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Investigation of hydrogen discharging and recharging processes of Ti-doped NaAlH₄ by X-ray diffraction analysis (XRD) and solid-state NMR spectroscopy

B. Bogdanović, M. Felderhoff, M. Germann, M. Härtel, A. Pommerin, F. Schüth^{*}, C. Weidenthaler, B. Zibrowius

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

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Abstract

The processes occurring in the course of two sequential hydrogen discharging and recharging cycles of Ti-doped sodium alanate were investigated in parallel using XRD analysis and solid-state NMR spectroscopy. Both methods demonstrate that in hydrogen storage cycles (Eq. (1)) the majority phases involved are NaAlH₄, Na₃AlH₆, Al and NaH. Only traces of other, as yet unidentified phases are observed, one of which has been tentatively assigned to an Al–Ti alloy on the basis of XRD analysis. The unsatisfactory hydrogen storage capacities heretofore observed in cycle tests are shown to be due entirely to the reaction of Na₃AlH₆ with Al and hydrogen to NaAlH₄ (Eq. (1), 2nd hydrogenation step) being incomplete. Using XRD and NMR methods it has been shown that a higher level of rehydrogenation can be achieved by adding an excess of Al powder.

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1. Introduction

One of the main goals associated with the development of Ti (or other metal)-doped NaAlH₄ as hydrogen storage materials [1–6] is to achieve the highest possible hydrogen storage capacity in a large number of cycles. The calculated hydrogen storage capacity of neat NaAlH₄ (Eq. (1)) is 5.5 wt.% H₂. However, in practice the capacity is always lower, due to the added weight of the dopant and, in some cases, also due to the consumption of a fraction of NaAlH₄ in the doping reaction. In general, the lower the dopant concentration the higher is the maximum storage capacity. If the stoichiometry of the doping reaction is known, the theoretically achievable storage capacity can be calculated.

A major disadvantage of the NaAlH₄ storage materials investigated previously is that storage capacities in cycle tests were always lower than the theoretically expected capacity. One of the primary goals of the present work was

LH₄ storage materials ge capacities in cycle theoretically expected 5-2373; fax: +49-208-306pg.de (F. Schüth). The X-ray powder patterns for qualitative and quantitative phase analysis were collected on a Stoe STADI P transmission diffractometer with a primary monochromator and a linear position sensitive detector. The data were collected in the range between 15° and 120° 2θ with a step width of 0.01° 2θ . The samples were filled in a glove box into glass capillaries (\emptyset 0.5 mm) which were sealed to prevent contact with air during the measurement. The

2. Experimental

of ball-milling on LiAlH₄.

therefore to investigate the causes for this detrimental effect by means of XRD analysis and solid state NMR

spectroscopy. In the course of these investigations, both

methods proved to be excellent tools for providing in-

formation about the processes occurring in the material on

a microscopic level during hydrogen discharging and

recharging. While an in situ X-ray diffraction study of the decomposition of NaAlH₄ has already been published by

Gross et al. [7], solid-state NMR spectroscopy has very recently been used by Balema et al. [8] to study the effect

^{*}Corresponding author. Tel.: +49-208-306-2373; fax: +49-208-306-2995.

E-mail address: schueth@mpi-muelheim.mpg.de (F. Schüth).

recorded patterns were evaluated qualitatively by comparison with entries from the PDF-2 powder pattern database and theoretical patterns calculated from literature data.

The quantitative phase analysis was performed by Rietveld refinements using the program FullProf2000 by Rodríguez-Carvajal [9]. Phases which could not be identified (their concentration is estimated to be well below 5 wt.%) were neglected during the refinement and therefore only the ratios of the analyzed crystalline phases are correctly determined, but not their absolute values. Another source of error is the amount of amorphous phase. The quantity of amorphous phase has to be determined by the addition of an exactly defined amount of internal standard. Due to the sample handling under protective gas, the admixture and homogenization of an internal standard to a defined amount of sample is not trivial. If the preparation of sample and standard is not exact, the analysis of the amorphous phase will have a large error. Therefore, no quantification of the amorphous fraction has been attempted. The content of phases at different stages of a cycle test as determined by Rietveld analysis is given in Table 1.

