Enhanced hydrogen storage properties of NaAlH4 co-catalysed with niobium fluoride and single-walled carbon nanotubes

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Keywords
niobium, fluoride, single, walled, carbon, nanotubes, properties, catalysed, co, naalh4, enhanced, hydrogen, storage

Disciplines
Engineering | Physical Sciences and Mathematics

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/339
Enhanced hydrogen storage properties of NaAlH₄ co-catalysed with niobium fluoride and single-walled carbon nanotubes†

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Received 29th August 2011, Accepted 16th November 2011
DOI: 10.1039/c1ra00645b

The effects of single-walled carbon nanotubes (SWCNTs) as a co-catalyst with NbF₅ on the dehydrogenation and hydrogenation kinetics of NaAlH₄ were investigated by X-ray diffraction, Fourier transform infrared spectroscopy, differential thermal analysis, temperature-programmed desorption, and isothermal hydrogen ab/desorption techniques. It has been revealed that there is a synergistic effect of SWCNTs and NbF₅ on the de/rehydrogenation of NaAlH₄, which improves the hydrogen de/absorption performance when compared to adding either SWCNTs or NbF₅ alone. For example, the apparent activation energy for the first-step and the second-step dehydrogenation of the co-doped NaAlH₄ sample is estimated to be 85.9 and 96.2 kJ mol⁻¹, respectively, using Kissinger's approach, which is lower than the pristine, SWCNT-, and NbF₅ doped NaAlH₄, respectively, indicating a reduced kinetic barrier. These results are attributed to the active Nb-containing species and the function of F anions, as well as the nanosized pores and high specific surface area of the SWCNTs, which facilitates the dissociation and recombination of hydrogen molecules on its surface and the atomic hydrogen diffusion along the grain boundaries and inside the grains, and decreases the segregation of bulk Al after the desorption. Hence, the combined catalytic mechanism is presented.

Introduction

Clean energy sources such as wind, solar, and hydropower are needed to meet the challenges of global warming and to address the finite nature of fossil fuel based energy resources. However, for the environmentally friendly use of the energy produced by these sources in final applications, a clean, efficient, and safe energy carrier is necessary. Since the development of the proton exchange membrane (PEM) fuel cell, which is fuelled by hydrogen and oxygen, and produces only water, hydrogen has been seen to be the most promising solution.1 However, the use of hydrogen for fuel-cell powered mobile applications requires materials that not only store hydrogen at high density, but that can operate reversibly at ambient pressure and temperatures below approximately 100 °C.2

Among the many materials studied for hydrogen storage, complex hydrides of light metals containing borohydride,3 amide,4 and alanate5,6 anions have high hydrogen capacity and, thus, have been studied extensively. However, the thermodynamic and kinetic properties of the borohydrides limit their ability to cycle hydrogen at low temperatures. On the other hand, the elimination of ammonia gas in using amides for hydrogen storage is the most important issue, because a very small amount of ammonia (ppm level) poisons the catalysts of proton exchange membrane (PEM) fuel cells. In this regard, sodium alanate has offered good prospects due to the high purity of its released hydrogen, its high reversible hydrogen storage capacity, and its optimal thermodynamic stability for reversible hydrogen storage at moderate temperatures, since Bogdanovic and Schwickerdi demonstrated that transition-metal dopants can considerably lower the kinetic barriers for both hydrogenation and dehydrogenation of NaAlH₄.6 It is well known that NaAlH₄ decomposes to release hydrogen in three steps according to the following reactions:

\[
\text{NaAlH}_4 \leftrightarrow 1/3\text{Na}_3\text{AlH}_6 + 2/3\text{Al} + 3/2\text{H}_2 \quad 3.7 \text{ wt\% H}_2 \quad (1)
\]

\[
\text{Na}_3\text{AlH}_6 \leftrightarrow 3\text{NaH} + \text{Al} + 3/2\text{H}_2 \quad 1.9 \text{ wt\% H}_2 \quad (2)
\]

\[
\text{NaH} \leftrightarrow \text{Na} + 1/2\text{H}_2 \quad 1.9 \text{ wt\% H}_2 \quad (3)
\]

