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# Synthesis and hydriding/dehydriding properties of nanosized sodium alanates prepared by reactive ball-milling

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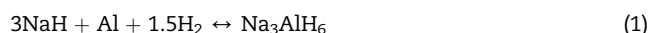
## ABSTRACT

TiF<sub>3</sub>-doped NaH/Al mixture was hydrogenated into Na<sub>3</sub>AlH<sub>6</sub> and NaAlH<sub>4</sub> complex hydrides by reactive ball-milling at room temperature through the optimization of milling duration and hydrogen pressure. The analysis of the preparation of NaAlH<sub>4</sub> samples during reactive ball-milling process has been performed by XRD and TG/DSC. It has been found that Na<sub>3</sub>AlH<sub>6</sub> was formed under 0.5 MPa hydrogen pressure and 30 h milling duration, while NaAlH<sub>4</sub> was formed under 0.8 MPa hydrogen pressure and 45 h milling duration. The process of preparing NaAlH<sub>4</sub> by ball-milling was found accomplished via two reaction steps, namely: (1) NaH + Al + H<sub>2</sub> → Na<sub>3</sub>AlH<sub>6</sub> and (2) Na<sub>3</sub>AlH<sub>6</sub> + Al + H<sub>2</sub> → NaAlH<sub>4</sub>. As the hydrogen pressure and milling duration increase, the synthetic yield of NaAlH<sub>4</sub> and its corresponding dehydriding capacity are both increased. With increased hydrogen pressure (0.8–3 MPa) and milling duration (45–60 h), the cell volume of Na<sub>3</sub>AlH<sub>6</sub> decreases while that of NaAlH<sub>4</sub> increases gradually. The abundance of Na<sub>3</sub>AlH<sub>6</sub> phase decreases from 57.76 (x = 0.8, y = 45) to 8.69 wt.% (x = 3, y = 60), and the abundance of NaAlH<sub>4</sub> phase increases from 20.63 (x = 0.8, y = 45) to 86.50 wt.% (x = 3, y = 60). All the samples prepared in this way have fairly good activation behavior and fast hydriding/dehydriding reaction kinetics, which are capable of absorbing 4.26 wt.% hydrogen at 120 °C and desorbing 4.12 wt.% hydrogen at 150 °C, respectively. The improvement of hydriding/dehydriding properties is ascribed to the favorable microstructure and ultrafine particle features of nanosized NaAlH<sub>4</sub> formed during ball-milling at the optimum synthetic condition.

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## 1. Introduction

Complex hydride has been regarded as one category of promising materials for mobile hydrogen storage [1], since Bogdanović et al. first discovered that Ti-catalyzed NaAlH<sub>4</sub> had good reversible hydrogen storage properties under moderate temperature and pressure conditions and that the hydrogenation/dehydrogenation reactions proceeded according to the following two-step reactions [2,3],



Theoretically, the above reactions (1) and (2) are capable of absorbing and desorbing 3.7 wt% and 1.9 wt% amount hydrogen reversibly, respectively. It has been proved that the kinetics of the above reversible reactions of NaAlH<sub>4</sub> is improved markedly by doping with a suitable catalyst, such as TiCl<sub>3</sub> or TiF<sub>3</sub> [4,5]. It is also well known that Ti-doped NaAlH<sub>4</sub> can be synthesized by a two-step method of hydrogenating the ball-milling composite of NaH and Al doped with Ti-based

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catalyst [6–8]. In early days these hydrogenation processes were generally carried out at about 120 °C and under high hydrogen pressure of 100–150 bar, and proceeded rather slowly [8]. Currently, Felderhoff et al. demonstrated that one step synthesis of Ti–NaAlH<sub>4</sub> is realized by direct ball-milling the NaH, Al and TiCl<sub>3</sub> mixtures at 50–70 °C under the initial hydrogen pressure of 8.3 MPa [9]. Eigen et al. further demonstrated that NaAlH<sub>4</sub> can be obtained by first partially hydrogenating NaH/Al with TiCl<sub>4</sub> catalyst during milling at the low hydrogen pressure of 1.2 MPa [10], however, it was shown that a fully converted NaAlH<sub>4</sub> process required further activation of the sample by hydrogenation with 100 bar hydrogen pressure or a lengthy dry milling process of more than 100 h under the low hydrogen pressure of 1.2 MPa [10]. Moreover, Wang and Ritter et al. reported a new procedure for the direct synthesis of NaAlH<sub>4</sub> through hydrogenation of NaH and Al in the presence of TiCl<sub>3</sub> as catalyst and a liquid complexing agent [11]. This technique involves three steps. Firstly, dry high-pressure ball-milling (HPBM) the blended NaH and Al with TiCl<sub>3</sub> catalyst under hydrogen. Secondly, hydrogenate the NaH, Al and TiCl<sub>3</sub> composite using HPBM in THF and under hydrogen. Finally, obtain the high yield of NaAlH<sub>4</sub> by vacuum filtration and drying process. However, these studies [9–11] still demanded either high hydrogen pressure or long milling duration during ball-milling, or the synthesis procedure was rather complex. Therefore, they were not favored and accepted in practice.