NMR measurements were performed on a Bruker Avance 500WB spectrometer operating at a magnetic field of 11.74 T. The corresponding resonance frequencies of ²³Na and ²⁷Al are 132.26 and 130.29 MHz, respectively. A 4-mm MAS probehead with dry nitrogen as driving and bearing gas was used. The rotors were filled in a glove box and stored under argon prior to the measurements. Spinning rates of up to 15 kHz were used. In the case of some of the dehydrogenated samples, eddy currents generated in metallic particles in the sample prevented us from using high spinning rates. (Warning: an attempt to spin such samples at higher rates can lead to a substantial temperature rise resulting in a sudden release of hydrogen.) All the dehydrogenated samples caused a strong spinning rate-dependent de-tuning of the probe.

The spectra were recorded using single pulse excitation employing short pulses and small flip angles (²³Na: 0.9 μ s, $\pi/8$; ²⁷Al: 0.6 μ s, $\pi/12$). The ²³Na and ²⁷Al NMR spectra were referenced with respect to aqueous solutions of sodium chloride and aluminum nitrate, respectively.

2.1. Preparation of samples of Ti-doped NaAlH₄

All experiments were carried out under an argon atmosphere, using a glove box or the Schlenk technique.

Experiment A: 4.06 g (75 mmol) of recrystallized NaAlH₄ [2] were suspended in 50 ml of toluene and 0.51 g (1.5 mmol) of Ti(OC₄Hⁿ₉)₄ were added to the stirred suspension using a syringe. The hydrogen evolution taking place during stirring of the suspension at room temperature was recorded by means of a thermovolumetric apparatus [1]. The hydrogen evolution took place with constant rate and stopped abruptly after 70 h giving 78 ml of H₂ (1.9 mol H₂/mol Ti). The black suspension was filtered, the solid washed with toluene and pentane and dried in vacuum until the constant weight (4.40 g) was achieved.

A sample of Ti-doped NaAlH₄ (1.10 g) was heated in a thermovolumetric apparatus at first to 120 °C and then to 180 °C (Fig. 1) and the hydrogen evolution taking place at the same time (—) was recorded. The heating was stopped for a short time and the glass vessel taken out of the oven to remove small samples for XRD and NMR measurements. These events are marked by circles in Fig. 1. Hydrogenations were carried out at 100 °C/100 bar for 12 h in a 35-ml autoclave. Hydrogen capacities (Fig. 1): (1) cycle, 4.5 wt.%; (2) cycle 4.0 wt.% H₂.

Experiment B: In a parallel experiment, a sample of

Table 1

Quantitative Rietveld analyses of the phase contents in the course of dehydrogenation and rehydrogenation of Ti-doped NaAlH₄

Sample code	Cycle number	Stage of the cycle test ^a	Phase content (mol%)					Al/Na ₃ AlH ₆ ratio	
			NaAlH ₄	Na ₃ AlH ₆	Al	NaH	By- product	From XRD	From ²⁷ Al MASNMR
A0	1	Starting material	100	_	_	_	_	_	_
A1	1	Dehydrogenated, about 50% of the 1st step	49	15	36	_	+	2.4	1.0
A2	1	Dehydrogenated, 1st step	7	30	63	_	+	2.1	1.3
A3	1	Dehydrogenated, 2nd step	_	1	46	53	+	46	_
A4	1	Rehydrogenated ^b	46	3	51	-	+	17	0.9
A5	2	Dehydrogenated, 2nd step	_	_	44	56	+	_	_
A6	2	Rehydrogenated ^b	61	15	24	-	+	1.6	_
B4	1	Rehydrogenated ^b	43	16	37	4	+	2.3	1.4
B5	1	Milled and rehydrogenated ^b	70	9	21	-	+	2.3	0.2
B6	1	Al added to B4, milled and rehydrogenated ^b	80	_	20	_	_	_	-

^a The cycle test is represented in Fig. 1.

