Hydrogen desorption from NaAlH₄ catalyzed by ball-milling with carbon nanofibers

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Abstract. The effect of ball-milling NaAlH₄ with carbon nanofibers on the hydrogen desorption rates is reported. The rates are strongly dependent on the ball to powder ratio and milling time. The use of an Arrhenius equation corrected for the dependence of hydrogen pressure allows a comparison with other literature data, performed in different conditions. It shows that ball-milling at high energy is the most favorable route to increase the desorption rate and lower the activation energy for hydrogen desorption.

1. Introduction
A technical challenge for the development of fuel cell powered vehicles is a suitable material for on-board hydrogen storage with 6.5 wt%H storage capacity. Sodium alanate has been considered as a potential hydrogen storage material with its theoretical capacity of 5.6 wt%H resulting from the first two desorption steps. The discovery of the catalytic effect of Ti on hydrogen desorption kinetics from NaAlH₄ by Bogdanovic and Schwickardi [1] attracted the interest in this relatively cheap hydrogen storage material because the desorption can be lowered near the working temperature of the PEM fuel cells. A large number of studies recently reviewed [2] have been focused on a wide range of catalysts and procedures, aiming to lower the desorption temperature and to increase the desorption rates. Ball-milling with doping agents proved to result both in high capacity reversible storage with excellent kinetics and a „one-step direct synthesis method” from NaH and Al powder [3].
A loss of capacity appears due to the irreversible reaction between the hydride and some dopants [4,5] which led to investigations of various forms of carbon as catalyst [6-8]. The positive effect of carbon was assigned to the inhibition of grain aggregation [8]. This paper reports the effects of ball-milling (BM) NaAlH₄ with carbon nanofibers on hydrogen desorption.

2. Experimental
In a glove box under dry nitrogen, 2 g Aldrich tech. NaAlH₄ were mixed with 0.2 g herringbone type carbon nanofibers (CNF) of 100-500 nm diameter, synthesized as described elsewhere [9], in the vial of 25 cm³ and 10 bar of pure hydrogen. The characteristics of the planetary mill are: revolution radius 150 mm, vial radius 12.5 mm, rotation to revolution angular velocity Wᵥ/Wₚ = 2.47.

With 24 balls of 6 mm diameter the ball/powder ratio is 10.3 and the transferred power calculated according to [10] is P* = 8 Wh/g which is in the range of medium energy ball-milling.

Alternatively, Pd (10%)/CNF were used, obtained by impregnation of CNF with Pd nitrate, calcined at 500°C and reduced under hydrogen flow at 300°C. The hydrogen desorption was
performed in a Sievert type apparatus, with a 6000 cm$^3$ volume, to ensure a pressure increase not higher than ~0.1 bar at the end of reaction, allowing thus measurements at rather constant pressure. The desorption was measured at constant temperature, starting from 1.1 bar H$_2$ pressure. The rehydrogenation was performed at, 120 bar using 99.999% H$_2$, 20 h at 110°C; each desorption run was started after maintaining the reactor for at least 1 h at the reaction temperature at a hydrogen pressure usually 50 bar H$_2$ higher than the equilibrium desorption pressure calculated from [11].

3. Results and discussion

The literature reports two types of (overall) kinetic curves of hydrogen desorption corresponding to the first desorption step from NaAlH$_4$: sigmoid type, associated to a nucleation and growth mechanism or

$$\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2$$

$$\leftrightarrow \text{NaH} + \text{Al} + \frac{3}{2} \text{H}_2$$

(1)

curves with decreasing slopes, corresponding to reactions proceeding evenly on the entire surface of all reactant particles [12]. However, in the later case a rather constant slope is observed for NaAlH$_4$ in a wide concentration range. In some cases, the type of curve changes with cycling or the catalyst as can be seen from data reported by Wang et al [13]. This might indicate that the catalyst is involved sometimes in a reaction as suggested by the comments on the differences between Sc and Ti catalysts [13] where the positive effect of Sc was assigned to the inhibition of aggregation of Al particles. The segregation of Al particles was reported by Bogdanovic et al [11] and Brinks et al [14] proposed that the formation of stable Ti-Al compounds would prevent the reverse (hydrogenation) reaction, leading to a loss of storage capacity.

The scope of this paper has not been to elucidate the reaction mechanism but rather to find some correlations with the hydride processing, able to identify simple and convenient ways to improve the overall reaction rates. Some typical hydrogen desorption curves obtained are given in figure 1. They are of the second type noted above, similar to other reported isothermal desorption curves for carbon [6] or other dopants such as TiCl$_3$ [15], Ti(Zr) [16]. This suggests that carbon is not implied in a reaction with Al, as reasonably may be assumed, in agreement with the observation of Cento et al. That the role of carbon “could be rather physical than chemical probably inhibiting the grain aggregation” [7].

