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Recording of hydrogen evolution—a way for controlling the doping process of sodium alanate by ball milling

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Abstract

A simple equipment was developed which allows to monitor gas evolution or absorption occurring in the course of a ball milling process. The equipment has been applied to characterize via hydrogen evolution the reduction process of metal halides used as doping agents in the preparation of sodium alanate hydrogen storage materials. The gas flow curves resulting from the measurements (Figs. 2–4) deliver useful informations concerning the rate, progress and completion of each of the involved reduction process, so that the stoichiometry of the underlying chemical reactions could be conceived or confirmed (Eqs. (3)-(7)). In the preparation of sodium alanate hydrogen storage materials, the presented method can help to find out ball milling parameters necessary to produce an optimal catalytic activity of a dopant. © 2003 Elsevier B.V. All rights reserved.

Keywords: Sodium alanate for hydrogen storage; Ball milling; Monitoring of gas evolution (absorption)

1. Introduction

The ball milling of NaAlH₄, NaH + Al mixtures, or lithium alanates together with the doping agent, e.g. TiCl₃, is at present almost generally adopted as a doping method for the preparation of catalyzed alanates for hydrogen storage [1-6]. The ball milling method has also been applied for the preparation of earth alkali metal alanates [7]. The disadvantage of the ball milling as a doping method, however, is the poorly definable nature of milling procedure, so that equipment and milling conditions (e.g. milling apparatus, weight of milling balls relative to milled material, duration of the milling procedure etc.) have to be purely empirically chosen and optimized. In order to overcome this problem, an attempt was made to characterize the ball milling process by recording hydrogen evolution during the process. The prerequisite for doing this is that in the course of the doping process the doping agent is being reduced with evolution of hydrogen. In fact, hydrogen evolution gives an evidence that the doping agent during the doping procedure is being reduced. As will be shown in the following, the rate of hydrogen evolution and the quantity of hydrogen evolved can give useful informations about the ball milling doping process. We describe here a simple set-up for performing this kind of measurements and discuss the results thus obtained.

2. Experimental

2.1. Description of the set-up for measuring hydrogen evolution during ball milling

In the jacket of the 25 ml volume milling vial (lengths 5 cm, diameter 21.8 mm) of the Retsch ball-mill (model 200 MM, 30 Hz) was welded a Swagelok gas connection supplied with a filtering element (Fig. 1). The connection is reinforced by an external steel tube welded as a corset. A K-type thermocouple (Ni–Cr–Ni) is situated in the wall of the milling vial. The vial is connected to a 250 ml automatic gas burette [8,9] via a standard laboratory vacuum rubber tube. The movements of the piston of the burette and the temperature inside the vial during milling are recorded on a two-channel recorder.

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Fig. 1. Experimental set-up for recording hydrogen (gas) evolution or absorption during ball milling.

2.2. Carrying out of the measurement

In a typical experiment, 2-3 g of NaAlH₄ (or of a NaH + Al mixture) are weighed in a glove box in the vial of the mill, and the desired (weighed) amount of the doping agent (typically a transition metal halide or a mixture thereof)

added. After adding the milling ball(s) the vial is closed and connected to set-up (Fig. 1). Good results with the above mentioned vial were obtained for example using one stainless steel ball of $\emptyset = 20 \text{ mm} (32 \text{ g})$. During ball milling hydrogen evolution is recorded on the paper strip of the recorder. According to our experience, optimal results in the

subsequent cycle tests are obtained when the milling time is prolonged well above the time required for the reduction of the dopant (see discussion). As a possible reason for error in measurements, it can happen that the gas outlet tube becomes clogged with the finely dispersed milled material, thus impairing of even stopping the hydrogen flow. If a doubt concerning this exists, after the measurement the outlet tube should be inspected and the measurement repeated.