In principle, gives 3.7 wt% hydrogen and the second one 1.9 wt% upon heating. The last reaction, eqn (3), however, occurs at over 300 °C, releasing another 1.9 wt% of hydrogen. This temperature is high, and hence, the desorption of NaH is not considered a useful capacity for practical purposes. By doping with a few mol% of selected catalyst, NaAlH₄ can reversibly release and take up hydrogen, as described above for the first two-step reaction. During the past decade, various catalysts, such as carbon,7 transition metal,8 and rare earth metal9 based materials have been found to be active in
significantly enhancing the reaction kinetics of NaAlH₄. However, further improvements in the dehydrating and hydriding kinetics of NaAlH₄ are highly desirable. In addition, an understanding of the hydrogen desorption/absorption of NaAlH₄ doped with a metal based catalyst is still unclear. For example, several Ti-containing species including Ti–Al alloy, Ti hydrides, and Ti cations in the NaAlH₄ lattice are proposed as the active species in Ti doped NaAlH₄, but none of them has been conclusively confirmed.⁸

More recently, it was demonstrated that the catalytic effects of transition metals such as Ti and Zr combined with porous materials such as carbon nanotubes (CNTs) and porous SiO₂ as mixed dopants lead to significant acceleration of hydrogen dissociation and diffusion, approaching the goal of rapid hydrogenation kinetics at practically meaningful low temperatures.¹⁰ For example, Wang et al.¹⁰ found that all five carbons SWCNTs, multiwalled CNTs (MWCNTs), activated carbon (AC), fullerenes (C₆₀), and graphite G) exhibited significant, sustaining, and synergistic co-catalytic effects on the dehydrogenation and hydrogenation kinetics of Ti-doped NaAlH₄ that persisted through charge and discharge cycling, in which SWCNTs were the best co-catalyst. This indicates that the synergistic interaction among metals and carbon nanotubes may be an effective strategy to significantly lower the operating temperature and to increase hydrogenation kinetics. Despite this progress, the dehydrogenation and hydrogenation kinetics still fall short of the requirements for practical applications. It is therefore desirable to further explore and develop the synergistic effects of CNTs with other metallic catalysts in order to achieve faster kinetics.

In our previous work, we demonstrated that the hydrogen desorption/absorption of NaAlH₄ can be significantly improved by introducing NbF₅ through the in situ formation of active Nb-containing catalysts and the function of F⁻ anions.¹¹ In this paper, we investigate the effects of single walled carbon nanotubes (SWCNTs) as a co-dopant on the hydrogen desorption/absorption of NbF₅-doped NaAlH₄. By comparing the hydrogen release/uptake kinetics with those of pristine NaAlH₄, SWCNT-doped NaAlH₄, and NbF₅-doped NaAlH₄, which possesses state-of-art kinetics among the various forms of doped NaAlH₄, we will show how SWCNTs can improve the hydrogen release/uptake kinetics of NbF₅-doped NaAlH₄ by a series of dehydrogenation/rehydrogenation measurements. Moreover, in order to acquire detailed information about the kinetics of the reactions, the non-isothermal Kissinger method has been used to evaluate the activation energy. At the end of the article, on the basis of these findings and the previous investigations, the active species and the catalysis are discussed.

**Experimental procedures**

The chemicals NaAlH₄ (hydrogen-storage grade, ≥93% purity), NbF₅ (98%), and single walled carbon nanotubes (SWCNTs) were all purchased from Sigma-Aldrich and used directly without pretreatment. All sample storage and handling were performed in an Ar filled glove box (MBraun Unilab). A QM3SP2 planetary ball mill was employed to prepare the pristine NaAlH₄, NaAlH₄-3 mol% NbF₅, NaAlH₄-5 wt% SWCNT and NaAlH₄-3 mol% NbF₅-5 wt% SWCNT samples, under an argon atmosphere at 450 rpm. Each time, about 1 g of a sample was prepared with 2 h of ball milling, with a ball-to-powder ratio of around 30 : 1.

The hydrogen desorption/absorption properties were measured in a Sieverts apparatus (Advanced Materials Corporation, USA), where the temperatures and pressures of the sample and the gas reservoirs were monitored and recorded by Grsc;LV-LabVIEW-based control program software during the sorption process. Temperature programmed desorption (TPD) curves were determined by volumetric methods starting from vacuum. The temperature was increased from ambient to ~300 °C at 2 °C min⁻¹. The hydrogen desorption kinetic measurements were performed at the desired temperature starting from vacuum. The hydrogen absorption measurements were performed at 150 or 160 °C and 55 or 65 bar hydrogen pressure. The sample was thoroughly dehydrogenated at 300 °C under dynamic vacuum before the rehydrogenation measurement. Other than specified, the H-capacity was calculated using the total weight of the samples to allow for an evaluation of the practical hydrogen storage properties.

