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Direct formation of Na₃AlH₆ by mechanical milling NaH/Al with TiF₃

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 Na_3AlH_6 can be directly formed by mechanical milling NaH/Al with TiF₃ under hydrogen atmosphere. The hydrogenation fraction of NaH increases with increasing the milling time, and reaches up to 0.61 after 20 h milling. Thus-formed Na_3AlH_6 exhibits unexpected polymorphic transformation and decomposition behaviors. This, together with the unusual hydrogen storage performance of the mechanically prepared materials, provides us a suggestive perspective to probe the favorable modification of the thermodynamics of Na_3AlH_6 and nature of active Ti-species in Ti-doped $NaAlH_4$. © 2005 American Institute of Physics. [DOI: 10.1063/1.2001756]

A key technical challenge in advancing "hydrogen economy" is to develop a viable on-board hydrogen storage medium. Among various potential approaches, materialbased reversible hydrogen storage has long been appreciated for its significant advantages on safety, energy efficiency and cost issues.¹ However, decades of extensive research efforts on metal/alloy hydrides and nanostructured carbon and related materials have led to no material system which can provide hydrogen source for on-board fuel cell application within combined constrains of energy density, operation conditions, and efficiency.¹⁻³ Recently, Bogdanović and Schwickardi had made a substantial breakthrough on sodium aluminum hydrides that brings the promise of clean hydrogen energy a big step forward.⁴ It was found that, upon doping with catalytic amount of selected transition metal compounds, NaAlH₄ might undergo reversible hydrogen storage at moderate temperatures. This finding immediately stimulated worldwide study on developing doped NaAlH₄ and other light-metal hydrides as viable hydrogen storage media for on-board applications. $^{5\!-\!18}$

The hydrogen storage in $NaAlH_4$ is accomplished via a reversible two-step process involving the reactions seen in Eq. (1),

$$NaAlH_4 \leftrightarrows 1/3Na_3AlH_6 + 2/3Al + H_2$$
$$\leftrightarrows NaH + Al + 3/2H_2. \tag{1}$$

Although both steps of de-/hydrogenation processes can be kinetically enhanced upon doping with Ti species, the practical availability of NaAlH₄ for on-board application is still largely hampered by the thermodynamic property of Na₃AlH₆. According to the literature, the plateau pressure of Na₃AlH₆/NaH+Al+H₂ equilibrium is less than 1 atm at temperature below 110 °C.^{7,10} Therefore, the study on the intermediate Na₃AlH₆ stage is critical in developing Tidoped NaAlH₄ as practical on-board hydrogen storage media. In this regard, however, the investigations hitherto performed, in particular focusing on the decomposition behavior and modification of thermodynamics, are rather limited.^{4,19} Partially, such situation should be attributed to the difficulty involved in the preparation of Na₃AlH₆. The traditional methods of preparing Na₃AlH₆ involve the utilization of high

pressure hydrogen (several hundred bar), organic solvent and complicated purification processes.²⁰⁻²² Additionally, controlled thermal decomposition of NaAlH₄ was also proposed as an alternative method.²² Recently, Huot *et al.* reported a simple solid-state approach, in which β -Na₃AlH₆ was synthesized by mechanical milling the mixture of NaAlH₄ +2NaH.²³

Quite recently we found that β -Na₃AlH₆ could be directly formed during mechanical milling of NaH/Al with TiF₃ under hydrogen atmosphere. More significantly, thus-formed Na₃AlH₆ presents unexpected polymorphic transformation and decomposition behaviors, in comparison with the literature results.^{23–25} Furthermore, the mechanically prepared materials starting from NaH+Al+4 mol % TiF₃ exhibit unusual hydrogen storage performance, which possibly relates to the *in situ* hydrogenation of the materials.

The starting materials of NaH (95%, 200 mesh), Al powder (99.95+%, ~200 mesh), and TiF₃ powder were all purchased from Sigma-Aldrich Co. and were used as-received. The mixture of NaH+Al+4 mol % TiF₃ was mechanically milled by using stainless steel pot and balls in a Fritsch 6 Planetary mill at 400 rpm. The milling was performed under hydrogen atmosphere, with an initial pressure of about 0.85 MPa. The ball-to-powder ratio was about 40:1. All the sample operation was performed in an Ar-filled glove-box.

