Rehydrogenation of Dehydrogenated NaAlH₄ at Low Temperature and Pressure

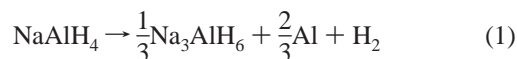**Dalin Sun,*,† Sesha S. Srinivasan,† Tetsu Kiyobayashi,‡ Nobuhiro Kuriyama,‡ and Craig M. Jensen†**

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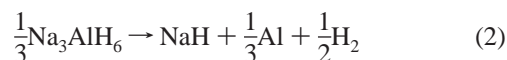
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NaAlH₄ is considered as a promising material for onboard storage of hydrogen. It is generally thought that high temperature (>120 °C) and high pressure (>15 MPa) are needed for rehydrogenation of dehydrogenated NaAlH₄. However, for practical application, reducing the rehydrogenation temperature and pressure as much as possible would be highly desirable. We have found that the dehydrogenated NaAlH₄, in either the undoped or titanium-doped state, can be rehydrogenated at temperatures of 25−120 °C and pressures of 2−12 MPa. This finding is confirmed by the subsequent dehydrogenation at 160 °C. In addition to that, after rehydrogenation under the same conditions, the amount of evolved hydrogen from the titanium-doped NaAlH₄ was much higher than that of the undoped NaAlH₄. This clearly indicates that the addition of titanium species enhances kinetically not only the dehydrogenation, but also the reverse process, the rehydrogenation reaction of the dehydrogenated NaAlH₄.

Introduction

The dehydrogenation or the decomposition of sodium aluminum hydride (NaAlH₄) consists of two consecutive steps that occur at about 220 °C and 250 °C, respectively,

$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \qquad (1)$$

and

$$\frac{1}{3}Na_3AlH_6 \rightarrow NaH + \frac{1}{3}Al + \frac{1}{2}H_2 \qquad (2)$$

Reaction 1 gives off about 3.7 wt % hydrogen and reaction 2, 1.9 wt %, with a total hydrogen release of 5.6 wt % for the overall reaction. In 1997, Bogdanovic et al.[1] discovered that the onset temperatures for reactions 1 and 2 were reduced to 100 °C and 140 °C, respectively, upon doping the hydride with a few mole percent of selected transition metal complexes. This has invoked intense attention and investigation in the area of hydrogen storage materials.[2−17] The superiority of NaAlH₄ over conventional metal hydrides (e.g., LaNi₅H₆, TiFeH₂, and Mg₂-NiH₄) is in its lightweight and high hydrogen storage capacity per unit weight, which makes it more promising for application in fuel cell vehicles.[18]

Effects of catalyst-doping on the dehydrogenation of NaAlH₄ have been studied extensively in recent years.[2−17,19] However, the rehydrogenation, i.e., the reverse of reactions 1 and 2, has not received as much attention. It is generally thought that severe conditions, such as high temperature and high pressure, are needed for the rehydrogenation. According to Ashby et al.,[20−22] the reverse reactions of (1) and (2) could only occur at 150 °C under a hydrogen pressure of 10−35 MPa in a solvent medium.

In the absence of a solvent medium, a temperature of 280 °C and a hydrogen pressure of 17−18 MPa are necessary.[23] Obviously, these conditions are too extreme to be realized for practical applications, therefore, a reduction of rehydrogenation temperature and pressure would be much preferable.

Recently, Bogdanovic et al.[24] reported that the small addition of the titanium species, Ti(OBu)₄, to mixtures of NaH and Al can reduce the rehydrogenation temperature to 120 °C. However, hydrogen pressure as high as 15 MPa was still required. In our effort toward studying the reaction mechanism, we accidentally found that the rehydrogenation of the dehydrogenated NaAlH₄ could be achieved even at temperatures as low as 25 °C. Further studies confirmed this finding, and reaction characteristics below 120 °C and 15 MPa were systematically studied. The results obtained on both pristine and titanium-doped NaAlH₄ are reported in this paper.