3. Results and discussion

The stoichiometries of the doping reactions of Ti(OBu)₄, Bu = n-C₄H₉, and of Ti(OBu)₄/Fe(OEt)₂ combinations with NaAlH₄ has been earlier investigated in toluene via measurement of hydrogen evolution and IR-spectra of the reaction products. On the basis of results thus obtained, it was concluded that the doping reactions proceed according to Eqs. (1) and (2) [10]. At this place should be mentioned that Eqs. (1) and (2) as well as the following ones (Eqs. (3)–(7)) represent only the overall stoichiometry of the reduction processes, without referring to the post-reduction changes of finely dispersed metals, e.g. formation of alloys [6,10].

$$x$$
NaAlH₄ + Ti(OBu)₄ $\xrightarrow{\text{toluene}}$ $(x - 1)$ NaAlH₄ + Ti
+ NaAl(OBu)₄+2H₂ \uparrow (1)

$$x \text{NaAlH}_4 + \text{Ti}(\text{OBu})_4 + \text{Fe}(\text{OC}_2\text{H}_5)_2$$

$$\xrightarrow{\text{toluene}} (x - 1.5) \text{NaAlH}_4 + \text{Ti} + \text{Fe}$$

$$+ 1.5 \text{NaAl}(\text{OC}_2\text{H}_5)_2\text{OBu} + 3\text{H}_2 \uparrow \qquad (2)$$

For the ball milling (b.m.) of NaAlH₄ with TiCl₃, based on reflections of NaCl found in the XRD of the milled product,

the reaction Eq. (3) has been proposed [11].

$$x \text{NaAlH}_4 + \text{TiCl}_3 \xrightarrow{\text{b.m.}} (x - 3) \text{NaAlH}_4 + \text{Ti} + 3\text{Al} + 3\text{NaCl} + 6\text{H}_2 \uparrow$$
(3)

In the present work, the described set-up (Fig. 1) has been applied to record the hydrogen evolution during b.m. of NaAlH₄ with some titanium, zirconium and iron halides as doping agents (Table 1).

B.m. of NaAlH₄ with 2 mole% of TiCl₃ (Fig. 2 (\bullet)) vielded in the course of 4 h, in accordance with Eq. (3), almost exactly 6 mole H₂/mole TiCl₃. The hydrogen evolution curve for the case of b.m. of NaAlH₄ with 4 mole% of TiCl₃ (\blacksquare) is characterized by a relatively high evolution rate during the first 4 h, and, after a bend in the curve, by a slower hydrogen evolution in the remaining 12h of milling time. The amount of hydrogen evolved until the bend in the curve is again in good agreement with that calculated for 6 mole H_2 /mole TiCl₃ (Eq. (3)). The steeper part of the hydrogen evolution curve represents apparently the process of reduction of TiCl₃ to metallic Ti, while the subsequent slower hydrogen evolution is the result of hydrogen liberation from NaAlH₄, catalyzed by the reduced doping agent. In a parallel experiment (4 mole% TiCl₃, \blacklozenge) the milling ball used was exchanged by a considerably smaller (lighter) one with the result that only ~ 5 mole H₂/mole TiCl₃ were released after 10h of milling time and that the milled sample was inferior in the subsequent hydrogen dis- and recharging test than the precedent sample [12]. This indicates that recording of hydrogen evolution can give valuable hints concerning optimization of the milling procedure, as well as toward an improving of hydrogen storage properties of the milled samples.

The so called "direct synthesis" of doped sodium alanate for the purpose of hydrogen storage [13] is usually carried out by b.m. of a NaH/Al mixture with a doping agent,

Monitoring of hydrogen evolution during ball milling of $NaAlH_4 + Al$ or of a NaH + Al mixture, with doping agents^a

Doping agent	Mole% relating to NaAlH ₄	Milling time (h)	Figure number	H ₂ (mole)/ dopant (mole)
TiCl ₃	2	5	Fig. 2	6
TiCl ₃	4	16	Fig. 2	6
TiCl ₃	4 ^b	10	Fig. 2	~ 5
TiCl ₃	4 ^c	8	Fig. 2	~ 1
TiCl ₂	4	13	Fig. 3	3.6
TiCl ₄	3 ^d	10	Fig. 3	8
TiCl ₃ ·1/3 AlCl ₃	4	10	Fig. 3	8
TiF ₃	2	21	Fig. 3	1.3
ZrCl ₄	2	5.5	Fig. 4	6.2
FeCl ₂	2.6	2.5	Fig. 4	2.5
FeCl ₂	4	2.5	Fig. 4	2.7
FeCl ₃	2	2.5	Fig. 4	4.5

^a If not otherwise noted, a milling ball of $\emptyset = 20 \text{ mm}$, 32 g was used.

