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## Mechanisms of partial hydrogen sorption reversibility in a 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite

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A new hydrogen storage composite containing NaBH<sub>4</sub> and a 3d transition metal fluoride, 3NaBH<sub>4</sub>/ScF<sub>3</sub>, was synthesized *via* ball milling. The composite shows no reaction during milling and its dehydrogenating process can be divided into three steps upon heating: (i) partial substitution of H<sup>-</sup> by F<sup>-</sup> in NaBH<sub>4</sub> to form NaBH<sub>x</sub>F<sub>4-x</sub> at the early stage, releasing about 0.19 wt% of hydrogen; (ii) formations of Na<sub>3</sub>ScF<sub>6</sub>, NaBF<sub>4</sub> and ScB<sub>2</sub> through the reaction between NaBH<sub>4</sub> and ScF<sub>3</sub>, with 2.52 wt% of hydrogen release and a dehydrogenating activation energy of 162.67 kJ mol<sup>-1</sup> H<sub>2</sub>; (iii) further reaction of residual NaBH<sub>4</sub> and Na<sub>3</sub>ScF<sub>6</sub> to form NaF, B and ScB<sub>2</sub>, with a dehydrogenating activation energy of 169.37 kJ mol<sup>-1</sup> H<sub>2</sub>. The total hydrogen release of the composite reaches 5.54 wt% at 530 °C. The complete dehydrogenated composite cannot be rehydrogenated while the products after the second dehydrogenating step can be hydrogenated with an absorption activation energy of 44.58 kJ mol<sup>-1</sup> H<sub>2</sub>. These results demonstrate that by adding 3d transition metal fluorides into NaBH<sub>4</sub>, a partial reversibility in NaBH<sub>4</sub> can be achieved.

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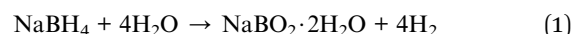
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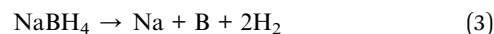
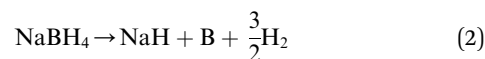
### 1 Introduction

Hydrogen is one of the most promising alternative and attractive clean energy sources that can substitute fossil fuels, with sufficient energy density and environment-friendliness.<sup>1,2</sup> Nevertheless, almost a century since the concept of “hydrogen economy” was introduced by Jules Verne,<sup>3,4</sup> it is still challenging to find reliable, flexible and cost-efficient hydrogen media for on-board, stationary and portable applications.<sup>5,6</sup> In the past few decades, great attention has been paid to both hydrogen production technologies and a variety of hydrogen storage methods,<sup>7-10</sup> including the use of different compounds,<sup>11,12</sup> especially complex hydrides, of which borohydrides are typical representative.<sup>13-15</sup> These solid-state hydrogen storage materials offer some advantages over high pressure gaseous storage and low temperature liquid storage, such as high capacity, high safety, and low cost. In particular, alkali metal borohydrides are regarded as possible hydrogen carriers, ascribed to their contribute to their high gravimetric and volumetric hydrogen density, together with good stability.<sup>16</sup> However, current research results showed that few technologies regarding the use of metal borohydrides as hydrogen storage carriers are able to fulfill the requirements established by the US Department of Energy.<sup>17</sup>

Early investigations into borohydrides have shown that, compared to other borohydrides such as LiBH<sub>4</sub> and KBH<sub>4</sub>, NaBH<sub>4</sub> is stable under alkaline conditions, and undergoes hydrolysis through the following reaction:<sup>18</sup>



However, the use of NaBH<sub>4</sub> as a hydrogen generator through hydrolysis faces several issues related to the catalyst durability, and/or poisoning, as well as storage vessels.<sup>19-21</sup> In contrast, thermal decomposition of NaBH<sub>4</sub> has emerged as potential alternative method for hydrogen storage. J. Urgnani *et al.* investigated the thermal decomposition behaviors of NaBH<sub>4</sub>, and proposed that NaBH<sub>4</sub> would decompose in two steps according to the following reactions:<sup>22</sup>