Because for hydrides the absorption/desorption kinetics depends on the hydrogen pressure [12], a comparison of the activation energies and pre-exponential factors from different literature results (often performed in different conditions, for example desorption in [13] is against 3.4 bar), the reaction rate must take into account the pressure dependence. Therefore, the activation energies and pre-exponential factors from our data and other reported results with available details of the experiments, have been evaluated from the desorption rate $r^d$ containing the term $(P_{eq}-P)$ as thermodynamic driving force of the desorption, with $P_{eq}$ – the hydrogen equilibrium pressure for the first step, evaluated from [11] and $P$ – the pressure at which the desorption is measured. The Arrhenius equation as in [17] has been used

$$r^d = A(P_{eq}-P)\exp(-E_a/RT)$$

(2)

where $A$ is the pre-exponential factor, $E_a$ – the activation energy and $R$ – the universal gas constant. The results obtained with the equation (2), by dividing the literature desorption rates with $(P_{eq}-P)$ are given in table 1. The CNF show activation energy and pre-exponential factors rather close to the literature data [6] for 10% carbon. The most important finding is that the overall desorption rate increases.
Figure 1. Hydrogen desorption at 130°C from ball-milled NaAlH₄ with 9% “herringbone” type carbon nanofibers obtained after 5 absorption/desorption cycles.

Table 1. Activation energy (Eₐ), pre-exponential factor (A) and balls/NaAlH₄ weight ratios RBP for hydrogen desorption from 2 g NaAlH₄ ball-milled with carbon nanofibers (CNF).

| Catalyst    | RBP | Eₐ (kJ/molH₂) | A   | r at 110°C (wt%H/h) | Conditions   | Ref     |
|-------------|-----|---------------|-----|---------------------|--------------|---------|
| 9%CNF       | 10.3| 51.5          | 12.2| 0.36                | 24 balls 3h  | This work |
| 9%Pd/CNF    | 10.3| 58.5          | 14.0| 0.25                | 24 balls 3h  | This work |
| 9%CNF       | 21.5| 53.1          | 13.7| 1.0                 | 50 balls 7h  | This work |
| 10%Carbon   | 15  | 57.0          | 13.7| 0.32                | Vibratory BM | [6]      |
| 2mol%TiCl₃ | -   | 45.2          | 11.2| 1.2                 | -            | [15]     |
| 4% Sc       | -   | 38.7          | 10.2| 2.6                 | High-energy BM | [13]     |
| 8%Ti+2%Zr   | 30  | 24.9          | 5.9 | 3.0                 | -            | [16]     |
| ~54% ScCl₃ | -   | -             | 5.6 | -                   | -            | [3]      |

Some literature data obtained from recalculated r" and measured desorption rates r at 110°C are also given for comparison significantly with the increasing RBP and milling time, parameters which increase the efficiency of BM due to a higher energy transfer from balls to powder [10]. The comparison with literature also show that high energy BM [13] or higher RBP [16] results in even higher desorption rates and a significant decrease of activation energy. This is consistent with the type of desorption curves suggesting a reaction which proceeds over the entire surface, when the initial slope is a product of the rate constant at the interface with the initial surface area [12] as the surface area can be increased by a more efficient BM. It should be noted that though Pd is efficient for hydrogen absorption/dissociation and transfer to the alanate, it does not result in any improvement of desorption characteristics.

It was noted [3] that NaAlH₄ seems to be closest to the demands for automotive applications in combination with advanced fuel cells working at 150°C. However, the heat management for absorption/desorption at these temperatures brings about additional difficulties and the calculations show [17] that the total weight of the storage tank increases by a factor of 1.6-2.
4. Conclusions
The carbon nanofibers are good catalysts for improving the hydrogen desorption kinetics of NaAlH₄ by ball-milling. The desorption rates can be increased by increasing the ball/powder ratio and milling time. An Arrhenius equation involving the dependence on the hydrogen pressure allows a unitary evaluation of the activation energy and pre-exponential factors for a comparison of literature data. High-energy ball-milling is a suitable way to achieve high desorption rates. Though rather close to the requirements for mobile applications, the heat management is a serious disadvantage for NaAlH₄. Materials with good storage capacity but low heat of hydrogen absorption seem much more suitable for a lower total weight of storage tank.

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