^b Hydrogenation conditions: 100 °C/100 bar/12 h.

^c The effects of final bandwidths of excitation and probe are neglected (see text).



Fig. 1. De- and rehydrogenation cycles carried out with a sample of Ti-doped NaAlH₄ (2 mol%). The circles with the corresponding numbers indicate the stages at which samples were taken for XRD and NMR analyses. Solid line, hydrogen evolution; dotted line, sample temperature; dashed line, rehydrogenation step.

Ti-doped NaAlH₄ was subjected to one dehydrogenation/ rehydrogenation cycle in the same way as in experiment A. To 0.44 g of the rehydrogenated sample (B4) 65 mg (2.4 mmol) of Al grindings (Al bronze, 'Lunasol', Schopflocher, Frankfurt/M.; 12 m²/g) were added in a glove box. The mixture was ball-milled for 30 min/30 Hz in a 10-ml steel vessel together with two high-grade steel balls (\emptyset =12 mm) using a Retsch high energy ball mill. Thereafter the sample was hydrogenated at 113 °C/135 bar for 20 h. Blank test (B5): Repeated ball-milling and hydrogenation of sample B4 without addition of Al powder at the same conditions as for B6.

3. Results and discussion

The samples of Ti-doped NaAlH₄ used for XRD and NMR investigations were prepared by doping of NaAlH₄ with Ti(OC₄Hⁿ₉)₄ (2 mol%) in toluene [2]. One of the doped samples was subjected to two complete dehydrogenation/rehydrogenation cycles (Fig. 1). The taking of samples at different stages of the cycle test is marked by circles and the samples labeled as A0–A6. In Table 1 the samples A0–A6 are assigned to dehydrogenation and

rehydrogenation processes of Ti-doped $NaAlH_4$ according to Eq. (1).

$$NaAlH_{4} \stackrel{1. \text{ dehydrogenation step}}{\underset{2. \text{ hydrogenation step}}{\rightleftharpoons}} \frac{1/3Na_{3}AlH_{6} + 2/3 \text{ Al} + 1}{\underset{1. \text{ hydrogenation step}}{\rightleftharpoons}} NaH + Al + 3/2H_{2}$$
(1)

Fig. 2 shows a part of the powder diagram of the starting material (A0) after the final Rietveld run. For the refinement of the structure of $NaAlH_4$, the crystal structure data of Lauher et al. [10] were used. All the observed reflections belong to NaAlH₄. The reported [11] changes of the crystal lattice parameters of Ti-doped NaAlH₄ are not observed in our study. Two additional series of samples with different concentrations of the Ti catalyst (1 and 3 mol.%) were prepared and investigated by X-ray analysis. An increase or decrease in the lattice constants for the NaAlH₄ phase cannot be confirmed in any of the samples. The ²³Na and ²⁷Al NMR spectra of Ti-doped sodium alanate at different stages of dehydrogenation (cf. Table 1) are given in Figs. 3 and 4, respectively. The high quality of the sodium alanate used as starting material in combination with the comparably high magnetic field and the spinning speeds applied allows the spectral parameters (chemical



Fig. 2. Powder pattern of Ti-doped $NaAlH_4$ after the final Rietveld run. The observed data points (cross), the calculated points (solid line), and the difference curve are given. The peak positions are marked by lines in the lower part of the pattern.

shift, quadrupole coupling) for NaAlH₄, Na₃AlH₆ and NaH to be determined with an accuracy and reliability superior to all previously published data [12,13]. A more detailed presentation of the NMR results will be published in a forthcoming paper (B. Zibrowius, unpublished). For identifying and monitoring the different compounds in the course of dehydrogenation/rehydrogenation cycles the positions of the resonance lines are sufficient. These line positions are summarized in Table 2.