For the sake of improving the thermodynamic and kinetic properties of the thermal decomposition of NaBH<sub>4</sub>, many strategies have been taken, such as adding catalyst, building thermodynamic destabilization system, nano-engineering and chemical modifications.<sup>13,23-25</sup> For instance, NaBH<sub>4</sub>/MgH<sub>2</sub> system could fulfil its decomposition before melting due to the formation of MgB<sub>2</sub> in the system.<sup>26</sup> Czujiko *et al.* suggested that pure Mg could lower down the desorption temperature of NaBH<sub>4</sub> through catalytic effect.<sup>27</sup> In addition, the decomposition of NaBH<sub>4</sub> may occur at lower temperatures with some reversibility through the addition of Ni-based catalysts,<sup>28</sup> which

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facilitates hydrogen release and improves the reversibility to some extent.<sup>29</sup> Moreover, the chemical reaction that regenerates borohydrides from metal-borides occurs much easier over the regeneration from boron since less energy is required for breaking the chemical bond between B-M (M means metal) relative to the B-B's.<sup>30</sup>

In previous works, many research works regarding hydrogen storage composite systems have been carried out, and some of them have explored how rare earth element (RE) addition can effect the thermodynamics and kinetics properties of metal borohydrides based systems, *i.e.*, NaBH<sub>4</sub>-YF<sub>3</sub>,<sup>31</sup> NaBH<sub>4</sub>-ScCl<sub>3</sub>,<sup>32</sup> LiBH<sub>4</sub>-YCl<sub>3</sub>,<sup>33</sup> *etc.* In particular, hydrogen sorption reversibility was achieved in 3NaBH<sub>4</sub>/LnF<sub>3</sub> systems with good thermodynamic and kinetic properties.<sup>34</sup>

Considering that scandium lies in the III B column of the periodic table as the lanthanide elements, we attempt to prepare a new hydrogen storage system, 3NaBH<sub>4</sub>/ScF<sub>3</sub>, through ball milling method. Our previous investigations on NaBH<sub>4</sub>-MF<sub>3</sub> (M = metal) systems proved that the molar ratio of 3 : 1 was the best one, *i.e.* 3NaBH<sub>4</sub>/LnF<sub>3</sub> (Ln = La, Ce, Nd, Gd, Yb),<sup>34</sup> 3NaBH<sub>4</sub>/YF<sub>3</sub>,<sup>31</sup> 3NaBH<sub>4</sub>/PrF<sub>3</sub> and 3NaBH<sub>4</sub>/HoF<sub>3</sub>.<sup>35,36</sup> If the molar ratio of NaBH<sub>4</sub> to MF<sub>3</sub> is higher than 3 : 1, some NaBH<sub>4</sub> will be left after the desorption due to the incomplete reaction. While if the ratio is less than 3 : 1, MF<sub>3</sub> is excessive, and the overall hydrogen sorption capacity is reduced since MF<sub>3</sub> can neither release nor absorb hydrogen. Consequently, the ratio of NaBH<sub>4</sub> to ScF<sub>3</sub> is set as 3 : 1 in the present work. We conducted a detailed study of hydrogen sorption behaviors of the 3NaBH<sub>4</sub>/ScF<sub>3</sub> system, and proposed mechanisms of hydrogen sorption in this composite, depending on experimental analyses.

## 2 Experimental

### 2.1 Sample preparation

NaBH<sub>4</sub> (Aladdin Reagent Database Inc., 96%) and ScF<sub>3</sub> (Aladdin Reagent Database Inc., 98%) were used as starting materials without further purification and mixed in the molar ratio of 3 : 1 in a planetary ball miller whose type is QM-1SP2. The stainless steel vessel with 100 ml volume was used to load 0.3928 g of NaBH<sub>4</sub> and 0.3530 g of ScF<sub>3</sub> powders together with 25 stainless steel balls (diameter of 5 mm, average weight of 0.8950 g each). The ball to powder weight ratio is approximately 30 : 1. Ball milling is conducted at a rotation speed of 400 rpm for 180 min. The prearrangement, manipulation and storage of specimen were carried out in an Ar-filled Lab 2000 glove box (Etelux inert gas system Co., Ltd.) in which neither moisture nor oxygen concentration beyonds 10 ppm.

