

# One-step direct synthesis of a Ti-doped sodium alanate hydrogen storage material

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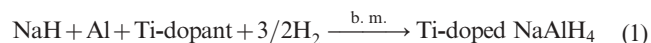
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Titanium-doped NaAlH<sub>4</sub> which has among the best reported hydrogen adsorption–desorption rates, has been synthesized in a one-step direct hydrogenation process under ball-milling in a special mill, allowing process parameters such as temperature and pressure to be recorded *in situ*.

The so-called “direct process”<sup>1–5</sup> for the synthesis of sodium alanate hydrogen storage materials<sup>6</sup> is usually carried out by ball-milling of NaH–Al mixtures in conjunction with a doping agent, *e.g.* TiCl<sub>3</sub> (the doping step), followed by hydrogenation of the milled mixture under pressure.<sup>6</sup> Earlier, preparations of NaAlH<sub>4</sub>, Na<sub>3</sub>AlH<sub>6</sub> and Na<sub>2</sub>LiAlH<sub>6</sub> in the solid state by ball-milling of NaH–AlH<sub>3</sub>,<sup>7</sup> NaH–NaAlH<sub>4</sub> or NaH–LiH–NaAlH<sub>4</sub> mixtures respectively, have been described<sup>8,9</sup> and recently the synthesis of Mg<sub>2</sub>FeH<sub>6</sub> by ball-milling of MgH<sub>2</sub>–Fe mixtures under hydrogen (7 bar) has been reported.<sup>10</sup> A report on the doping of NaAlH<sub>4</sub> with Ti powder under hydrogen (7 bar) has been published recently.<sup>11</sup> We give here an account of an improved one-step synthesis process, which leads directly to the doped alanate, and of the properties of the material obtained. The doping and hydrogenation proceed in one step, that is, by ball-milling of NaH–Al–dopant mixtures under hydrogen (eqn (1)).<sup>11</sup>



Since it is necessary to follow the course of the reaction in such a process, it was necessary to construct a system which allows recording of pressure and temperature during milling. Attempts to connect sensors to the milling vessel with cables failed, since connections broke after very short times due to the vibrations. We therefore constructed a system where pressure and temperature are transmitted *via* a radio signal, thus avoiding all mechanical connections. A commercial milling vial for a Fritsch Pulverisette 7 planetary mill was modified. A lid with connections to a hydrogen valve and a Gems Minimap 1000 miniature pressure sensor (range: 0–160 bar) from Synotech GmbH was made from stainless steel. A shortened K-type thermocouple was also affixed to the lid. The vial was inserted into a pressure-resistant sleeve matching the lid. The whole assembly constituted a pressure-resistant vessel with a design limit of 200 bar. The assembly was itself inserted into a plastic jacket containing six 1.5 V batteries, which supplied a CAESAR radio emitter located on the holding bracket of the planetary mill. The whole construction rotated at 500 rpm and sent

the data to an external, non-rotating receiver and data acquisition computer.

For the one-step direct synthesis of the storage material, a mixture of NaH (0.8 g, Aldrich, 95%; according to an XRD evaluation, the applied NaH contained 3–5 wt% NaOH as impurity), Al powder (0.9 g, Strem Chemicals, 99.7%, 325 mesh) and TiCl<sub>3</sub> (molar ratio 1 : 1 : 0.04, Aldrich, 99%) was milled in the autoclave of the “radio mill” under hydrogen (99.999%, 83 bar initial pressure, 3 2/3 h, 7 stainless steel balls, each ball 14 g) without external heating. As can be seen in Fig. 1, the temperature in the autoclave increased during ball-milling from room temperature to 70 °C, caused mainly by internal friction. The absorption of hydrogen started at about 50 °C and stopped after 1 1/2 h at 70 °C. The total hydrogen pressure drop (15 bar) corresponds roughly to that calculated according to eqn (1) (expected: 18 bar). After the one-step synthesis, samples show only the XRD reflections (Fig. 2a) of NaAlH<sub>4</sub>, NaCl and Al (due to loss of NaH from the reaction with TiCl<sub>3</sub>), which suggests the quantitative course of the reaction shown in eqn (1). The storage capacity found after the synthesis (Table 1, cycle 1, 3.96 wt%) is in satisfactory agreement with the calculated one (4.13 wt%).<sup>12†</sup>

