated at 115 bar at 120 °C in a calibrated Sievert's apparatus from LESCA Co., Japan, with a high-precision pressure transducer and a silicon oil bath.

SR-PXD data at 22 °C were collected at the Swiss−Norwegian Beam Line (station BM01B) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.5 mm boron−silica−glass capillaries. Intensities were measured in steps of $\Delta(2\theta) = 0.003-0.005°$. The wavelengths 0.49962 and 0.51979 Å were obtained from a channel-cut Si(111) monochromator.

Rietveld refinements were carried out using the program Fullprof (version 2.80).[21] X-ray form factors were taken from the Fullprof library. Thompson−Cox−Hastings pseudo-Voigt profile functions were used, and backgrounds were modeled by interpolation between manually chosen points. Information about the microstructure was obtained from isotropic broadening effects included in the Rietveld refinements. The instrumental resolution was determined with a LaB_6 standard.

3. Results and Discussion

$Al_{1-y}Ti_y$ with $y \approx 0.15$ is formed during cycling of $NaAlH_4$ with Ti catalyst according to the total reaction given by eq 3 [20]

$$NaAlH_4 + xTiCl_3 = (1 - kx)NaAlH_4 + 3xNaCl + x/yAl_{1-y}Ti_y + lxNa_3AlH_6 + (2k - 3l)xH_2 \quad (3)$$

with

$$k = \frac{3 - 6y}{2y} \quad \text{and} \quad l = \frac{1 - y}{2y} - {}^3/_2$$

To compensate for the Al trapped in $Al_{1-y}Ti_y$ that leaves some unreacted Na_3AlH_6 after rehydrogenation $NaAlH_4$ with 2 and 4 mol % $TiCl_3$ was ball-milled with extra Al. When $2lx$ Al is added, the total reaction becomes

$$NaAlH_4 + xTiCl_3 + 2lxAl = (1 - 3x)NaAlH_4 + 3xNaCl + x/yAl_{1-y}Ti_y + 2kxH_2 \quad (4)$$

In the case of $y = 0.15$ and 2 and 4 mol % $TiCl_3$, 5.3 and 10.7 mol % Al are needed, respectively, to prevent deficiency of Al for reaction with Na_3AlH_6 to $NaAlH_4$. The addition of Al according to eq 4 increases the theoretical storage capacity compared to eq 3. In Figure 1, these two models are compared for 4 mol % $TiCl_3$. The theoretical capacity, i.e., complete consumption of free Al when $y = 0.15$, is increased from 3.94 to 4.25%. The corresponding numbers for 2 mol % $TiCl_3$ are 4.73 and 4.88%.

Because the chemical reactions may be hindered by diffusion through $NaAlH_4$ product layers, additional Al in the two samples was also tested to aim at complete consumption of Na_3AlH_6. This may increase both the storage capacity and the kinetics in applied systems. The reaction then becomes

$$NaAlH_4 + xTiCl_3 + (2lx+w)Al = (1 - 3x)NaAlH_4 + 3xNaCl + x/yAl_{1-y}Ti_y + wAl + 2kxH_2 \quad (5)$$

The amount ~7 mol % additional Al ($w \approx 0.07$) was chosen, because this could be large enough to affect the reversibility and still small enough to give an increased theoretical capacity compared to no extra Al as in eq 3. The samples were then cycled three times with a final rehydrogenation of 9 h for the 2 mol % $TiCl_3$ samples and >20 h for the 4 mol % $TiCl_3$ samples.

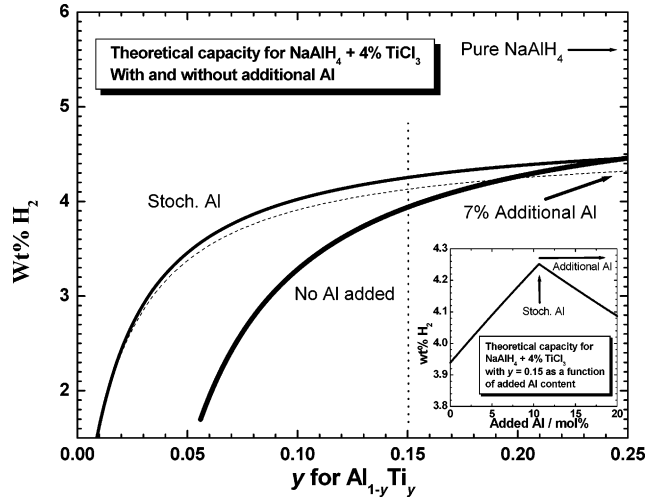

Figure 1. Theoretical storage capacity of $NaAlH_4$ + 4 mol % $TiCl_3$ with ($w \approx 0.07$) and without additional Al as a function of the composition of $Al_{1-y}Ti_y$. The inset shows the wt % H_2 for 4 mol % $TiCl_3$ and $y = 0.15$ as a function of the amount of added Al, having a maximum at $2lx$.