Differential scanning calorimetry (DSC) analysis of the dehydrogenation process was carried out on a Mettler ToledoTGA/DSC 1. About 2–6 mg of the sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the DSC apparatus. An empty alumina crucible was used as the reference material. The samples were heated from room temperature to 300 °C under 1 atm flowing argon atmosphere, and the heating rate was 2 °C min⁻¹.

The phase structures of various samples at different stages were identified by a GBC X-ray diffractometer with Cu-Kα radiation at 40 kV and 25 mA. In order to avoid oxidation during the X-ray diffraction (XRD) measurement, samples were mounted on a glass slide 1 mm in thickness in the Ar-filled glove box and sealed with an airtight hood composed of amorphous tape. To obtain the information of Al–H bond, the obtained samples were ground with KBr and pressed into a sample cup, and the vibration spectra of the species were then identified using a Shimadzu Prestige 21 Fourier transform infrared spectrometer (FTIR) in absorbance mode.

**Results and discussion**

**Hydrogen desorption**

Fig. 1 reveals the effects of NbF₅ and the SWCNTs, when used separately as single catalysts or together as co-catalysts, on the dehydrogenation of NaAlH₄ by means of TPD curves. It was observed that the pristine NaAlH₄ starts to release a small amount of hydrogen at around 183 °C, which is probably due to the melting of NaAlH₄. Most of the hydrogen was released starting at 210 °C, and release was completed at 283 °C. The total amount of hydrogen evolved is about 5.5 wt%, which is very close to the theoretical value from eqn.(1) and (2), but these two steps of dehydrogenation were not distinct. In contrast, a significant catalytic effect was observed in the curves for the NbF₅-doped, SWCNT-doped, and NbF₅ and SWCNT co-doped samples, which exhibited two distinct dehydrogenation steps at much lower dehydrogenation temperatures. For the NbF₅-doped...
NaAlH₄ sample, the first-step dehydrogenation could be finished at around 178 °C. Further heating led to a second decomposition, which was completed at 225 °C. For the SWCNT-doped NaAlH₄ sample, the first and second dehydrogenation steps could be finished at 181 and 223 °C, respectively. Clearly, the dehydrogenation temperature of the NaAlH₄ is reduced by addition of either NbF₅ or SWCNTs, suggesting that a catalytic effect occurred. Furthermore, the NbF₅ and SWCNT co-doped NaAlH₄ sample can complete its first and second-step dehydrogenation at 159 and 201 °C, respectively, which is lower than for the NbF₅ or the SWCNT doped samples. These results further confirmed the synergistic effect of NbF₅ and SWCNTs towards the decomposition of NaAlH₄.

A comparative evaluation of the isothermal dehydrogenation kinetics of NaAlH₄ with single catalysts (NbF₅, SWCNTs) and co-catalysts (NbF₅ and SWCNTs together) at 155 °C was performed, as shown in Fig. 3. For the pristine NaAlH₄, no appreciable hydrogen desorption is detected within 120 min at 155 °C (results not shown here). However, the NbF₅-doped sample releases around 2.5 wt% hydrogen within 50 min. The hydrogen evolved from the SWCNT-doped NaAlH₄ sample is 2.4 wt% in 50 min, which is a little lower than for the NbF₅-doped sample. The results indicate that the hydrogen released from the SWCNT- and NbF₅-doped samples at 155 °C is attributable to the first-step dehydrogenation of NaAlH₄ according to eqn. (1). However, the dehydrogenation curves for the co-doped sample showed a two-step decomposition feature, corresponding to the first reaction stage (1) and the second reaction stage (2) of NaAlH₄, respectively. The co-doped sample releases about 2.5 wt% hydrogen in 6 min and another decomposition of the NaAlH₄, the decomposition of molten NaAlH₄ to NaAlH₆ (195–252 °C), a phase transition of α–Na₃AlH₆ to β–Na₃AlH₆ (~264 °C) and the decomposition of Na₃AlH₆ into NaH and Al (171–286 °C). However, only two endothermic peaks are seen in the dehydrogenation of the doped NaAlH₄ samples. In the case of the NbF₅-doped sample, the first peak at about 178 °C is attributed to the dehydrogenation of NaAlH₄, and the second peak at 215 °C corresponds to the dehydrogenation of Na₃AlH₆. For the SWCNT-doped sample, the first and second peaks were observed at 179 and 219 °C, corresponding to the decomposition of NaAlH₄ and Na₃AlH₆, respectively. As a whole, the DSC curves for the co-doped NaAlH₄ sample were similar to those of the NbF₅ or SWCNT doped samples, displaying only two endothermic peaks, corresponding to eqn. (1) and (2), respectively, but both endothermic peaks had moved to lower temperatures. The first peak at about 169 °C is attributed to the dehydrogenation of NaAlH₄, and the second peak at 209 °C corresponds to the dehydrogenation of Na₃AlH₆. A phase transition of Na₃AlH₆ is also observed at 264 °C. These results further confirmed the synergistic effect of NbF₅ and SWCNTs towards the decomposition of NaAlH₄.