The dehydrogenation to approximately half of the first dissociation step (A1) leads to the formation of Na₃AlH₆ beside aluminum. The main crystalline phase detected by XRD at this stage is NaAlH₄, followed by Na₃AlH₆, and Al, respectively (Fig. 5). The crystal structure data reported by Rönnebro et al. [14] were used for the simulation of Na₃AlH₆. At 12.9° and 20.6° 2θ (Fig. 5) two reflections are observed which cannot be assigned to any of the identified phases. These reflections are considered to belong to impurities with no relevance to the overall process because they were detected only in some of the experiments which were otherwise identical to the others with respect to the kinetics and storage capacities. NMR data (traces A1 in Figs. 3 and 4) are in full agreement with

the XRD data: present at this stage are $NaAlH_4$, Na_3AlH_6 and Al.

The XRD (Fig. 5, A2) indicates that after dehydrogenation at 120 °C for 4 h the sample still contains some small amount of NaAlH₄, while aluminum and Na₃AlH₆ are the main crystalline phases (Table 1). The impurity phase observed for the sample A1 is still present. The ²³Na NMR spectrum of this sample (Fig. 3, A2) shows no NaH at all, but only Na₃AlH₆. Because of the small difference in the line positions observed for NaAlH₄ and the Na(2) position of Na₃AlH₆ (Table 2), it would be difficult to identify the small amount of NaAlH₄ detected by XRD in the ²³Na MAS NMR spectrum. However, the ²⁷Al MAS NMR spectrum (A2, Fig. 4) shows a line with low intensity corresponding to NaAlH₄, confirming the XRD data. The first stage of the dehydrogenation process (Eq. (1)) is thus almost complete at this stage. Complete dehydrogenation could certainly be achieved by prolonging the heating under these conditions.

In the completely dehydrogenated sample, NaH could be detected as a new phase both by XRD (A3, Fig. 5) and NMR spectroscopy (A3, Fig. 3). For Rietveld analysis, the structure data of NaH given by Shull et al. [15] were used.



Fig. 3. 23 Na MAS NMR spectra (240 scans, 15 s recycle delay) of the samples A0–A4 (Table 1). The spinning rates applied are 15 kHz (A0, A1, and A4), 12 kHz (A2), and 10 kHz (A3).

The content of aluminum at this stage (Table 1, A3) is almost equal to that of NaH, as required by the stoichiometry, while the content of Na₃AlH₆ is almost negligible. The unidentified phase observed for the samples A1 and A2 is still present. The existence of a by-product can also be inferred from ²⁷Al MAS NMR spectroscopy. The additional line at about -70 ppm (marked with asterisks in the right column of Fig. 4) is probably caused by some aluminum oxide introduced into the parent material A0 by the aluminum source. Since the aluminum used in the synthesis of the materials is a very fine particle grade, the surface aluminum oxide present can be detected in the NMR experiments. The intensity of the resonance line of this by-product varied with the batch of sodium alanate, corresponding to different amounts of surface oxide present in the starting material.

The rehydrogenated sample (Table 1, A4) contains $NaAlH_4$ as the main component (based on weight) besides aluminum and Na_3AlH_6 . NMR spectroscopy also detected primarily Na_3AlH_6 , $NaAlH_4$ and metallic aluminum, together with a small amount of NaH (less than 3% of the



Fig. 4. ²⁷Al MAS NMR spectra (9600 scans, 5 s recycle delay) of the samples A0–A4 (Table 1). The spinning rates applied are 15 kHz (A0), 13.5 kHz (A1 and A4), 12 kHz (A2), and 11 kHz (A3).