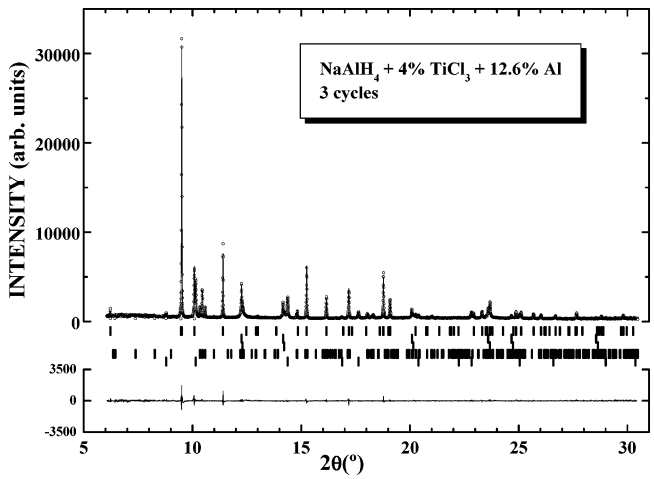

Figure 2. Observed SR-PXD intensities (circles) and calculated intensities from Rietveld refinements (upper line) of $NaAlH_4$ with 4 mol % $TiCl_3$ and 12.6% Al after three cycles, measured at 22 °C at BM01B, ESRF. Positions of Bragg reflections are shown with bars for $NaAlH_4$, Al, $Al_{1-y}Ti_y$, Na_3AlH_6, and NaCl (from top). The differences between observed and calculated intensity are shown with the bottom line.

SR-PXD experiments confirmed that $NaAlH_4$, Na_3AlH_6, Al, and $Al_{1-y}Ti_y$ were present in all samples. Rietveld refinements give a decent fit to the observed data, as shown for 4 mol % $TiCl_3$ + 12.6 mol % Al in Figure 2.

In Figure 3, observed data are compared for 4 mol % $TiCl_3$ treated in different ways, with 12 mol % Al and 19 mol % Al. The data were measured with slightly different wavelengths and are therefore shown in the Q-range ($2\pi/d$). The intensities are normalized to the integrated intensity of NaCl, which according to eqs 3 and 4 only depends on the amount of additive, because all of the chloride added is bound in NaCl. It is evident that adding more Al than 12 mol % increases the observed amount of $NaAlH_4$. Prolonged rehydrogenation with 19 mol % Al further increases the amount of $NaAlH_4$. In this case, basically all of the Na_3AlH_6 has been consumed.

When the addition of Al is increased from 12 to 19 mol % Al, the amount of free Al in the sample increases as expected. In agreement with eq 4, the $Al_{1-y}Ti_y$ shoulder has the same intensity for all samples. The unit-cell dimensions are the same

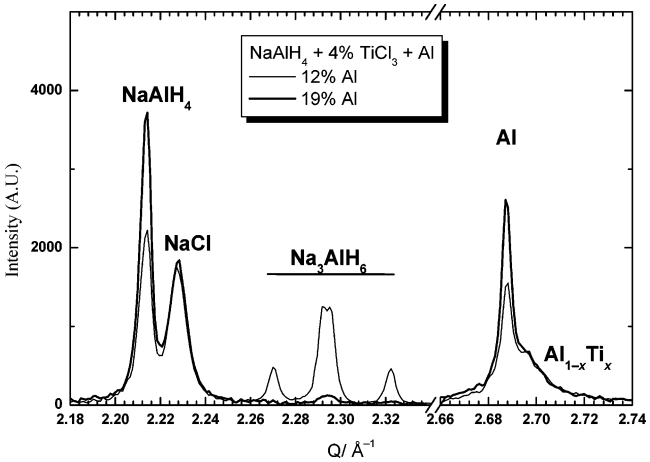

Figure 3. SR-PXD data of $NaAlH_4$ + 4% $TiCl_3$ and different Al amounts after three cycles with a prolonged last rehydrogenation, with intensities normalized to the NaCl reflections. Additional Al ($w \approx 0.07$) improves the reversibility, whereas the $Al_{1-y}Ti_y$ content appears to be independent of the Al content.