Experimental Section

Materials and Sample Preparation. Raw NaAlH₄ was obtained from Aldrich Chemical. Aluminum residual present in the raw NaAlH₄ was removed by filtration following dissolution of the hydride in a minimal amount of tetrahydrofuran (THF). Analytically pure NaAlH₄ was precipitated by addition of pentane to the THF solution. The hydride was then isolated by filtration, washed with several portions of pentane, and dried at 50 °C for 24 h under high vacuum. Two samples were used in the present study—one was undoped NaAlH₄, and the other was NaAlH₄ doped with 2 mole percent of titanium butoxide (Ti(OBu)₄, Aldrich Chemical), referred to as Ti-doped NaAlH₄ hereafter. The doping process was realized by ball-milling, which has been described in detail elsewhere.[19]

Dehydrogenation and Rehydrogenation. Both dehydrogenation and rehydrogenation were carried out volumetrically with a Sievert's-type apparatus (LESCA Co. Japan) that was carefully calibrated for hydrogen absorption and desorption measurements by using LaNi₅ alloy as a standard. This ensured the reliability in the measured data for NaAlH₄ in our experiments. The
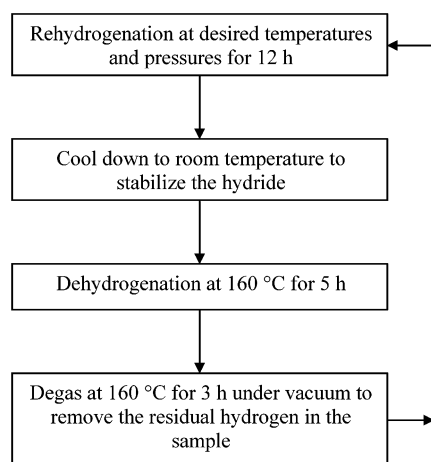
Figure 1. Procedure used for rehydrogenation and dehydrogenation after the first dehydrogenation.
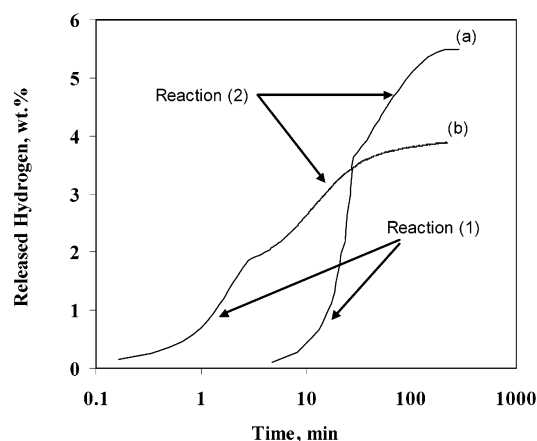

Figure 2. The dehydrogenation isotherms of (a) undoped NaAlH$_4$ at 250 °C, and (b) Ti-doped NaAlH$_4$ at 160 °C. Two distinct dehydrogenation steps corresponding to reactions 1 and 2, respectively, were shown.
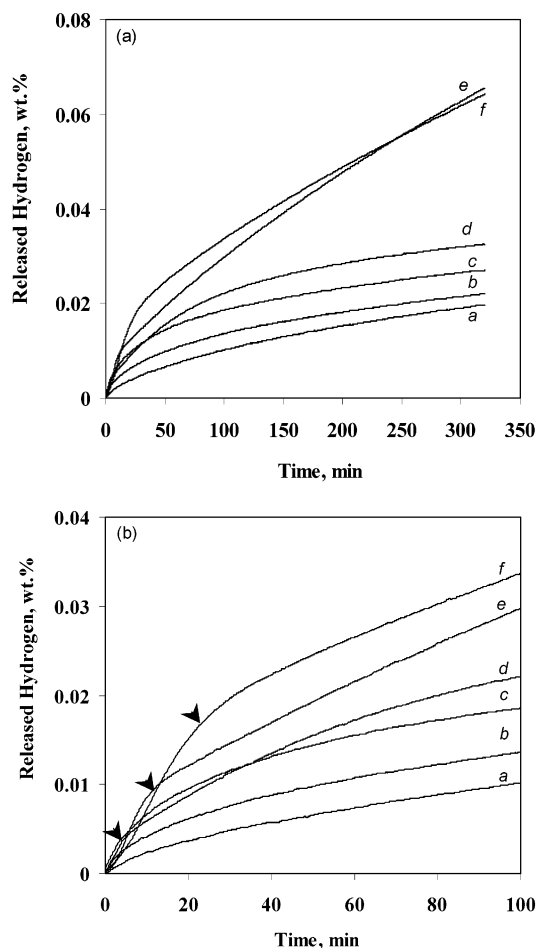