### 2.2 Characterization

The analyses of phase composition for the ball milled, dehydrogenated and rehydrogenated samples were accomplished using an X-ray diffraction apparatus (D/max 2550VL/PC), equipped with a Cu-K $\alpha$  radiation source. For XRD tests, composite powder at different states were kept into specific sample holders with arched glass on both sides and airtight PVC tape on the top, to isolate them from air. Meanwhile, the

broad peak at around  $2\theta = 15^\circ$  in the patterns is caused by the tape. Using a Spectrum Nicolet iS5 produced by Thermo Fisher Scientific Inc., Fourier transform infrared spectroscopy (FTIR) tests were performed on samples with different states in an Ar filled glove box. In principle of volumetric methods, we carried out temperature-programmed-desorption (TPD) measurements on 0.2 g of the 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite sample from room temperature to about 530 °C under an initial vacuum condition, with a heating rate  $R_H$  of 3 °C min<sup>-1</sup>. Evaluations of hydrogen absorption performance were implemented for 10 h at various temperatures under around 3.2 MPa H<sub>2</sub> pressure.

Dehydrogenation behaviors of composites were determined by synchronous thermal analyzer (Differential Scanning Calorimetry/Thermal Gravimetry, DSC/TG), in a Netzsch, STA 449 F3 Jupiter equipment, in which  $R_H = 3$  °C min<sup>-1</sup>, 5 °C min<sup>-1</sup>, 7 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup>, respectively, starting from room temperature to about 500 °C, under the protection of 0.1 MPa Ar flow. To compare the properties of hydrogen storage performances of different composites, data of weight percent considering hydrogen release and uptake during the tests was assessed based on the samples' initial weight value.

## 3 Results and discussions

### 3.1 Dehydrogenation of the 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite

The effect of the ScF<sub>3</sub> addition on the hydrogen desorption behaviors of NaBH<sub>4</sub> was examined by DSC measurements at different  $R_H$ , namely 3 °C min<sup>-1</sup>, 5 °C min<sup>-1</sup>, 7 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup>, as well as TG measurement at the  $R_H$  of 10 °C min<sup>-1</sup>, as Fig. 1 showed.

Two major endothermic peaks upon heating appeared on the DSC curves, indicating that two main desorption steps took place during dehydrogenation. According to the starting point of dehydriding in DSC profiles, the first major dehydrogenation begins at 356 °C with  $R_H = 3$  °C min<sup>-1</sup> heating rate condition. In contrast, pure NaBH<sub>4</sub> shows a dehydrogenation temperature of 517 °C under the same condition.<sup>31</sup> In addition, a subsequent broad endothermic peak was also recorded. TG curve obtained at the heating rate of 10 °C min<sup>-1</sup> shows that the total mass loss reaches 4.10 wt% at 500 °C. According to the DSC/TG profiles, the dehydrogenation enthalpies of the first and second major desorption reactions are determined to be  $27.43 \pm 5$  kJ mol<sup>-1</sup> H<sub>2</sub> and  $29.54 \pm 2$  kJ mol<sup>-1</sup> H<sub>2</sub>, respectively.

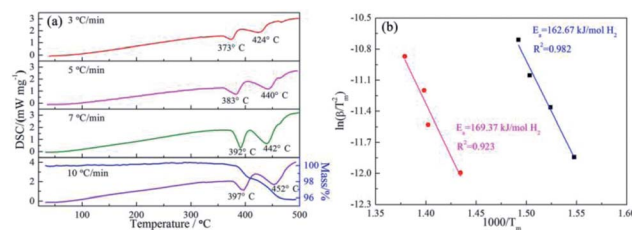


Fig. 1 DSC curves of 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite samples under heating rates of 3 °C min<sup>-1</sup>, 5 °C min<sup>-1</sup>, 7 °C min<sup>-1</sup> and 10 °C min<sup>-1</sup> and TG profile at the heating rate of 10 °C min<sup>-1</sup> (a) and the corresponding Kissinger plots for the two major endothermic desorption steps (b).