TABLE 1: Results of SR-PXD of $NaAlH_4$ + $x$$TiCl_3$ + zAl[a]

	SR-PXD samples			
mol % $TiCl_3$	2.00	2.00	4.01	4.00
mol % Al	6.2	12.0	12.6	19.0
rehydrogenation time, h	9	9	24	90
mol % $NaAlH_4$	63.0	62.8	60.5	69.5
mol % Na_3AlH_6	8.3	6.7	5.2	0.2
mol % Al	17.8	22.5	9.8	10.9
mol % $Al_{1-y}Ti_y$	6.0	3.9	14.3	11.5
mol % NaCl	4.8	4.1	10.2	7.9
% Al after rehydrogenation, SR-PXD	1.2	9.1	−0.6	10.5
% Al after rehydrogenation, calculated	0.9	6.7	1.9	8.3
wt % H_2 for dehydrogenation to NaH/Al, SR-PXD	4.2	4.2	3.9	4.3
wt % last rehydrogenation	2.37	3.21	3.35	3.70

[a] The upper third shows sample preparation, the middle third gives the mole fractions after three cycles, and the bottom third shows derived values of free Al after assumed complete rehydrogenation (compared to expected values from eq 4) and wt % H_2 for dehydrogenation to NaH/Al (PXD results compared to observed rehydrogenation amount).

as published earlier for $NaAlH_4$ + $TiCl_3$.[10,20] Hence, it seems that extra Al does not influence the $Al_{1-y}Ti_y$ phase but obviously facilitates the formation of $NaAlH_4$ from Na_3AlH_6.

The molar ratio of the phases after three cycles were derived from the Rietveld refinements and shown in Table 1. All samples but the sample with 4 mol % $TiCl_3$ and 19 mol % Al contain 5−8 mol % Na_3AlH_6, whereas the last sample only contains 0.2 mol %. With additional Al and prolonged rehydrogenation it is hence possible to remove basically all of the hexahydride.

There is an $Al_{1-y}Ti_y$ shoulder on the high-angle side of each Al reflection. In the refinements it is possible to distinguish $Al_{1-y}Ti_y$ from pure Al. By subtraction of 2 times the observed amount of Na_3AlH_6 from the amount of pure Al (cf. eq 1), it is possible to determine the real amount of excess Al after assumed complete rehydrogenation. As can be seen in Table 1, the observed amounts of excess free Al after cycling are in good agreement with excess Al calculated on the basis of the formation of $Al_{1-y}Ti_y$ with $y = 0.15$. This is in agreement with the results in ref 20. Furthermore, it confirms that samples with 2 and 4 mol % $TiCl_3$, where the trapping of Al in $Al_{1-y}Ti_y$ has been close to exactly counteracted by adding extra Al, have been successfully prepared. In addition, samples with ∼7 mol % additional Al were prepared.

The released and absorbed amount of hydrogen (wt %) during the cycling are shown in Figures 4 and 5. The values are considerably below the theoretical values as shown for the samples with 4 mol % $TiCl_3$ in Figure 1. From the storage capacities alone, this can be explained by both incomplete rehydrogenation and incomplete dehydrogenation to NaH + Al, but determination of mole fractions after cycling with PXD brings more insight into this; see below.

One important observation for both 2 and 4 mol % $TiCl_3$ is that the reversible hydrogen storage capacity was increased significantly by adding more Al than needed for the complete reaction with Na_3AlH_6. For 2 mol % $TiCl_3$, the capacity in the final rehydrogenation was increased from 2.37 to 3.21% by the 7 mol % additional Al (cf. Figure 4), whereas for 4 mol % the improvement was from 3.35 to 3.70 wt % (cf. Figure 5). Even though the theoretical capacity decreases by this additional Al (from 4.25 to 4.14% for 4 mol % $TiCl_3$), the observed capacity, at least in these first cycles, is increased. The observed capacity, as a fraction of the theoretical capacity, is increased from 49 to 68% for 2 mol % $TiCl_3$ and from 79 to 89% by this additional Al for 4 mol % $TiCl_3$. The sensitivity of the kinetics on the Al amount is an indication that Al may limit the kinetics of the dehydrogenation/rehydrogenation reaction.

In Table 1, the wt % remaining H_2 in different samples are shown, calculated from the fraction of the different phases determined by PXD. Furthermore, the observed wt % from the last rehydrogenation is given. The hydrogen content is significantly larger than the last observed rehydrogenation, and this clearly means that the second dehydrogenation reaction from Na_3AlH_6 to NaH/Al is not complete. The same result was obtained for cycled $NaAlH_4$ with $Ti(OBu)_4$ additive.[20] It appears that the incompleteness of the second dehydrogenation reaction is more severe for samples with 2 mol % $TiCl_3$ compared to 4 mol % $TiCl_3$.