The thus obtained Ti-doped NaAlH<sub>4</sub> was subjected to a 22-cycle test, the first 12 cycles being carried out in a manual apparatus<sup>13</sup> under decreasing hydrogenation pressure during hydrogenation, and the remaining cycles in a fully automated cycling set under isobaric conditions. The results of the test are compiled in Tables 1 and 2. Under decreasing pressure conditions (Table 1, Fig. 3), with the sample preheated to the nominal‡ hydrogenation temperature (125 °C, cycles 4, 6–9), hydrogenations at 116–93 bar were completed in ~20 min. After two hydrogenations under extremely

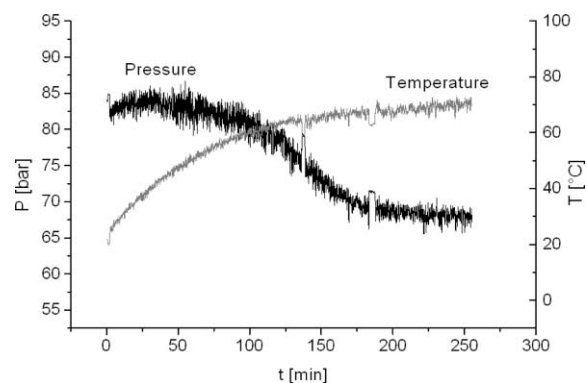
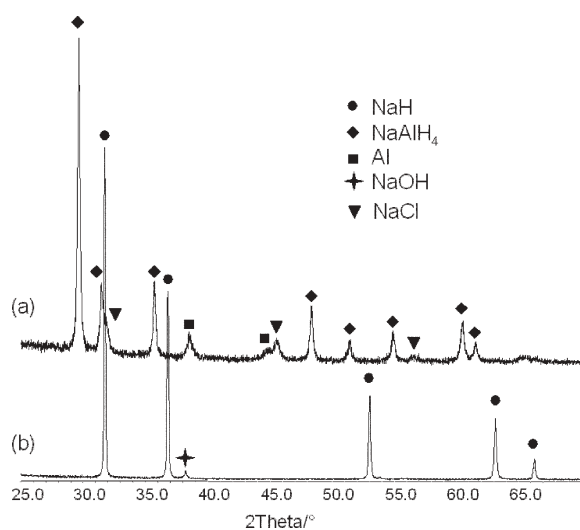


Fig. 1 The one-step direct synthesis of Ti-doped sodium alanate recorded by the “radio mill”.

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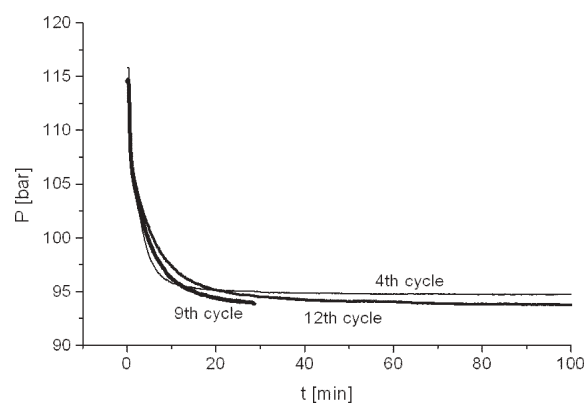
**Fig. 2** (a) X-Ray diffraction pattern of Ti-doped NaAlH<sub>4</sub> obtained via the one-step direct synthesis; (b) X-ray diffraction pattern of the commercial NaH.

**Table 1** Cycle test carried out with a sample (1.325 g) of Ti-doped NaAlH<sub>4</sub> prepared by ball-milling of a NaH–Al–TiCl<sub>3</sub> mixture (molar ratio 1 : 1 : 0.04) under hydrogen; dehydrogenation at 120 and 180 °C, normal pressure

Cycle	Hydrogenation conditions [°C/bar]	Hydrogenation time/min	wt% H <sub>2</sub> <sup>a</sup> [1st step/1st + 2nd step]
1	10–70/83–65 <sup>b</sup>	—	2.57/3.96
2 <sup>c</sup>	125/113–108	40	2.18/3.52
3 <sup>c</sup>	125/106–101	40	2.18/3.53
4	125/116–95	20	2.18/3.56
5 <sup>c</sup>	125/113–108	40	2.11/3.47
6–8	125/115–95	20	2.08/3.44
9	125/115–93	20	1.99/3.35
10	80/26–17	23 h	0.38/1.69
11	80/26–16	45 h	0.87/2.2
12	125/116–95	40	2.08/3.41