The as-prepared materials were characterized by x-ray diffraction (XRD, Rigaku D/MAX-2500, Cu $K\alpha$ radiation) and synchronous thermal analyses [thermogravimetry (TG) and differential scanning calorimetry (DSC), Netzch 449C Jupier]. It should be noted that special caution had been taken to minimize the H₂O/O₂ contamination during the measurements. In the thermal analysis measurement, highpurity Ar (purity>99.999%) was used as purge gas. The heating rate was 10 K/min. Hydrogen absorption/desorption behavior was examined by using a carefully calibrated Sievert's-type apparatus, the details of which can be found in Refs. 17 and 18. A typical cyclic experiment entailed desorption at 150 °C and absorption at 120 °C with an initial pressure conditions of <1 Torr and ~10 MPa, respectively. The weight of dopant precursor was taken into account in the determination of H-capacity.

Upon doing with TiF₃, NaH/Al can be directly hydrogenated to β -Na₃AlH₆ during mechanical milling under H₂ atmosphere. Figure 1 presents the XRD profiles of the materials milled for a period ranging from 1 to 20 h. It was ob-

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FIG. 1. XRD patterns of NaH+Al+4 mol % TiF₃ mechanically milled under H₂ atmosphere for different periods.

served that the intensive milling of the first 5 h only led to a markedly decreased diffraction intensity of the starting materials, especially that of NaH. When the milling time was increased to over 10 h, the diffraction peaks (220) and (400) of metastable β -Na₃AlH₆ appeared. The as-formed β -Na₃AlH₆ was nanocrystalline, the average grain size of which was estimated to be about 16 nm according to the Scherrer equation. In a comparative investigation, we failed in our attempt to synthesize Na₃AlH₆ from the mixture of NaH/Al under identical milling conditions. Therefore, active Ti-species may be produced in the milling process and play a critical role in the in situ hydrogenation.

A quantitative characterization of the in situ hydrogenation during mechanical milling was further achieved by TG measurement of thus-prepared samples. As shown in Fig. 2, for the samples milled for longer than 2 h, a significant weight loss was observed to start around 470 K and terminate around 570 K. Clearly, the weight loss should come from the hydrogen evolution from the formed Na₃AlH₆, as was confirmed by the XRD examination (the result not shown here) of the samples after being heated to 573 K. The amount of formed β -Na₃AlH₆ increased with increasing the milling time. As shown in the inserted figure in Fig. 2, the hydrogen amount desorbed from the material milled for 20 h reaches up to 1.11 wt. %, which corresponds to a hydrogenation fraction of NaH of 0.61. These values agree well with the measurement results by using volumetric methods.

The synchronous thermal analyses of thus-formed β -Na₃AlH₆ revealed that its decomposition behavior and



FIG. 2. TG profiles of NaH+Al+4 mol % TiF₃ mechanically milled under hydrogen atmosphere for different periods. The heating rate was 10 K/min. The inserted figure gives the desorbed H-amount and the corresponding hydrogenation fraction of NaH determined by TG measurement.



FIG. 3. Synchronous TG/DSC profiles of the material NaH+Al+4 mol % TiF_3 milled for 10 h (top) and 20 h (bottom). The heating rate was 10 K/min.