This shows that both the first reaction step (eq 1 during rehydrogenation) and the second step (eq 2 during dehydrogenation) are incomplete. Because there should be enough Al seeds from the first step during dehydrogenation, excess Al is not expected to increase the completeness of the second step (eq 2) substantially. However, the present experimental results tend to confirm the idea that additional Al leads to a more complete first reaction step; i.e., the rehydrogenation becomes more complete.

This study confirms formation of an $Al_{1-y}Ti_y$ phase (a = 4.037 Å), which is more Al-rich than Al_3Ti. This metastable phase has a composition close to $Al_{0.85}Ti_{0.15}$.[20] The amount of this phase appears only to be dependent on the amount of added Ti, i.e., after normalization to the NaCl content. Furthermore, the positions, i.e., the unit-cell dimensions, are not changed. This is in line with eq 4 and shows that any additional Al does not influence y.

Ti-based additives obviously result in a Ti species that has a catalytic effect on alanates. Clearly, most of the Ti ends up as the $Al_{1-y}Ti_y$ phase after a few cycles. An obvious question is whether this is the catalyst or an unavoidable byproduct. One possible involvement of $Al_{1-y}Ti_y$ in the reaction could be that this phase transports and eventually stores Al during cycling, i.e., acts as a source of Al during rehydrogenation and a sink during dehydrogenation. This would eventually affect the composition and the unit-cell dimension of the phase.

This hypothesis was tested by taking the $NaAlH_4$ sample with 10 mol % $TiCl_3$ from ref 20 and partially dehydrogenating it and carrying out SR-PXD measurements at room temperature. Two different samples, with different extents of dehydrogena-