sodium, below the detection limit of the X-ray diffraction). Careful integration of the intensities of the central transition (excluding contributions from overlap with satellite transition spinning side bands but including side-band intensities from the central transition) of the ²³Na and ²⁷Al MAS NMR spectra allowed the molar ratio of Na₃AlH₆ to NaAlH₄ to be estimated as 0.27 ± 0.03 . Since there is almost no NaH left in the sample, according to Eq. (1) the amount of Na₃AlH₆. This intensity ratio was not observed for the resonance lines in the ²⁷Al MAS NMR spectrum of A4

Table 2

Positions of the NMR lines (in ppm) of the compounds detected in dehydrogenated sodium alanate

Compound	²³ Na	²⁷ Al
NaAlH ₄	$-9.4{\pm}0.2$	95.2±0.5
Na ₃ AlH ₆	Na(1): 22.8±0.2	-42.7 ± 0.3
	Na(2): -10.2±0.2	
NaH	18.3 ± 0.2	_
Al _{met}	-	1639.5±0.5



Fig. 5. Comparison of the powder patterns of the analysed samples A0–A6, the reflections of the crystalline phases are marked by symbols. The reflections which could not be assigned to any known phase are marked by '?'.

(Fig. 4), but for quantitative analysis one has to take into account that the cubic structure of metallic aluminum leads to vanishing quadrupolar coupling. Therefore, the resonance line of metallic aluminum contains the contributions of all the five possible transitions [16]. To compare its intensity with that of the central transition observed for Na_3AlH_6 , it has to be multiplied by a factor of 9/35. The thus derived Al_{met}/Na_3AlH_6 ratio for sample A4 is 0.86. Even smaller values have been found by NMR spectroscopy for other rehydrogenated samples (cf. Table 1). By shifting the frequency offset and tuning to the resonance line of the metallic aluminum, it was found that only part of the missing signal intensity for metallic aluminum in the spectrum of sample A4 can be explained by unequal rf excitation and optimization of the probe tuning for the central transition of NaAlH₄.

The skin effect occurring in larger metallic particles present in the sample and an inhomogeneous distribution of these metallic particles in the batch are very probably the reason for the discrepancy between the expected and observed Al_{met}/Na₃AlH₆. The fast sample spinning itself might have led to a further aggregation of the rather large metallic aluminum particles (several 100 nm in size) detected by electron microscopy. At a spinning rate of 10 kHz the acceleration exerted at the inner wall of a 4-mm MAS rotor is about 600 000 times the standard acceleration of gravity g. Spinning the sample at several kHz was always found to increase irreversibly the de-tuning effect observed for the dehydrogenated samples. As noted in the experimental part, the generation of eddy currents was so pronounced for some samples that spinning at high rates was impossible and appreciable heating of the sample occurred. Hence, the application of the calibration procedure used by Balema et al. [8] to quantify the amount of aluminum in ball-milled LiAlH_4 would not solve the problem.

The ratio of Na₃AlH₆ to aluminum as determined from the Rietveld analysis also does not correspond to the ratio of 1:2 expected from the stoichiometry, and the NaAlH₄/ Na₃AlH₆ ratio determined from the XRD does not agree with the one calculated from the NMR results. This is attributed to the formation of amorphous or very small domain size Na₃AlH₆ which cannot reliably be refined using the procedure applied here (see Section 2). In other samples or subsequent cycles (A6, for instance) such discrepancies did not occur. The ratio determined by Rietveld analysis of 15/24 for sample A6 corresponds to 1:2 within the error of the determination. These problems only occurred with some of the samples, but they are discussed in some detail here to highlight the problems in analyzing the composition of such complex and highly inhomogeneous samples. Thus, two independent methods such as XRD and NMR spectroscopy should be used to fully analyze the processes during cycling such hydrides.