<sup>a</sup> Based upon the amount of hydrogen evolved at dehydrogenation (120 and 180 °C). <sup>b</sup> Ball-milling under hydrogen, represented in Fig. 1. <sup>c</sup> After pressurizing with hydrogen, the temperature was slowly (30 min) increased up to the nominal temperature.

low pressure (26–16 bar, cycles 10 and 11), in the following cycle a small but distinct decrease in the hydrogenation rate (Fig. 3) is observed. It is notable (Table 1) that the initial storage capacity of ~4.0 wt% H<sub>2</sub> obtained for the direct hydrogenation during



**Fig. 3** Cycle test carried out with the Ti-doped NaAlH<sub>4</sub> prepared by the one-step direct synthesis (Table 1); (re)hydrogenation curves under decreasing hydrogen pressure.

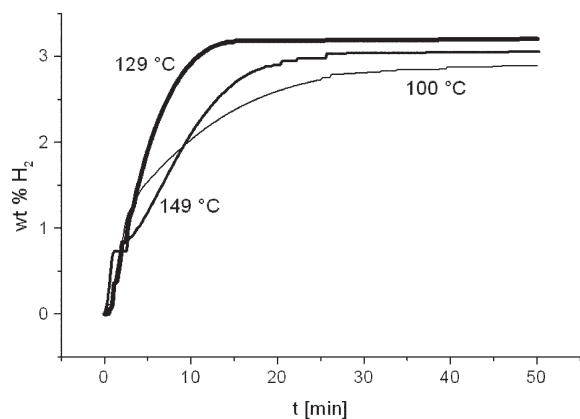
synthesis under ball-milling dropped to 3.4–3.5 wt% H<sub>2</sub> and from then on remained constant. This reduction of storage capacity in such cases has been shown by XRD and NMR studies<sup>14</sup> to be entirely caused by the incomplete formation of NaAlH<sub>4</sub> from the intermediate Na<sub>3</sub>AlH<sub>6</sub> and Al (the second hydrogenation step). It has been proposed that in the course of the hydrogenation process metallic aluminium particles become more and more coated with a layer of NaAlH<sub>4</sub> which prevents their reaction with Na<sub>3</sub>AlH<sub>6</sub> (product inhibition). It has also been shown that a high level of (re)hydrogenation can be achieved by adding an excess of fresh Al powder.<sup>14</sup>

Under isobaric conditions (Table 2) hydrogenation pressure was kept in the range of 97–100 bar, except in the 13th cycle. The (nominal<sup>†</sup>) hydrogenation temperature was varied between 91 and 149 °C. Under constant hydrogen pressure, with increasing temperature, the hydrogenation rate is expected<sup>6</sup> to pass a maximum. In the present case (Fig. 4), the maximum of the hydrogenation rate is found at 129 °C, (18th cycle); 90% of the total hydrogenation is accomplished in 10 min. This is, for TiCl<sub>3</sub> as a dopant, among the shortest yet achieved hydrogenation times. Upon further increase of hydrogenation temperature (134 and 149 °C) the hydrogenation rate decreases, because of proximity to thermodynamic equilibrium conditions.

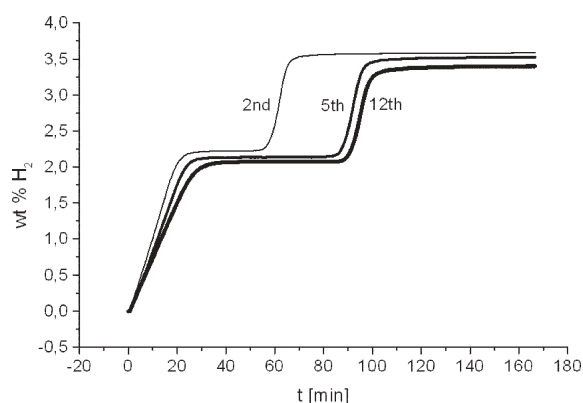
At 120 and 180 °C and normal pressure (Table 1), the dehydrogenation rates of the present reversible system (Fig. 5) appear to be stable. The automatic cycling equipment allows the dehydrogenation rate to be investigated as function of the applied hydrogen backpressure. As can be seen in Fig. 6, the hydrogen