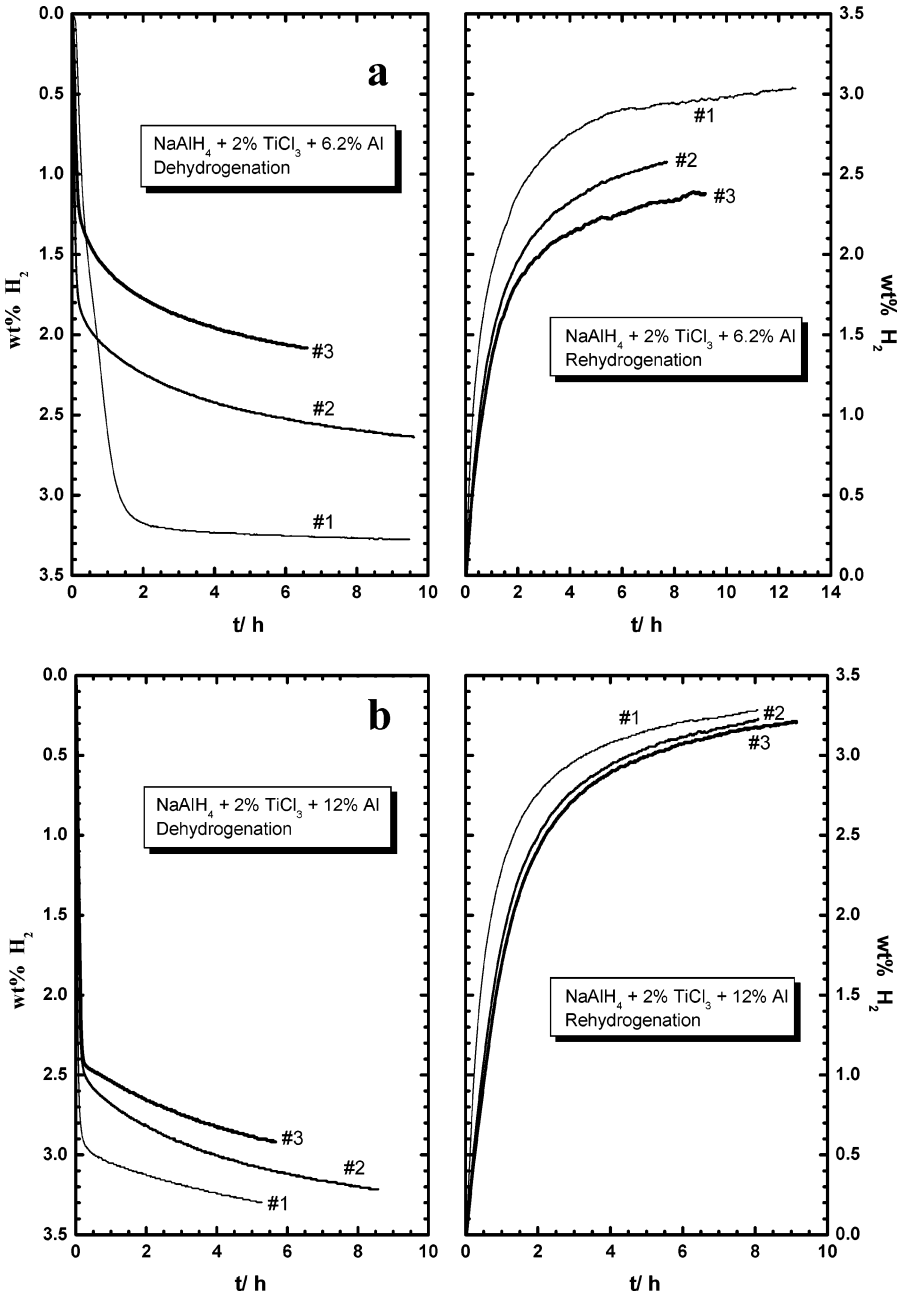

Figure 4. Storage capacity (wt %) during dehydronation and rehydrogenation of $NaAlH_4$ with 2 mol % $TiCl_3$ and (a) 6.2 mol % Al and (b) 12.0 mol % Al. Three cycles were carried out.

tion, were prepared at 160 °C, and the samples from the SR-PXD were estimated to be 3 and 46% dehydrogenated into the second step, respectively. In Figure 6, the SR-PXD results from the three samples are compared on a *Q*-scale around the strongest Al reflection. There is a large difference in the amount of free Al, but the positions of $Al_{1-y}Ti_y$ are not changed. The refined unit-cell dimensions are 4.0368(1), 4.0376(1), and 4.0376(1) Å, respectively, and there are no signs of $Al_{1-y}Ti_y$ changing composition during cycling of Ti-enhanced $NaAlH_4$.

Recent kinetics studies based on the John−Mehl−Avrami approach indicate that the limiting factor for the dehydrogenation reaction is changed from nucleation and growth to diffusion by adding Ti-based additives.[22] The same was found for V-based additives for $LiAlD_4$.[23] It is a possibility that the $Al_{1-y}Ti_y$ phase may facilitate nucleation and growth of the phases involved, but it is not improbable that the diffusion is improved as well. Contrary to interstitial metal hydrides, cycling of complex hydrides such as $NaAlH_4$ requires, as evident from eqs 1 and 2, diffusion of metal species. From the grain sizes this is on the order of 100 nm.

The grain sizes, determined from SR-PXD, of the present cycled samples with 2 and 4 mol % $TiCl_3$, are about 200 nm for $NaAlH_4$, whereas refinements of the considerable broader reflections for $Al_{1-y}Ti_y$ give an average grain size of about 30 nm. Hence, $Al_{1-y}Ti_y$ is forming grains that appear to be significantly smaller than $NaAlH_4$, which would result in large interfaces between the two phases with a minimum amount of $Al_{1-y}Ti_y$. This is in line with what would be desired for a heterogeneous catalyst.

The ideal microstructure would probably be small grain size of $NaAlH_4$ with a heterogeneous catalyst well spread in the sample as tiny grains in the grain boundaries of $NaAlH_4$. This will give broad PXD reflections that complicate the detection of phases that are only present in small fractions and will