Recently, we found out that NaAlH<sub>4</sub> can be directly synthesized in one step by ball-milling NaH/Al with TiF<sub>3</sub> as catalyst under hydrogen pressure of ~2.5 MPa for 50 h [12]. The aim of the present work is to develop this technique by further studying the synthesis mechanism and hydriding/dehydriding properties of sodium alanates (Na<sub>3</sub>AlH<sub>6</sub> and NaAlH<sub>4</sub>) through controlling the ball-milling duration (0.5–60 h) and hydrogen pressure (0.5–3 MPa) during reactive ball-milling NaH/Al with 4 mol% TiF<sub>3</sub> catalyst at the ambient temperature. Favorable results were obtained by the phase structures and thermal decomposition properties of the synthesized samples were investigated by X-ray diffraction (XRD) and thermogravimetry united differential scanning calorimetry (TG/DSC). The synthesized NaAlH<sub>4</sub> can absorb 4.26 wt.% hydrogen at 120 °C and desorb 4.12 wt.% hydrogen at 150 °C and has fast reaction kinetics as well as stable cycling hydriding/dehydriding capacities. Moreover, as NaH and Al are cheaper and easier to prepare than Na<sub>3</sub>AlH<sub>6</sub> and NaAlH<sub>4</sub>, we believe this technology will have a good market in the future.

## 2. Experimental method

The starting materials were NaH powder (95%, ~74 μm), Al powder (99%, 74–154 μm) and TiF<sub>3</sub> powder (99%). All were purchased from Sigma–Aldrich Co. and used as received. Each mixture of NaH/Al + 0.04TiF<sub>3</sub> (NaH, Al and TiF<sub>3</sub> powders were weighted in 1:1:0.04 mol ratio) was introduced into a stainless steel vial together with stainless steel balls (∅ = 8 mm). The ball-to-powder weight ratio was 30:1. The vial was then evacuated, and filled with 0.5–3 MPa supra-pure hydrogen. The mixture was ball-milled for 0–60 h at 350 rpm at ambient

temperature. All the operations were carried out in a glove box under purified argon atmosphere (99.999%).

The hydriding/dehydriding tests on the as-prepared samples were carried out on a Sieverts type apparatus. The hydriding temperature was set at 120 °C, pressure at 10 MPa for 1 h duration, and the dehydriding temperature was set at 150 °C against 0.1 MPa for 2 h duration. The hydrogen absorption capacity was calculated into weight percent of the weight of NaH/Al with the weight of TiF<sub>3</sub> powder included.

The crystal structures and surface morphology of the as-prepared samples were studied and compared by means of X-ray diffraction (XRD, Rigaku D/Max PC2500) and scanning electron microscopy (SEM, HITACHI S-570) with an energy dispersive analysis for X-rays (EDS). The crystal structures were carried out by XRD with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at operating parameters of 150 mA, 40 kV, with step size 0.02° and speed 2°/min. The crystalline lattice parameters and cell volumes were measured from the XRD diffraction peaks, the grain size was calculated by Scherrer equation ( $L = K \cdot \lambda / \beta \cos \theta$ ), and the phase abundances were calculated quantitatively by K value method (plotting the peak intensity ratio  $I/I_c$  to calculate the mass fraction of the phase) using MDI Jade software, and the details of calculation procedures can be found in some references [13–15]. The XRD sample was covered with a special plastic tape to prevent the contact of the sample with water vapor and oxygen from air during experimentation. The thermal decomposition properties of the samples were also measured synchronously by thermogravimetry united with a differential scanning calorimetry (TG/DSC, SDT Q600 DSC). The heating rate of thermal analyses was 4 K/min and the flow rate of argon protective gas was 100 ml/min.

## 3. Results and discussion

For realizing the variation of phase structures during the synthesis of NaAlH<sub>4</sub> in ball-milling process, the X-ray diffraction (XRD) measurements of (NaH/Al + 0.04TiF<sub>3</sub>) mixture ball-milled under different hydrogen pressures (0.5–3 MPa) and for different milling-durations (0.5–60 h) were made and their results are shown in Figs. 1 and 2. With the increase of milling duration and hydrogen pressure, the synthesis of NaAlH<sub>4</sub> complex hydride can be divided into two different stages. Fig. 1 shows the XRD patterns of (NaH/Al + 0.04TiF<sub>3</sub>) mixture ball-milled under different hydrogen pressures (0.5–0.8 MPa) and for different milling-durations (0.5–30 h). It can be seen that the NaH and Al diffraction peaks become weaker and broader, as the milling duration increased from 0.5 to 15 h with a constant hydrogen pressure of 0.5 MPa. This indicates that reactive ball-milling under hydrogen actually induces the decrease of crystallite size and the increase of internal stress in the sample. But as the NaH and Al cannot be hydrogenated under such low hydrogen pressure of 0.5 MPa within 15 h, because no new phase has been found in the samples under these ball-milling conditions. As the milling duration is prolonged to 30 h under 0.5 MPa hydrogen pressure, the Na<sub>3</sub>AlH<sub>6</sub> diffraction peak is obviously detected, and the NaH diffraction peaks are disappeared almost entirely. Furthermore, with the hydrogen pressure further increased to 0.8 MPa, the intensity of Na<sub>3</sub>AlH<sub>6</sub> is further

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