Figure 3. The dehydrogenation isotherms of (a) the undoped NaAlH$_4$ at 160 °C after rehydrogenated at various temperatures (25, 40, 50, 70, 100, and 120 °C, i.e., $a-f$) under pressure of 12 MPa for 12 h. (b) Redrawing of (a) using a shorter time scale. The arrows indicate the separation point between the two dehydrogenation steps.

samples of 0.5 g were loaded into stainless steel reactors in a nitrogen-filled glovebox (the oxygen content was 0.2 ppm, the dew point was −76 °C), and the reactors were then connected to the apparatus. After being degassed under vacuum at room temperature for 2 h, the samples were first fully dehydrogenated at 160 °C for the doped NaAlH$_4$ and 250 °C for the undoped NaAlH$_4$. The amount of evolved hydrogen as a function of time was measured by rapidly heating the samples up to the desired temperature. This was realized by immersing the sample reactor into an oil bath (with an accuracy of ±1 °C), which was preheated to a given temperature. After the first dehydrogenation, the samples were subjected to rehydrogenation and dehydrogenation in turn, by following the procedure as described in Figure 1. The temperature range for rehydrogenation was 25−120 °C, and the pressure range was 2−12 MPa. Hydrogen gas with a purity of 99.9999% was used. During these measurements, the samples were not removed from the reactors until they were completed.

Results and Discussion

Comparison of the First Dehydrogenation. The amount of evolved hydrogen as a function of time is shown in Figure 2, where two distinct steps can be identified. The first dehydrogenation step corresponds to the contribution of reaction 1, and the second step corresponds to reaction 2. In agreement with earlier reports,[1,5,7,9] an enhancement in the dehydro-

kinetics, resulting from the addition of titanium species, was observed. As compared to the undoped NaAlH$_4$, the hydrogen evolution from the Ti-doped sample was much faster, i.e., around 95% of the hydrogen was released from the Ti-doped NaAlH$_4$ in 40 min. The Ti-doped NaAlH$_4$ released 3.8 wt % hydrogen, about 1.7 wt % less than that of the undoped sample, which can be attributed to a partial release of hydrogen during the doping process. Note that the undoped NaAlH$_4$ released 5.5 wt % hydrogen, very close to the calculated value of 5.6 wt % from reactions 1 and 2. This confirms that the measurement system used in this study is reliable.

Rehydrogenation and Dehydrogenation. The dehydrogenated samples were subjected to rehydrogenation at 25−120 °C under a pressure of 12 MPa for 12 h. Unfortunately, the amount of hydrogen uptake with reaction time could not be calculated accurately due to scattering in the recorded pressure data under such a high-pressure range. Therefore, as an alternative, the extent of hydrogen uptake was inferred from the amount of hydrogen released in the subsequent dehydrogenation at 160 °C in 5 h.