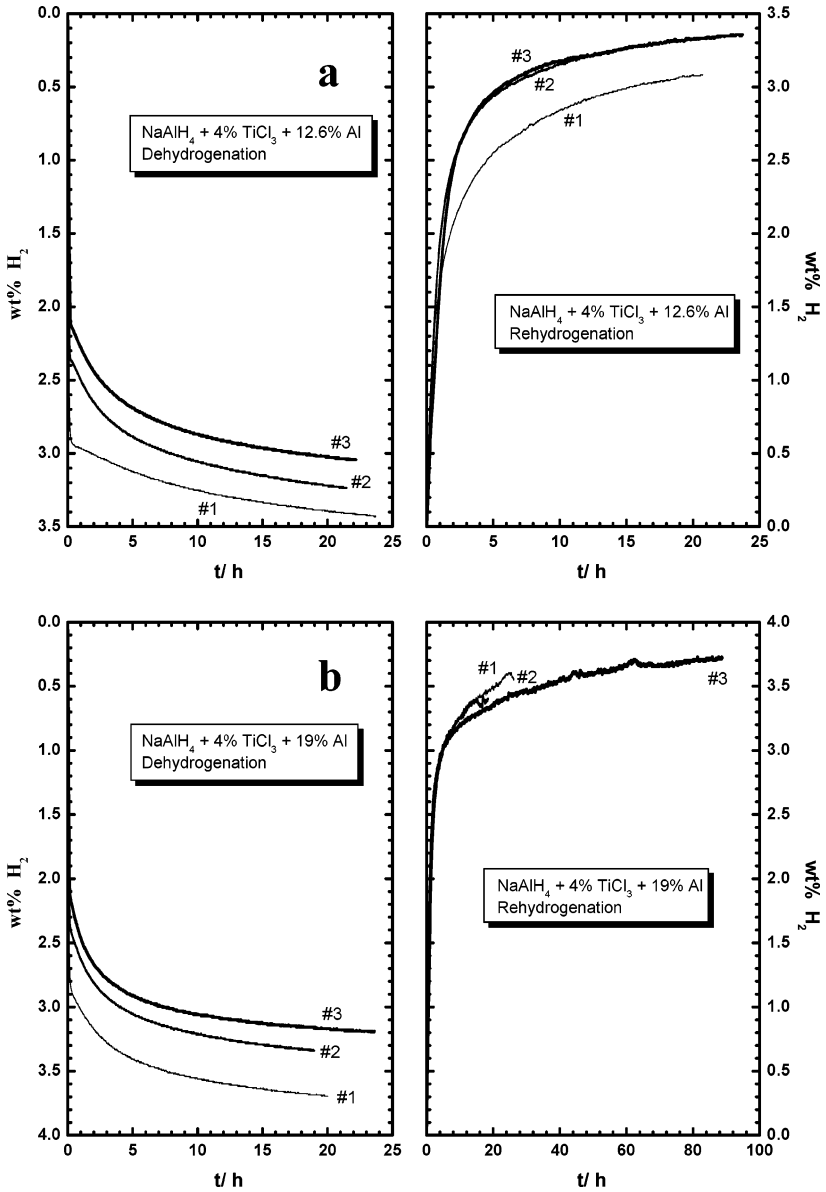

Figure 5. Storage capacity (wt %) during dehydronation and rehydrogenation of $NaAlH_4$ with 4 mol % $TiCl_3$ and (a) 12.6 mol % Al and (b) 19.0 mol % Al. Three cycles were carried out.

strongly correlate with the background in the Rietveld refinements. The detection limit by PXD is around 4−6 nm, depending on the fraction present. An ideal heterogeneous catalyst would hence be difficult to detect by X-ray or neutron diffraction. But electron diffraction could be a viable route to learn more about the effect of Ti, and some work has already been carried out for $NaAlH_4$ by Andrei et al.[24]

If the entire effect of the Ti additive is to produce a catalyst for splitting/recombination of hydrogen molecules, then it would have been expected that adding a fast interstitial metal hydride with the correct microstructure would be similarly efficient as a catalyst. This was tested in the present work by adding 8 mol % $TbNiAlH_{1.33}$ to $NaAlH_4$. $TbNiAlH_x$ forms three different interstitial metal hydrides ($x = 0.33$, 0.40−0.58, 0.90−1.40) and has very fast kinetics. [25−27] However, the dehydrogenation kinetics of $NaAlH_4$ (technical quality) was slightly improved by $TbNiAlH_{1.33}$ but was clearly inferior to the kinetics of $NaAlH_4$ with 2 mol % TiF_3. This indicates that other catalytic effects of the Ti additives than a simple catalytic splitting of H_2 are of larger importance. An uncertainty with this experiment, however, is that good catalytic effect demands good contact between the material and the catalyst, which clearly is achieved by the reactive milling with Ti halides, but this may not be optimized for the $NaAlH_4/TbNiAlH_x$ mixture.

X-ray absorption spectroscopy and electron spin resonance studies have proven that $TiCl_3$ is reduced, in particular after cycling, to a metallic state.[7−9,28] After a few cycles, the Ti species is mainly present as metastable $Al_{1-y}Ti_y$. Similar results are obtained with $Ti(OBu)_4$.[20] If $Al_{1-y}Ti_y$ is the catalyst, then it should be possible to add it directly and avoid the considerable capacity loss by the byproduct NaCl, but a suitable microstructure has to be assured.