^b Milling ball of $\emptyset = 11.6 \text{ mm}, 6.3 \text{ g}.$

Table 1

^c Direct synthesis of doped NaAlH₄ [9].

^d In this case hydrogen evolution took place without b.m., by stirring the NaAlH₄/TiCl₄ mixture in a closed system (see text).



Fig. 2. Hydrogen evolution curves in the case of NaAlH₄ (NaH + Al)/TiCl₃ ball milling (if not otherwise noted, a milling ball of $\emptyset = 20 \text{ mm}$, 32 g was used). (**•**) NaAlH₄/2 mole% TiCl₃; (**•**) NaAlH₄/4 mole% TiCl₃; (**•**) NaAlH₄/4 mole% TiCl₃ (milling ball of $\emptyset = 11.6 \text{ mm}$, 6.3 g); (**•**) NaAlH₄/4 mole% TiCl₃.

e.g. TiCl₃, followed by hydrogenation under pressure. In this case the monitoring of hydrogen evolution during b.m. brought a surprising result. As can be seen in Fig. 2 (\blacktriangle), an initial hydrogen evolution of a ~1 mole H₂/mole TiCl₃ is (reproducibly) followed by *absorption* of roughly 0.5 mole H₂/mole Ti, so that after the hydrogen flow stops, a net hydrogen uptake of ~0.5 mole H₂/mole Ti results. Whether and what kind of relation this phenomenon has to the course (mechanism) of the direct synthesis of doped sodium alanate remains yet to be explored. Provisionally, it may be assumed that simultaneously with reduction of TiCl₃ to Ti(0) (Eq. (4)), the highly reactive Ti(0) particles react with the hydrogen evolved with formation of titanium hydride TiH₂. Alternatively, there might be a Ti-catalyzed hydrogenation of the present NaH/Al mixture.

$$x \text{NaH} + x \text{Al} + \text{TiCl}_3 \xrightarrow{\text{b.m.}} (x - 3) \text{NaH} + x \text{Al} + 3 \text{NaCl} + \text{Ti} + 1.5 \text{H}_2 \uparrow \qquad (4)$$

B.m. of NaAlH₄ with TiCl₂ (4 mole%) as a doping agent (Fig. 3) led to the evolution of 4 mole H₂/mole TiCl₂, in accordance with the Eq. (5). On the other hand, using the set-up of Fig. 1 it was not possible to get reproducible hydrogen evolution curves for the NaAlH₄/TiCl₄ ball milling, since a rapid hydrogen evolution starts immediately upon dropwise addition of the liquid doping agent TiCl₄ to NaAlH₄ in the vial. This determination was therefore carried out by adding TiCl₄ to NaAlH₄ in closed system by means of a syringe. In this case hydrogen evolution took place even without b.m., by merely stirring the mixture at ambient temperature. The recorded hydrogen evolution curve (Fig. 3) is in good agreement with the expected 8 mole H₂ /mole TiCl₄ (Eq. (6)).



Fig. 3. Hydrogen evolution during ball milling, or stirring (TiCl₄), of $NaAlH_4$ with titanium halides.

B.m. of NaAlH₄ with TiCl₃·1/3 AlCl₃ as a dopant (Fig. 3) proceeded also with evolution of 8 mole H_2 /mole dopant, in accordance with the Eq. (7).

$$x \text{NaAlH}_4 + \text{TiCl}_2 \xrightarrow{\text{b.m.}} (x - 2) \text{NaAlH}_4 + \text{Ti} + 2\text{Al} + 2 \text{NaCl} + 4\text{H}_2 \uparrow$$
(5)

$$x \text{NaAlH}_4 + \text{TiCl}_4 \xrightarrow[\text{at 25 °C}]{\text{stirring}} (x - 4) \text{NaAlH}_4 + \text{Ti} + 4\text{Al} + 4 \text{NaCl} + 8\text{H}_2 \uparrow$$
(6)

$$x \text{NaAlH}_4 + (\text{TiCl}_3)_{\frac{1}{3}} \xrightarrow{\text{b.m.}} (x - 4) \text{NaAlH}_4 + \text{Ti} + 4\frac{1}{3}\text{Al} + 4\text{NaCl} + 8\text{H}_2 \uparrow$$
(7)