If the cycle is then repeated, the same sequence of phase transformations is essentially observed again, demonstrating the complete reversibility of the process. The only exception is the ratio of the different phases in the rehydrogenated sample, as already discussed above. In addition, kinetics and thus extent of rehydrogenation are improved, as is almost invariably observed for titanium-doped NaAlH₄ in the second and subsequent dehydrogenation/rehydrogenation cycles. This is tentatively interpreted as being due to improved dispersion of the titanium on the



Fig. 6. Powder pattern of sample A4. Aluminum reflection marked by the bar, exhibiting a clear asymmetry at the right side of the reflection.

atomic scale, since the dehydrogenation/rehydrogenation cycle is accompanied by a massive transfer of matter.

A possibly important effect is observed if one analyzes the XRD patterns carefully. The aluminum reflections of the rehydrogenated sample (A4) show a clear asymmetry on the side of higher θ values as an enlarged part of the powder pattern in Fig. 6 shows. The powder patterns of the samples with low aluminum content show that the asymmetry is actually a shoulder which might be assigned to the presence of another crystalline phase. It has been reported for LiAlH₄ that a titanium-catalyzed transformation to Al₃Ti alloy occurs upon ball-milling with TiCl₄ [8]. The shoulders on the right side of the aluminum reflections observed in this work does not match the reflections of the Al₃Ti phase or any other known Al–Ti alloy. However, since the intensity of the reflections increases with the amount of the applied catalyst, and since alloys like Al₂Ti [17] have their main reflections at 2θ values where the broad shoulders appear, we suggest that a crystalline Al-Ti alloy has formed during the phase transformation processes. The nature of this phase is at present unclear, but because of its possible relevance to the catalytic effect of the titanium, the formation of an Al-Ti phase during cycling of Ti-doped NaAlH₄ will be further investigated.

One of the main results of the present XRD and NMR investigations is that in the rehydrogenated samples A4 and A6 (Table 1 and Figs. 3–5) NaAlH₄, Na₃AlH₆ and Al, but only negligible amounts of NaH, could be observed. This means that the rehydrogenation of NaH with Al to Na₃AlH₆ (Eq. (1), 1st step) runs to completion, while the reaction of Na₃AlH₆, Al and hydrogen to NaAlH₄ (2nd step) stops before it is completed, at least on the time scale of the experiments.

The incomplete rehydrogenation of the Na_3AlH_6 is thus the reason for low storage capacities in cycle tests (cf. Section 1). A possible scenario could be a mass transfer problem: during dehydrogenation rather large metallic aluminum particles are formed, as evidenced by the occurrence of eddy currents in the NMR experiment and SEM investigations (not shown). During rehydrogenation metallic aluminum particles would first react with NaH to Na_3AlH_6 , and in parallel Na_3AlH_6 and the residual aluminum would react to $NaAlH_4$. The metallic aluminum particles would thus be coated by a layer of $NaAlH_4$. Those aluminum particles, which are rather big after dehydrogenation, would after some period of rehydrogenation consist of a center made of aluminum-coated with $NaAlH_4$. The aluminum in the particles core might then not be reached by the reactant Na_3AlH_6 formed in other parts of the sample, terminating the rehydrogenation reaction.

In order to test this hypothesis additional experiments were carried out. A regular sample was subjected to one dehydrogenation/rehydrogenation cycle. After this cycle, the powder pattern of the sample (Fig. 7, B4) again shows the presence of NaAlH₄, Na₃AlH₆, Al and NaH. After addition of a fine Al powder to the sample B4, the mixed sample was ball-milled for 30 min and again hydrogenated (B6). The XRD pattern of the sample thereafter (Fig. 7, B6) shows the complete absence of Na₃AlH₆ reflections. A reference experiment, where the sample B4 was just ball-milled and then exposed to a hydrogenation step without additional aluminum, shows only a small reduction of the amount of Na₃AlH₆ (B5). Hence, an excess of aluminum in the system results in complete rehydrogenation in the 2nd step, so that the full storage capacity can be exploited. Normalized to weight, the additional aluminum results in a lower overall storage capacity. Nevertheless, the results indicate that improved mass transfer in the system will result in a higher reversible hydrogen storage capacity. The pattern of the refinement after the final Rietveld run is given in Fig. 8.