The aforementioned TPD results are confirmed by the DSC curves shown in Fig. 2. Clearly, the plot for the pristine NaAlH₄ shows four distinct endothermic processes, which can be assigned to the melting of NaAlH₄ (~185 °C), along with slight decomposition of the NaAlH₄, the decomposition of molten NaAlH₄ to NaAlH₆ (195–252 °C), a phase transition of α–Na₃AlH₆ to β–Na₃AlH₆ (~264 °C) and the decomposition of Na₃AlH₆ into NaH and Al (171–286 °C). However, only two endothermic peaks are seen in the dehydrogenation of the doped NaAlH₄ samples. In the case of the NbF₅-doped sample, the first peak at about 178 °C is attributed to the dehydrogenation of NaAlH₄, and the second peak at 215 °C corresponds to the dehydrogenation of Na₃AlH₆. For the SWCNT-doped sample, the first and second peaks were observed at 179 and 219 °C, corresponding to the decomposition of NaAlH₄ and Na₃AlH₆, respectively. As a whole, the DSC curves for the co-doped NaAlH₄ sample were similar to those of the NbF₅ or SWCNT doped samples, displaying only two endothermic peaks, corresponding to eqn. (1) and (2), respectively, but both endothermic peaks had moved to lower temperatures. The first peak at about 169 °C is attributed to the dehydrogenation of NaAlH₄, and the second peak at 209 °C corresponds to the dehydrogenation of Na₃AlH₆, which is lower than for either the NbF₅ or the SWCNT doped samples. These results further confirmed the synergistic effect of NbF₅ and SWCNTs towards the decomposition of NaAlH₄.

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1.45 wt% in the following 120 min, almost all of the hydrogen in the post-milled sample. This phenomenon further indicates that a synergistic catalysis from the combination of NbF$_5$ and SWCNTs exists for NaAlH$_4$.

**Hydrogen absorption**

Fig. 4 presents a systematic comparison of the absorption behaviour between the NaAlH$_4$ samples with NbF$_5$ or SWCNTs as the sole additive and with NbF$_5$ and SWCNTs as co-additives. It was observed that the simultaneous addition of NbF$_5$ and SWCNTs further improves the absorption rate of NaAlH$_4$. At 150 °C and 55 bar in Fig. 4(a), the saturated hydrogenation process for the co-doped sample can be limited to within 20 min, which is lower than for the SWCNT doped sample (48 min) and much lower than for the NbF$_5$ doped sample (96 min). On increasing the hydrogenation temperature and pressure up to 160 °C and 6.5 MPa (see Fig. 4(b)), the rehydrogenation capacity remains unchanged for the three samples, but the absorption rate is increased, leading to saturated rehydrogenation times of 7, 14, and 49 min, respectively, for the co-doped, SWCNT doped, and NbF$_5$ doped samples. These results clearly show that the co-doped NaAlH$_4$ has better rehydrogenation kinetics than the samples doped with a single catalyst.