The apparent dehydrogenation activation energy ( $E_a$ ) of the  $3\text{NaBH}_4/\text{ScF}_3$  sample could be determined using the Kissinger method,<sup>37</sup> as described below:

$$\frac{d\left(\ln\frac{\beta}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E_a}{R} \quad (4)$$

where heating rate ( $\beta$ ), peak temperature ( $T_m$ ), and gas constant ( $R$ ) show a specific relationship. Table 1 gives the peak temperatures in DSC curves at various  $R_H$  obtained from Fig. 1a. The fitting plot displays that  $\ln(\beta/T_m^2)$  and  $1/T_m$  have good linearity, as shown in Fig. 1b. According to eqn (4), the  $E_a$  value is calculated to be  $162.67 \text{ kJ mol}^{-1} \text{ H}_2$  and  $169.37 \text{ kJ mol}^{-1} \text{ H}_2$  for the first major desorption step and second major desorption step, respectively.

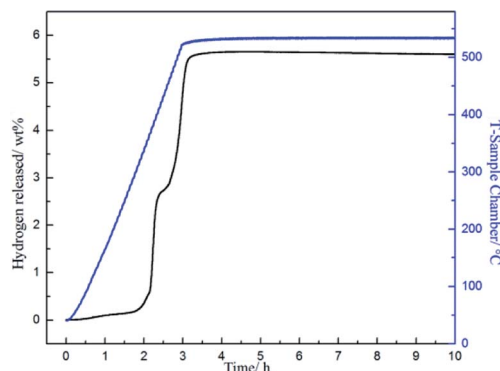
To obtain further information of dehydrogenation process of the target system, TPD measurement was performed on the ball-milled composite with a constant  $R_H$  of  $3 \text{ }^\circ\text{C min}^{-1}$  from ambient temperature to  $530 \text{ }^\circ\text{C}$  and the results are shown in Fig. 2. The results exhibit that  $3\text{NaBH}_4/\text{ScF}_3$  composite has an appropriate onset dehydrogenation temperature, which is actually lower than  $200 \text{ }^\circ\text{C}$  in vacuum. Meanwhile, the figure shows that the desorption behavior may be subdivided into three consecutive processes, with a small amount of hydrogen ( $\sim 0.19 \text{ wt}\%$ ) released at temperature lower than  $310 \text{ }^\circ\text{C}$  in the initial process, and the latter two steps range from  $310 \text{ }^\circ\text{C}$  to  $420 \text{ }^\circ\text{C}$ , and above  $420 \text{ }^\circ\text{C}$ , releasing about  $2.52 \text{ wt}\%$  and  $2.83 \text{ wt}\%$  of hydrogen, respectively. In comparison to the DSC measurements, the second and third desorption steps shown in TPD profile should correspond to the two major endothermic peaks on DSC curves.

The entire hydrogen release obtained from the experimental process up to  $530 \text{ }^\circ\text{C}$  is  $5.54 \text{ wt}\%$ , which is over 95% of the theoretical hydrogen content. Previous study shows that during dehydrogenation process of pure  $\text{NaBH}_4$  under the same condition, only  $0.68 \text{ wt}\%$  weight loss is observed when heated up to  $482 \text{ }^\circ\text{C}$ .<sup>19</sup> Thus, the hydrogen desorption properties of  $\text{NaBH}_4$  were significantly promoted by the addition of  $\text{ScF}_3$ . However, from Fig. 1, there is no endothermic peak present from ambient to  $300 \text{ }^\circ\text{C}$  in DSC curves. C. Bonatto Minella reported a related phenomenon and the difference between DSC analyses and volumetric measurements was ascribed to dissimilar experimental conditions.<sup>38</sup>

XRD analyses were performed on samples treated under a series of controlled conditions in order to have a better understanding of mechanisms of de/rehydrogenation in the

**Table 1** The DSC peak temperatures of the  $3\text{NaBH}_4/\text{ScF}_3$  at different heating rates under  $0.1 \text{ MPa}$  argon atmosphere

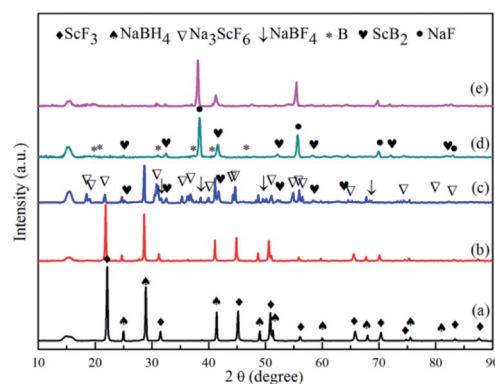
Sample	Heating rate/ $^\circ\text{C min}^{-1}$	Temperature of peaks/ $^\circ\text{C}$	
$3\text{NaBH}_4/\text{ScF}_3$	3	373	424
	5	383	440
	7	392	442
	10	397	452



**Fig. 2** TPD profile of the  $3\text{NaBH}_4/\text{ScF}_3$  sample at a heating rate of  $3 \text{ }^\circ\text{C min}^{-1}$ .