Figure 3a shows the evolution of hydrogen as a function of time for the undoped NaAlH$_4$. As the rehydrogenation temperature increased from 25 °C to 120 °C, the maximum amount of released hydrogen increased from 0.02 wt % to 0.07 wt %. Although these values are very low, they do indicate that the reverse reactions of (1) and/or (2) occur at 25−120 °C. This conclusion becomes more evident when Figure 3a is redrawn
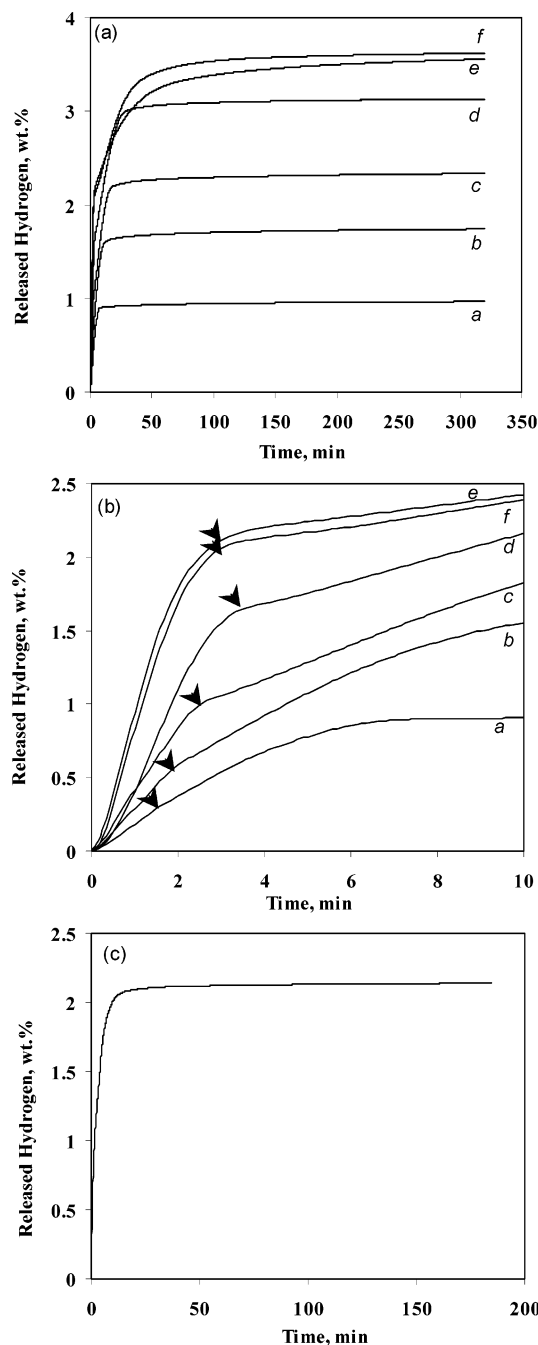
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Figure 4. The dehydrogenation isotherms of (a) the Ti-doped NaAlH$_4$ at 160 °C after rehydrogenated at various temperatures (25, 40, 50, 70, 100, and 120 °C, i.e., $a-f$) under pressure of 12 MPa for 12 h. (b) Redrawing of (a) using a shorter time scale. The arrows indicate the separation point between the two dehydrogenation steps. (c) The dehydrogenation curve at 160 °C after rehydrogenation at 25 °C under a pressure of 12 MPa for 100 h.
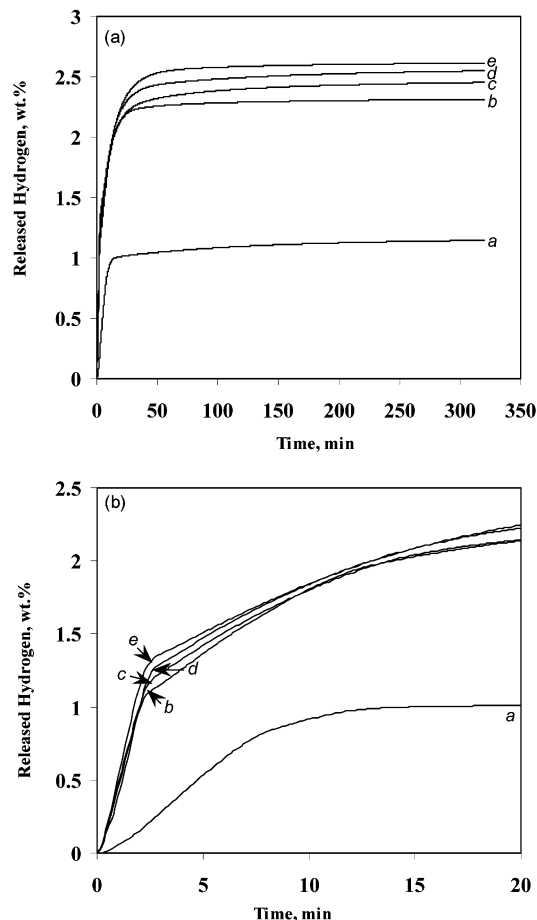
Figure 5. The dehydrogenation isotherms of (a) the Ti-doped NaAlH$_4$ at 160 °C after rehydrogenated at 70 °C under various pressures (2, 4, 6, 8, and 10 MPa, i.e., $a-e$) for 12 h. (b) Redrawing of (a) using a shorter time scale. The arrows indicate the separation point between the two dehydrogenation steps.