It is worth noting that the rehydrogenation capacity for the SWCNT-doped, NbF$_5$-doped, and SWCNT–NbF$_5$ co-doped samples is 1.78, 1.73, and 1.66 wt%, respectively. These values are similar to those found in the second-step dehydrogenation processes in these three samples, suggesting that the hydrogen released from the rehydrogenated sample is from the separate contributions of the reformed Na$_2$AlH$_6$. To confirm this, these rehydrogenation products for the three samples were examined by means of TPD, and the TPD curves are compared in Fig. 5. Fig. 5 presents the TPD curves for the first hydrogenation cycle of the three samples. All the curves show one hydrogen release step, starting at over 150 °C and completed before 240 °C, with a hydrogen capacity of between 1.5–1.7 wt%. All in all, these results indicate the recombination of Na$_2$AlH$_6$ in all three samples. The absence of NaAlH$_4$ in the rehydrogenated state is possibly due to the quite high equilibrium hydrogen pressure required for the transformation from Na$_2$AlH$_6$ to NaAlH$_4$ in the hydrogenation process by eqn. (1).12 Meanwhile, the dehydrogenation temperature for the rehydrogenated SWCNT doped sample is similar to that of the rehydrogenated NbF$_5$ doped sample. However, the co-doped sample has the lowest dehydrogenation temperature compared to the SWCNT and NbF$_5$ doped samples, further confirming the synergistic effect of NbF$_5$ and SWCNTs.

**Structure analysis**

An intriguing aspect of the co-doped NaAlH$_4$ sample after cycling through synthesis, dehydrogenation, and rehydrogenation is illustrated by the XRD patterns shown in Fig. 6. After ball milling, only peaks due to the NaAlH$_4$ and a small amount of Al are observed. The crystalline Al is most likely formed by the decomposition of a minor part of the NaAlH$_4$ during the ball milling, due to the effects of the NbF$_5$ and SWCNTs. Upon desorption of the hydrogen from the as-milled sample, the NaAlH$_4$ phase has disappeared, and more the crystalline Al and...
NaH are observed, indicating the complete decomposition of NaAlH$_4$ according to eqn. (1) and eqn. (2). After rehydrogenation, the peak due to the crystalline Al decreases in height, and the new phase Na$_3$AlH$_6$ is formed. Nevertheless, no crystalline NaAlH$_4$ is formed, which is possibly due to the quite high equilibrium hydrogen pressure required for the transformation of Na$_3$AlH$_6$ to NaAlH$_4$ in the hydrogenation process by eqn. (1).

In order to detect the existing state of C, Nb, and F in the NbF$_5$ and SWCNT co-doped NaAlH$_4$ sample, two samples of NaAlH$_4$-30 wt% NbF$_5$-15 wt% SWCNT and NaAlH$_4$-60 wt% NbF$_5$-30 wt% SWCNT were further prepared by increasing the amount of NbF$_5$ and SWCNT. Then, the XRD patterns of the as-milled samples were analysed, as shown in Fig. 7. Clearly, only NaAlH$_4$ and Al phases were observed in the case of NaAlH$_4$-30 wt% NbF$_5$-15 wt% SWCNT. However, for the NaAlH$_4$-60 wt% NbF$_5$-30 wt% SWCNT samples, the NaAlH$_4$ phase disappeared. Meanwhile, in addition to Al, the new phases of Al$_3$Nb, NbH$_x$, and NaF were identified although their diffraction peaks are weak and distorted (Fig. 7 and Fig. S1, ESI†). Since NaAlH$_4$ was stable when it was ball milled alone,\cite{11} the consumption of NaAlH$_4$ and the formation of Al$_3$Nb, NbH$_x$, and NaF in the case of NaAlH$_4$-60 wt% NbF$_5$-30 wt% SWCNT were very likely due to a chemical reaction between NaAlH$_4$ and NbF$_5$. The result agrees well with our previous report that Al$_3$Nb, NbH$_x$, and NaF were also detected in the NbF$_5$ doped NaAlH$_4$ sample after ball milling.\cite{11} Therefore, it can be deduced that similar to the case of NbF$_5$ doped NaAlH$_4$, the NbF$_5$ still prefer to react with NaAlH$_4$ during ball milling to generate the active Nb and F containing species in the case of NbF$_5$ and SWCNT co-doped sample.

Activation energy

To further study the effect of the co-catalyst on the kinetic barrier, the apparent activation energy (E$_a$) relating to the first and the second-step dehydrogenation of NaAlH$_4$ was estimated using the non-isothermal Kissinger method according to the following equation.\cite{13}

\[
\ln \left( \frac{b}{T_m^2} \right) = - \frac{E_a}{RT}
\]  

Fig. 7 XRD patterns of the (a) NaAlH$_4$-30 wt% NbF$_5$-15 wt% SWCNT and (b) NaAlH$_4$-60 wt% NbF$_5$-30 wt% SWCNT samples after ball milling.