From these results it is apparent that, contrary to other findings [14], independently of the oxidation state of Ti-chloride dopants 2, 3 or 4, the reduction with NaAlH₄ always proceeds up to the zerovalent stage of titanium.

In comparison to TiCl₃ (Fig. 2), the rate of hydrogen evolution upon b.m. of TiF₃ with NaAlH₄ (Fig. 3) is found to be extremely low. If one assumes that also in this case reduction of TiF₃ proceeds till the zerovalent stage of titanium, then after 10 h of milling time only a small fraction of TiF₃ could have been reduced. The incomplete reduction may explain the low catalytic activity of TiF₃ as a dopant in previous cycle tests [12]. In order to achieve better results with TiF₃ as a doping agent, evidently the milling time and/or the milling temperature must be increased.

The b.m. of NaAlH₄ with 2 mole% of ZrCl₄ (Fig. 4) delivered after 5.5 h of b.m. 6.2 mole H_2 /mole ZrCl₄, which is below the amount expected for the reduction of ZrCl₄ to Zr metal (8 mole H_2 /mole ZrCl₄). In order to complete the reduction process, also in this case an increase of milling time and/or temperature appear to be necessary. For the b.m. of NaAlH₄ with 2.6 or 4.0 mole% of FeCl₂ (Fig. 4), in both cases the hydrogen evolution stopped after release of ~2.5 mole H₂/mole FeCl₂. On the other hand, the b.m. of NaAlH₄ with 2 mole% of FeCl₃ (Fig. 4) resulted in 4.5 mole H₂/mole FeCl₃. Both for FeCl₂ and FeCl₃ the hydrogen evolution is thus found to be by the amount of ~1.5 mole H₂/mole Fe lower than the amount expected for the reduction of Fe chlorides to the zerovalent stage (4 and 6 mole H₂/mole Fe). Since in all three experiments with Fe chlorides the hydrogen evolution after 2–3 h stops, a partial reduction of FeCl₂ or FeCl₃ in the presence of excess NaAlH₄ seems improbable. The "lack" of 1.5 mole H₂/mole Fe upon b.m. of NaAlH₄ with Fe chlorides could be a hint for a possible formation of a hydride (Fe-Al hydride?), which is worth of further investigation.

4. Conclusion

From the preliminary results presented, it appears that for processes taking place with gas evolution or absorption during b.m., the monitoring of gas flow can be used as a way for characterization of b.m. processes. In particular, such measurements can deliver following informations.

- The rate of gas evolution (absorption) and the total amount of gas evolved (absorbed) can give direct evidence about an underlying chemical reaction, so that such a reaction can be conceived or confirmed.
- The recorded gas flow curves (Figs. 2–4) inform about the rate, progress and completion of a b.m. process giving rise to gas evolution. Thus, they can be used as a graphical representation of a specific performed b.m. experiment and also for controlling reproducibility of such experiments.



Fig. 4. Hydrogen evolution curves resulting from ball milling of NaAlH₄ with zirconium and iron chlorides.

- Furthermore, gas flow curves can help in choice of milling parameters (milling time, milling balls and their weight relative to the milled material etc.) and milling equipment. Monitoring of the gas flow during b.m. can also be used to compare the efficiency of different high energy ball mills, as f.i. in up-scaling of a b.m. process.
- In the use of the b.m. method for the preparation of doped sodium alanate hydrogen storage materials [1-3,10,11,13], the recording of hydrogen evolution during b.m. can be used to find out milling parameters necessary to achieve the optimal catalytic activity of a dopant (c.f. above, TiF₃ as dopant).
- Occasionally, measurements of gas flow during b.m. can bring about to trace out the presence of a known or un-known metal hydride.

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