$3\text{NaBH}_4/\text{ScF}_3$  composite, as shown in Fig. 3. The results show that no new product can be found in the sample after ball milling, except  $\text{NaBH}_4$  (JCPDS no. 09-0386) and  $\text{ScF}_3$  (JCPDS no. 46-1243), which means that only physical mixing takes place during milling process. Before dehydrogenation at various temperatures of  $300 \text{ }^\circ\text{C}$ ,  $420 \text{ }^\circ\text{C}$  and  $530 \text{ }^\circ\text{C}$ , the loaded sample container was first placed under a  $4.5 \text{ MPa}$   $\text{H}_2$  pressure, then followed by a quick temperature rising and heat preservation. At last, the sample chamber was evacuated and powders were treated at the expected temperature for 3 h. After dehydrogenation at  $300 \text{ }^\circ\text{C}$  under vacuum, it can be clearly seen in Fig. 4 that diffraction peaks from  $\text{NaBH}_4$  in the  $3\text{NaBH}_4/\text{ScF}_3$  composite shifted slightly from high angle side to lower angle side, demonstrating a lattice expansion of  $\text{NaBH}_4$  after the first dehydrogenation.

On the basis of the XRD patterns and using the RIR analysis, the lattice parameters of  $\text{NaBH}_4$  in ball milled sample is calculated to be:  $a = 0.6165 \text{ nm}$ ,  $b = 0.6184 \text{ nm}$ ,  $c = 0.6153 \text{ nm}$  and  $\alpha = \beta = \gamma = 90^\circ$ . After the first step dehydrogenation at  $300 \text{ }^\circ\text{C}$ , the lattice constants of  $\text{NaBH}_4$  changed into  $a = 0.6185 \text{ nm}$ ,  $b = 0.6225 \text{ nm}$ ,  $c = 0.6166 \text{ nm}$  and  $\alpha = \beta = \gamma = 90^\circ$ . Such a lattice expansion of  $\text{NaBH}_4$  might be attributed to the fact that  $\text{H}^-$  was partially substituted by  $\text{F}^-$  in the unit cell. Similar phenomenon was also observed in some previous



**Fig. 3** XRD patterns of the  $3\text{NaBH}_4/\text{ScF}_3$  composite after ball milling (a), dehydrogenated at  $300 \text{ }^\circ\text{C}$  (b), dehydrogenated at  $420 \text{ }^\circ\text{C}$  (c), fully dehydrogenated at  $530 \text{ }^\circ\text{C}$  (d) and rehydrogenated at  $420 \text{ }^\circ\text{C}$  (e).



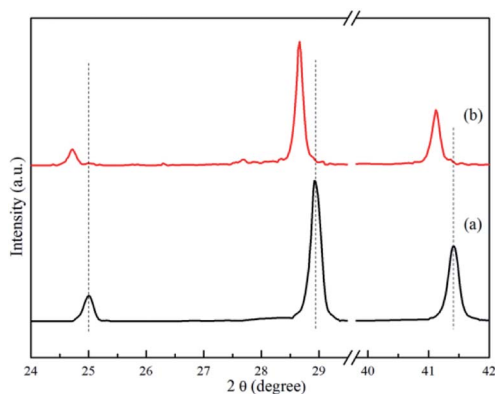
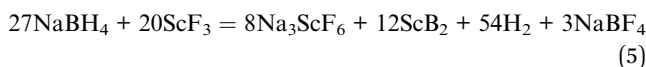
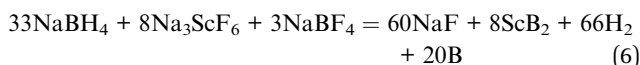


Fig. 4 XRD patterns of  $3\text{NaBH}_4/\text{ScF}_3$  composite after ball milling (a) and after dehydrogenation at  $300\text{ °C}$  (b) in the range of low diffraction angle.