phase transformation during the heating process were much more complicated than our current understanding.^{23–25} And excellent agreement was achieved among the measurements performed at different times. Figure 3 presents the TG/DSC profiles of the sample milled for 10 h (top) and 20 h (bottom). The broad exothermic peak centered around 410 K, according to the literature, $^{23-25}$ should originate from β -Na₃AlH₆ $\rightarrow \alpha$ -Na₃AlH₆ and was observed to shift to higher temperature upon increasing the milling time from 10 to 20 h. While the counter polymorphic transformation cannot be distinguished from DSC profiles during the following heating process. Actually, an endothermic peak centered at 525 K that was previously assigned to the polymorphic transformation from α - to β -Na₃AlH₆ was observed for both samples.^{23–25} However, the rapid weight loss detected by synchronous TG measurement provided clear evidence that this heat effect should, at least mainly, correspond to the decomposition of thus-formed Na₃AlH₆, rather than the polymorphic transformation. This is further supported by the XRD examination result that the diffraction peaks of β -Na₃AlH₆ disappeared after the sample being heated up to 573 K. One possible mechanism explaining the phenomenon is that thus-formed Na₃AlH₆ is in a highly disordered nanostructure characterized by a fine grain size and wide energy distribution. As a result, the small and wide peak arising from the polymorphic transformation may be masked by the large heat effect of thermal decomposition. Additionally, for both samples, another exothermic peak was observed around 490 K, but with the nature still unclear.

It was further found that decomposition behavior of the Na_3AlH_6 formed after 20 h milling was substantially different from that of 10 h sample. In great contrast to the single endothermic peak in the case of the 10 h sample, double endothermic effects were observed to be involved in the thermal decomposition of the Na_3AlH_6 formed after 20 h milling. Furthermore, as determined by combination of the calo-



FIG. 4. 150 °C dehydriding profiles (second cycle) of NaH+Al+4 mol % TiF₃ mechanically milled under H₂ atmosphere for different periods.

detected by TG, the enthalpy change for the solid-state dehydriding of Na_3AlH_6 to NaH/Al was found to decrease from 35 for the 10 h sample to 28.5 kJ/mol for the 20 h sample. And both of them are considerably lower than the literature values.^{7,10,25} These findings clearly suggest that the variation of the preparation condition may lead to a change of the microstructure of Na_3AlH_6 , possibly including local atomic arrangement, coordination environment and structural defects. And as a result, the phase transformation, decomposition behavior, and even thermodynamics of Na_3AlH_6 may be modified. A better understanding of the involved mechanism, including the possible role of Ti^{x+} and F^- played in such property change, is clearly of importance for achieving favorable modification of thermodynamics of Na_3AlH_6 .

Of particular interest, we found that the materials prepared by mechanical milling NaH/Al with TiF₃ under H₂ atmosphere underwent a serious degradation on the hydrogen storage performance upon increasing the milling time. Moreover, the marked difference on hydrogen storage performance arising from the variation of milling time was found to persist in the following de-/hydrogenation cycles. Figure 4 gives the typical dehydriding profiles (second cycle) at 150 °C of the materials milled for different periods. A careful examination of the dehydriding profiles found that almost all the capacity degradation came from the first decomposition step (NaAlH₄ \rightarrow Na₃AlH₆/Al), while the second step $(Na_3AlH_6 \rightarrow NaH/Al)$ was left almost intact. These results clearly indicate that the active Ti-species that are involved in the reversible dehydrogenation of Na₃AlH₆ may not necessarily contribute to the kinetic enhancement of $NaAlH_4/Na_3AlH_6+Al$ reactions. The possible reasons for the aggravated " "selective" deactivation" of Ti-species upon increasing the milling time include the modification of structural/chemical environment of the doped hydride, the distribution state and even the nature of the active Ti-species. Here, a key clue is available from the direct formation of β -Na₃AlH₆ because the *in situ* hydrogenation during the milling process may produce a critical influence on the distribution of the active Ti-species. Further investigation in this respect is currently under way.

In conclusion, for the first time, direct formation of β -Na₃AlH₆ from NaH/Al was achieved by mechanical milling with TiF₃ under H₂ atmosphere. The as-formed Na₃AlH₆ exhibits a series of unexpected phase transformation and decomposition behaviors. In particular, it was found that varying the milling time led to a modified thermodynamics of the dehydriding reaction of Na₃AlH₆. Additionally, possibly related to the in situ hydrogenation, the mechanically prepared Ti-doped materials were observed to undergo a serious degradation on the hydrogen storage performance upon increasing the milling time. A comprehensive understanding of these phenomena may lead to the elucidation of the nature of active Ti-species and the means of improving the hydrogen storage property of Ti-doped NaAlH₄.

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