Fig. 8 FTIR spectra of NaAlH$_4$, NaAlH$_4$-3 mol% NbF$_5$, NaAlH$_4$-5 wt% SWCNT, and NaAlH$_4$-3 mol% NbF$_5$-5 wt% SWCNT samples after ball milling.
Figure 9 Kissinger plots for the first and second dehydrogenation steps for the NaAlH4–3 mol% NbF5, NaAlH4–5 wt% SWCNT, and NaAlH4–3 mol% NbF5–5 wt% SWCNT samples.

Where \( E_a \) is the activation energy, \( \beta \) is the heating rate in \( ^\circ\text{C min}^{-1} \), \( T_m \) is the absolute temperature for the maximum desorption rate, and \( R \) is the gas constant. In this work, \( T_m \) was obtained using TPD measurement with the selected heating rates of 0.5, 1, 2 and 5 \( ^\circ\text{C min}^{-1} \). The detailed TPD curves are shown in Figures S2–S4 of the ESI.† Plotting \( \ln(\beta/T_m^2) \) versus \( 1/T_m \) yields a straight line with the slope of \(-E_a/R\). Fig. 9 shows the Kissinger plots for the first-step and second-step dehydrogenation of the co-doped NaAlH4 sample, together with NbF5– and SWCNT-doped samples for comparison. The intrinsic linearity of all of the curves indicates that the dehydrogenation kinetics of doped NaAlH4 is well represented by the non-isothermal Kissinger equation and that they follow a first order decomposition reaction.

The derived values of the activation energies, \( E_{a1} \), for the first step [i.e., eqn. (1)] and \( E_{a2} \) for the second step [i.e., eqn. (2)], are listed in Table 1. For comparison, \( E_{a1} \) and \( E_{a2} \) of pristine NaAlH4 are also included in Table 1.† Comparison of the activation energies for dehydrogenation reveals several phenomena as follows: (1) All of the present additives significantly enhance the dehydrogenation kinetics of NaAlH4 and Na3AlH6 (reducing \( E_{a1} \) and \( E_{a2} \)). (2) SWCNTs enhance the kinetics of NaAlH4, reducing \( E_{a1} \) from 118.1 to 95.8 kJ mol\(^{-1}\), and \( E_{a2} \) from 120.7 to 105.8 kJ mol\(^{-1}\), showing that the addition of SWCNTs reduces energy barriers for both eqn.(1) and eqn. (2). (3) Compared to the SWCNT-doped sample, the NbF5 doped sample has a lower \( E_{a1} \) (91.7 kJ mol\(^{-1}\)) and \( E_{a2} \) (103.1 kJ mol\(^{-1}\)), indicating that NbF5 is more effective for the decomposition of NaAlH4. It should be noted that the activation energies for the decomposition of NbF5 doped NaAlH4 are slightly different to that of our previous report, which is probably due to the fact that the \( T_m \) was obtained using TPD measurement in this paper but using DSC measurement in the previous report.† (3) The combination of SWCNTs and NbF5 was more efficient than those of SWCNTs or NbF5 alone, lowering the \( E_{a1} \) and \( E_{a2} \) to 85.9 and 96.2 kJ mol\(^{-1}\), respectively. This phenomenon indicates that a synergistic catalytic effect between the NbF5 and SWCNTs exists for NaAlH4.

Table 1 Apparent Activation Energies (\( E_a \)) for the first-step and second-step dehydrogenation of NaAlH4, respectively

<table>
<thead>
<tr>
<th>Samples</th>
<th>( E_{a1} ) (kJ mol(^{-1}))</th>
<th>( E_{a2} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlH4</td>
<td>118.1</td>
<td>120.7</td>
</tr>
<tr>
<td>NaAlH4–NbF5</td>
<td>91.7</td>
<td>103.1</td>
</tr>
<tr>
<td>NaAlH4–C</td>
<td>95.8</td>
<td>105.8</td>
</tr>
<tr>
<td>NaAlH4–C–NbF5</td>
<td>85.9</td>
<td>96.2</td>
</tr>
</tbody>
</table>