at a shorter time scale in Figure 3b. As shown in Figure 3, two dehydrogenation steps were also observed after rehydrogenation at 70, 100, and 120 °C. The separation points between the two steps were indicated by arrows in the figure. When the rehydrogenation temperature was lower than 70 °C, only one step was observed, which means that at 25, 40, and 50 °C, the reverse reaction of (2) occurs, whereas the reverse reaction of (1) does not. This was further confirmed by infrared spectroscopic analysis on these rehydrogenated samples, showing that the absorption band, corresponding to Na$_3$AlH$_6$, existed in the range of 1320−1340 cm^{-1} but the typical absorption band at ∼1650 cm^{-1} from NaAlH$_4$ was not observed. In the case of

the Ti-doped sample, two dehydrogenation steps can be seen after rehydrogenation at all of the temperatures observed (see Figure 4a,b). Moreover, the hydrogen released was about 1.0−3.6 wt %, 50 times as much as that of the undoped NaAlH$_4$. It should be stated here that an additional experiment showed that at 25 °C when the rehydrogenation time was prolonged from 12 to 100 h, the amount of released hydrogen increased up to 2 wt % (see Figure 4 c). Figure 5 represents the dehydrogenation kinetic curves of the Ti-doped NaAlH$_4$ after rehydrogenation at 70 °C under various hydrogen pressures. It can be seen that, as the rehydrogenation pressure decreased from 10 to 2 MPa, the amount of evolved hydrogen gradually decreased, but remained in the range of 4−10 MPa. The total amount of released hydrogen was around 2−2.5 wt %. When the pressure was reduced to 2 MPa, the released hydrogen was dramatically decreased to 1 wt %.

On the basis of the results obtained above on the pristine and the Ti-doped NaAlH$_4$, it is concluded that titanium doping enhances both the dehydrogenation and rehydrogenation of NaAlH$_4$. The nature of the catalytic effect of titanium species on the rehydrogenation is presently unclear. One of the most likely mechanisms is that the formation of [AlH$_6$]$^{3-}$ and [AlH$_4$]$^-$ is facilitated by the presence of titanium species.

Conclusions

In summary, we have demonstrated for the first time that the reverse of reactions (1) and/or (2) occur at temperatures of 25−

120 °C and pressures of 2−12 MPa for the dehydrogenated NaAlH4 both in the undoped and in the Ti-doped forms. This finding is confirmed by the observation of two distinct dehydrogenation steps after rehydrogenation. Under the same rehydrogenation conditions, the amount of evolved hydrogen from the Ti-doped NaAlH4 is about 50 times as much as that of the undoped NaAlH4. According to the present study, rehydrogenation may be possible at moderate conditions by optimizing the doping materials, temperature, and hydrogen pressure. Another important conclusion drawn from this study is that the addition of titanium species enhances kinetically not only the dehydrogenation process, but also the reverse rehydrogenation reactions of (1) and (2). Further investigations are needed to establish the underlying mechanism of why titanium species enhance the rehydrogenation.

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