Pure Ti with relatively small particle size has been shown to give kinetics comparable to $TiCl_3$, when thoroughly milled with $NaAlH_4$ or NaH/Al.[5,29] However, in this case present preliminary SR-PXD results indicate that Ti is not in a metallic state. NaH + Al + 0.04 Ti samples were ball-milled for 10 h in both Ar and H_2, and both directly after ball-milling and after one cycle, no $Al_{1-y}Ti_y$ or other Al−Ti phases were observed. On the contrary, in all four samples a phase with broad reflections and very similar positions (face-centered cubic with $a = 4.454$ Å) to TiH_2 was observed. Ti_3AlH_6 has a smaller unit-cell of $a =$

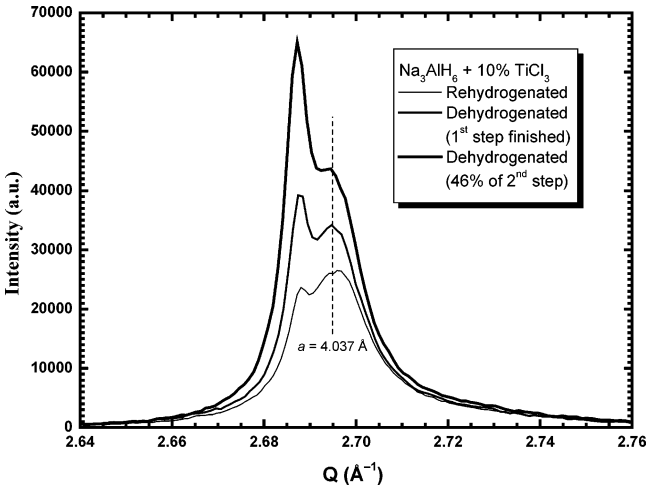

Figure 6. SR-PXD data at 22 °C of $NaAlH_4$ + 10% $TiCl_3$ after three cycles and during its fourth dehydrogenation. The strongest Al and $Al_{1-y}Ti_y$ peaks are shown, showing that the unit-cell dimension of $Al_{1-y}Ti_y$ is not altered during dehydrogenation. The intensity of the data are normalized by the NaCl peaks.

4.35 Å[30] and is not present in these samples. This indicates that ball-milling NaH/Al or $NaAlH_4$ with Ti^{III}/Ti^{IV} may give different products than ball-milling with metallic Ti.

An interesting aspect is which Ti-containing compound that is stable from a thermodynamic point of view. This was checked by the HSC program,[31] which also includes a database of thermodynamic data that was supplemented with enthalpies and entropies in agreement with the pressure−composition isotherms of $NaAlH_4$ and Na_3AlH_6 by Gross et al.[32] Stability calculations clearly show that for NaH/Al with Ti the stable Ti compound is Al_3Ti for the conditions of the cycling (the same as for the present excess Al samples), but at room temperature, TiH_2 is the most stable Ti compound above about 10 bar. Hence, for the sample ball-milled in H_2, the TiH_2 formed may have been thermodynamically stable, whereas for the other samples metastable and kinetically stable TiH_2 apparently forms during ball-milling.

However, for NaH/Al with $TiCl_3$, Al_3Ti is stable in both the dehydrogenated and the hydrogenated states. The NaCl formation stabilizes Al_3Ti because it changes the NaH/Al ratio.

Clearly, Ti is improving the kinetics of alanates even with two different crystalline Ti-containing phases, i.e., $Al_{0.85}Ti_{0.15}$ and TiH_2. This may be interpreted in different ways; either the real catalyst is none of these phases or both Ti phases have some common promoting effects, e.g., both catalyzing H_2 splitting/recombinations and/or both providing interfaces for nucleation and diffusion. Still more experiments are needed to fully reveal the effect of titanium in alanates.

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References and Notes

(1) Bogdanovic, B.; Schwickardi, M. *J. Alloys Compd.* **1997**, *253*, 1−9.

(2) Sandrock, G.; Gross, K.; Thomas, G. *J. Alloys Compd.* **2002**, *339*, 299−308.

(3) Srinivasan, S. S.; Brinks, H. W.; Hauback, B. C.; Sun, D.; Jensen, C. M. *J. Alloys Compd.* **2004**, *377*, 283−289.

(4) Fichtner, M.; Fuhr, O.; Kircher, O.; Rothe, J. *Nanotechnology* **2003**, *14*, 778−785.

(5) Wang, P.; Jensen, C. M. *J. Phys. Chem. B* **2004**, *108*, 15827−15829.

(6) Jensen, C. M.; Zidan, R.; Mariels, N.; Hee, A.; Hagen, C. *Int. J. Hydrogen Energy* **1999**, *24*, 461−465.

(7) Graetz, J.; Reilly, J. J.; Johnson, J.; Ignatov, A. Y.; Tyson, T. A. *Appl. Phys. Lett.* **2004**, *85*, 500−502.