**Table 2** Continued cyclisation of the sample from Table 1 in the automatic cycling equipment under isobaric hydrogenation and dehydrogenation conditions; dehydrogenation at 120 and 180 °C and variable H<sub>2</sub> backpressure

Cycle	Hydrogenation conditions [°C/bar]	Hydrogenation time/min	Dehydrogenation H <sub>2</sub> backpressure/bar	wt% H <sub>2</sub> [1st step/1st + 2nd step]
13	122/92	—	0.95	1.84/3.09
14	120/99	35	0.86	2.01/3.40
15	100/99	35	2.85	1.84/2.89
16	91/98	42	3.00	1.95/2.98
17	125/98	24	3.75	1.92/3.20
18	129/99	14	0.80	1.97/3.21
19	139/97	17	3.20	1.83/3.06
20	149/99	26	2.01	1.91/3.06
21	124/99	20	0.73	1.95/3.14
22	134/100	16	0.59	1.98/3.28



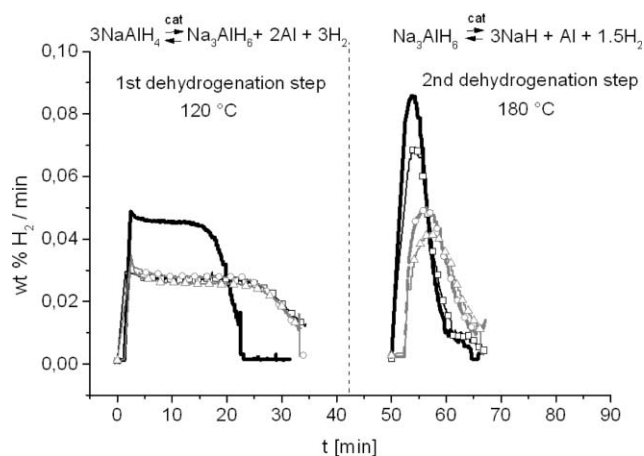
**Fig. 4** Cycle test carried out with the Ti-doped NaAlH<sub>4</sub> prepared by the one-step direct synthesis (Table 2); (re)hydrogenation curves under isobaric hydrogenation conditions.



**Fig. 5** Dehydrogenation curves for the 2nd, 5th and 12th cycles of the Ti-doped NaAlH<sub>4</sub> at normal pressure, heated successively to 120 and 180 °C.

delivery rate in the 1st dehydrogenation step, except for the 1 bar case, is independent of backpressure, and for the 2nd step decreases uniformly with the applied hydrogen backpressure.

In summary, ball-milling under hydrogen allows quantitative conversion of NaH–Al–TiCl<sub>3</sub> mixtures to Ti-doped NaAlH<sub>4</sub> in one step. Further advantages over the two-step direct synthesis<sup>3–5</sup> include lower temperature and pressure conditions, a considerably shorter reaction time and excellent kinetics of the synthesized material. Furthermore, *via* radio transmission, temperature and pressure changes during ball-milling can be monitored and thus the progress of the reaction (eqn (1)) controlled. From the rate of hydrogen absorption during ball-milling, the efficiency of the applied hydrogenation catalyst can be directly assessed. The properties of the resulting storage material under cycling conditions seem to compare favorably with those known for the two-step process, although more detailed data concerning the latter are not yet available.<sup>3–5</sup>



**Fig. 6** Dehydrogenation rates of the Ti-doped NaAlH<sub>4</sub> as a function of the hydrogen back pressure (Table 2); — 1 bar; –□– 2 bar; –○– 3 bar; –△– 3.75 bar.

It can be expected that ball-milling under hydrogen can be applied to the synthesis of other known or unknown hydrides. Initial experiments in our laboratories have already given promising results in this direction.

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## Notes and references

† In a parallel experiment, the quantitative course of the reaction was confirmed by the exact 2 : 1 ratio of hydrogen amounts evolved in the 1st and 2nd dissociation steps (2.68 *versus* 1.33 wt% H<sub>2</sub>).

‡ After pressurizing with hydrogen, the sample temperature rises instantaneously above the nominal temperature.

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