The beneficial effect of excess aluminum on the rehydrogenation is also corroborated by the ²³Na MAS NMR spectra in Fig. 9. The spectrum of the dehydrogenated and subsequently rehydrogenated sample B4 shows a significant amount of Na₃AlH₆. While ball-milling and a further rehydrogenation (B5) diminished the Na₃AlH₆ line already significantly, the addition of excess aluminum prior to the ball-milling and rehydrogenation under the same conditions (B6) resulted in an almost complete conversion of the intermediate Na₃AlH₆ into NaAlH₄. The same conclusion can also be drawn from the ²⁷Al MAS NMR spectra in Fig. 10.

4. Conclusion

On the basis of the results presented above, the following statements can be made with respect to hydrogen discharging and recharging processes of Ti-doped NaAlH₄:

1. XRD analysis and solid-state NMR spectroscopy are



Fig. 7. Powder patterns of the rehydrogenated sample B4, of the milled and rehydrogenated sample B5 and of the sample with the admixed aluminum B6. The different phases observed in the two samples are marked by symbols.

suitable tools to study the processes during dehydrogenation and rehydrogenation reactions of NaAlH₄.

2. While in most cases the results obtained with both analytical techniques applied agree perfectly, in some cases discrepancies were observed which can be rationalized by taking the peculiarities of the individual techniques into account. The skin effect occurring in larger metallic particles in the NMR experiments and the fact that amorphous phases are not considered in the quantitative Rietveld refinement lead to apparently



Fig. 8. Rietveld plot after final refinement of the sample B6. Observed data (cross), calculated data (line), and the difference curve. The reflection positions for the two phases are marked by vertical lines: upper row, Al; bottom row, $NAAH_4$.



Fig. 9. 23 Na MAS NMR spectra (60 scans, 20 s recycle delay) of the rehydrogenated samples B4–B6 (Table 1) recorded at a spinning rate of 13 kHz.

contradictory results for certain states of the potential hydrogen storage material. Both techniques should be applied in combination to obtain an adequate picture of the dehydrogenation and rehydrogenation processes.

3. Only NaAlH₄, Na₃AlH₆, Al metal and NaH were



Fig. 10. ²⁷Al MAS NMR spectra (2400 scans, 5 s recycle delay) of the rehydrogenated samples B4–B6 (Table 1) recorded at a spinning rate of 11 kHz. The resonance line of the metallic aluminium in the spectrum of sample B4 is cut at 35% of the full height.

observed in the X-ray powder diagrams to a significant extent. In addition, non-identified phases with a content of around 1-2 wt.% were observed. These minority phases, however, could not clearly be associated with particular steps in the dehydrogenation/rehydrogenation cycle and are thus probably not crucial in understanding the system behavior. Of particular interest, however, is a shoulder on the right side of the main Al reflection, the intensity of which increases with the amount of the applied catalyst, and which can be tentatively assigned to an Al–Ti alloy.

Rehydrogenation of a completely dehydrogenated sam-4. ple leads to the formation of NaAlH₄ and Na₃AlH₆ while some Al is left, but only traces of NaH are observed. This means that the rehydrogenation of NaH with Al to Na_3AlH_6 (Eq. (1), 1st step) runs almost to completion, while the reaction of Na₃AlH₆, Al and hydrogen to NaAlH₄ (2nd step) stops before it is This incomplete rehydrogenation of completed. Na₃AlH₆/Al is responsible for the storage capacity in cycle tests being lower than theoretically expected. It is suggested that this results from relatively large particles with an aluminum core which is covered by NaAlH₄. The aluminum is thus effectively separated from the other reagent, Na₃AlH₆, and mass transfer limitations prevent full rehydrogenation. In agreement with this hypothesis, the signal of Na₃AlH₆ almost completely disappears from the XRD pattern and the NMR spectrum, when a rehydrogenated sample is ball-milled with fresh Al powder and then hydrogenated again.

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