(8) Léon, A.; Kircher, O.; Rothe, J.; Fichtner, M. *J. Phys. Chem. B* **2004**, *108*, 16372−16376.

(9) Felderhoff, M.; Klementiev, K.; Grunert, W.; Spliethoff, B.; Tesche, B.; von Colbe, J. M. B.; Bogdanovic, B.; Hartel, M.; Pommerin, A.; Schuth, F.; Weidenthaler, C. *Phys. Chem. Chem. Phys* **2004**, *6*, 4369−4374.

(10) Brinks, H. W.; Jensen, C. M.; Srinivasan, S. S.; Hauback, B. C.; Blanchard, D.; Murphy, K. *J. Alloys Compd.* **2004**, *376*, 215−221.

(11) Weidenthaler, C.; Pommerin, A.; Felderhoff, M.; Bogdanovic, B.; Schuth, F. *Phys. Chem. Chem. Phys* **2003**, *5*, 5149−5153.

(12) Bogdanovic, B.; Felderhoff, M.; Germann, M.; Hartel, M.; Pommerin, A.; Schuth, F.; Weidenthaler, C.; Zibrowius, B. *J. Alloys Compd.* **2003**, *350*, 246−255.

(13) Zhang, F.; Lu, L.; Lai, M. O. *J. Alloys Compd.* **2000**, *297*, 211−218.

(14) Klassen, T.; Oehring, M.; Bormann, R. *Acta Mater.* **1997**, *45*, 3935−3948.

(15) Klassen, T.; Oehring, M.; Bormann, R. *J. Mater. Res.* **1994**, *9*, 47−52.

(16) Oehring, M.; Klassen, T.; Bormann, R. *J. Mater. Res.* **1993**, *8*, 2819−2829.

(17) Oehring, M.; Yan, Z. H.; Klassen, T.; Bormann, R. *Phys. Status Solidi A* **1992**, *131*, 671−689.

(18) Choi, J. H.; Moon, K. I.; Kim, J. K.; Oh, Y. M.; Suh, J. H.; Kim, S. J. *J. Alloys Compd.* **2001**, *315*, 178−186.

(19) Fan, G. J.; Gao, W. N.; Quan, M. X.; Hu, Z. Q. *Mater. Lett.* **1995**, *23*, 33−37.

(20) Brinks, H. W.; Hauback, B. C.; Srinivasan, S. S.; Jensen, C. M. *J. Phys. Chem. B* **2005**, *109*, 15780−15785.

(21) Rodríguez-Carvajal, J. *Physica B* **1993**, *192*, 55−69.

(22) Kircher, O.; Fichtner, M. *J. Appl. Phys.* **2004**, *95*, 7748−7753.

(23) Blanchard, D.; Brinks, H. W.; Hauback, B. C. *J. Alloys Compd.*, in press; doi: 10.1016/j.jallcom.2005.09.009.

(24) Andrei, C. M.; Walmsley, J. C.; Brinks, H. W.; Holmestad, R.; Srinivasan, S. S.; Jensen, C. M.; Hauback, B. C. *Appl. Phys. A* **2005**, *80*, 709−715.

(25) Yartys, V. A.; Gingl, F.; Yvon, K.; Akselrud, L. G.; Kolomietz, A. V.; Havela, L.; Vogt, T.; Harris, I. R.; Hauback, B. C. *J. Alloys Compd.* **1998**, *279*, L4−L7.

(26) Brinks, H. W.; Yartys, V. A.; Hauback, B. C.; Fjellvåg, H. *J. Alloys Compd.* **2002**, *330*−*332*, 169−174.

(27) Brinks, H. W.; Fossdal, A.; Bowman, R. C.; Hauback, B. C. *J. Alloys Compd.*, in press; doi: 10.1016/j.jallcom.2005.09.018.

(28) Kuba, M. T.; Eaton, S. S.; Morales, C.; Jensen, C. M. *J. Mater. Res.* **2005**, *20*, 3265−3269.

(29) Wang, P.; Jensen, C. M. *J. Alloys Compd.* **2004**, *379*, 99−102.

(30) Rudman, P. S.; Reilly, J. J.; Wiswall, R. H. *J. Less-Common Met.* **1978**, *58*, 231−240.

(31) Outukumpu. *HSC Chemistry for Windows*; version 5.1; ChemSW, Inc.: 1999.

(32) Gross, K. J.; Thomas, G. J.; Jensen, C. M. *J. Alloys Compd.* **2002**, *330*, 683−690.