**Discussion**

On the basis of the above results, it is evident that the dehydrogenation and rehydrogenation kinetics of NaAlH4 were enhanced by introducing NbF5 or SWCNTs. As discussed in our previous paper,† a much higher dispersion of Nb–Al and Nb–H active species may form on the hydride surface or grain boundaries during ball milling or after the heating process in the NbF5–doped NaAlH4, which may facilitate the dissociation/recombination of molecular hydrogen and mass transport. Meanwhile, the introduction of F-anions may also play a role, which has also been theoretically and experimentally demonstrated in the study of NaAlH4. Therefore, it was believed that both Nb and F containing species play critical roles in the dehydrogenation/hydrogenation process of the NaAlH4 sample with added NbF5. The reasons for the improvement in the dehydrogenation of NaAlH4 doping with SWCNTs can be understood from the following three aspects: (1) SWCNTs exhibit a prominent “catalytic” effect in NaAlH4. Based on the experimental observations and theoretical calculations, Berseth et al. provided a general understanding of the catalytic mechanism by the carbon catalysts that interaction of NaAlH4 with an electronegative substance such as carbon nanotube affects the charge donation from Na to AlH4, consequently weakening the Al–H bond and decreasing the dehydrogenation temperatures as well as facilitating the rehydrogenation reaction.† Actually, the weakening of Al–H bond in the NaAlH4 lattice was confirmed by FTIR in the case of NaAlH4–5 wt% SWCNTs, compared with pristine NaAlH4 sample (Fig. 8). (2) Because of the nanosize and strength, the SWCNTs can penetrate in NaAlH4 matrix either nearly vertically or in an inclined orientation. Therefore, the presence of SWCNTs may facilitate the atomic hydrogen diffusion both inside the phase grains and along the grain boundaries. (3) The presence of SWCNTs may also modify the grain interfaces of dehydrogenated phases due to its high specific surface area, especially by inhibiting the aggregation of Al particles. All these are responsible for the decrease in both the onset dehydrogenation temperature and the activation energy in the SWCNT-doped NaAlH4.

It was also shown that co-doping with NbF5 and SWCNTs exhibits superior de/rehydrogenation properties to that doping with single NbF5 or SWCNTs, indicating a favorable synergistic effect. It is already well known that combined utilization of catalytically active metal nanoparticles and nanostructured carbon materials is effective for improving the dehydridding/rehydridding properties of metal hydrides, and this strategy has been intensely developed over the past several decades,\(^{10,16}\) where the carbon nanotubes are expected to form a net-like structure after being milled together with host metal hydrides.
thus creating a microconfined environment for the decomposition/restoration of hydrides, while the metal nanoparticles have high catalytic activity. In our case, we also believe that both NbF₅ and SWCNTs play important roles in the dehydrogenation/hydrogenation process of the co-doped NaAlH₄. Similar to the NbF₅ doped NaAlH₄, the active species of NbHₓ, AlₓN_b, and NaF were also found in the co-doped sample (Fig. 7). The results indicate that NbF₅ prefers to react with NaAlH₄ during ball milling to generate the active Nb and F containing species in the NbF₅ and SWCNT co-doped sample. The role of SWCNTs in the co-doped sample could be more “physical” than “chemical” compared with the catalytic role of NbF₅ in that it modifies the grain surface of the dehydrogenated phases probably due to the inhibition of grain aggregation. As a consequence, a favourable synergistic effect on the dehydrogenation and rehydrogenation of NaAlH₄ is achieved in the co-doped NaAlH₄ sample through the formation of Nb- and F-containing species, and the presence of SWCNTs. All these complex factors resulted in the improvement of the hydrogen storage performances of NaAlH₄.

Conclusions

The effects of SWCNTs as a co-catalyst with NbF₅ on the dehydrogenation and hydrogenation kinetics of NaAlH₄ are presented in the present study. Either the SWCNTs or the NbF₅ alone can improve the hydrogen de/absorption properties of NaAlH₄. Moreover, a synergistic effect on the dehydrogenation of NaAlH₄ occurs when SWCNTs are added as a co-dopant with NbF₅. For example, the synergistic effect results in the apparent activation energy for the first-step and the second-step dehydrogenation of NaAlH₄ being reduced to 85.9 kJ mol⁻¹ and 96.2 kJ mol⁻¹, respectively. These positive effects can be ascribed to the in situ formation of Nb- and F-containing species in the NbF₅, as well as the presence of nanosized pores and the high specific surface area of the SWCNTs.

Acknowledgements

We would like to acknowledge support from the University of Wollongong, as well as critical reading by Dr Tania Silver.

References

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