works,<sup>29,39–43</sup> for which the lattice expansion was attributed to the formation of an intermediate compound  $\text{NaBH}_x\text{F}_{4-x}$ . In the present work, the formation of  $\text{NaBH}_x\text{F}_{4-x}$  occurred at the first desorption step between  $\text{NaBH}_4$  and  $\text{ScF}_3$ , together with releasing small amount of hydrogen, as also seen in the  $3\text{NaBH}_4/\text{NdF}_3$ ,  $3\text{NaBH}_4/\text{PrF}_3$ ,  $3\text{NaBH}_4/\text{HoF}_3$  systems,<sup>19,35,36</sup> and was regarded as an energy favorable process in theory.<sup>44</sup> Upon heating at temperatures higher than  $310\text{ °C}$ , along with the reduction of  $\text{NaBH}_4$  and disappearance of  $\text{ScF}_3$  (Fig. 3c),  $\text{Na}_3\text{ScF}_6$  appeared in the system, indicating that a major reaction between  $\text{NaBH}_4$  and  $\text{ScF}_3$  occurred. It has been also indicated by Radovan Cerny *et al.* that in the case of  $\text{NaBH}_4/\text{ScCl}_3$  system,  $\text{Na}_3\text{ScCl}_6$  and  $\text{NaSc}(\text{BH}_4)_4$  formed as a result of the reaction between  $\text{NaBH}_4$  and  $\text{ScCl}_3$ .<sup>32</sup> Chong *et al.* reported that the reaction occurred at  $250\text{ °C}$  between  $\text{NaBH}_4$  and  $\text{HoF}_3$  could produce  $\text{NaHo}(\text{BH}_4)_4$  and  $\text{NaHo}_2\text{F}_7$  phases.<sup>36</sup> In the  $3\text{NaBH}_4/\text{ScF}_3$  composite,  $\text{NaSc}(\text{BH}_4)_4$  might form upon heating and then decomposed to  $\text{ScB}_2$  and  $\text{H}_2$ . Based on the XRD analysis, the second dehydrogenation step before  $420\text{ °C}$  can be described as:



Such a reaction has a theoretical hydrogen release of 2.53 wt%, close to the value measured from TPD for the second step dehydrogenation. At around  $500\text{ °C}$ , the remaining  $\text{NaBH}_4$  reacts with  $\text{Na}_3\text{ScF}_6$  and  $\text{NaBF}_4$  to produce  $\text{NaF}$ ,  $\text{ScB}_2$  and B, as shown in the indexed XRD pattern of Fig. 3d. Thus, the third dehydrogenation step can be described as follows:



with a theoretical hydrogen desorption value of 3.08 wt%. This value is also close to what is observed in the TPD analysis for the third dehydrogenation step. According to Garroni *et al.*,<sup>45</sup>  $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$  is usually a byproduct during desorption of  $\text{NaBH}_4$  based composites, which forms in an intermediate step and is still present at the end of reaction.  $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$  is found to be

a stable byproduct and cannot be re-hydrogenated to  $\text{NaBH}_4$ , thus is regarded as an unfavorable product for the reversibility.<sup>46,47</sup> However, the  $\text{Na}_2[\text{B}_{12}\text{H}_{12}]$  phase was not found in the XRD pattern of the partial or the complete dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  samples, which means that very small amount or even no such a byproduct was generated during the decomposition of the  $3\text{NaBH}_4/\text{ScF}_3$  composite.

### 3.2 Rehydrogenation in the $3\text{NaBH}_4/\text{ScF}_3$ composite

Fig. 3e shows the XRD pattern of the complete dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite ( $530\text{ °C}$  for 3 h) that is maintained under a pressure of 3.2 MPa  $\text{H}_2$  at  $420\text{ °C}$  for 10 h. The pattern shows no change compared to that of the complete dehydrogenated composite, which means that the latter one has no hydrogen absorption ability.

As the complete dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite shows no reversibility, the hydrogen absorption after the second dehydrogenation step was attempted to study the possible reversibility. The profiles of hydrogen absorption are given in Fig. 5a, which are obtained under the condition of  $380\text{ °C}$ ,  $400\text{ °C}$  and  $420\text{ °C}$  at 3.2 MPa  $\text{H}_2$  pressure for the sample that has gone through dehydrogenation at  $420\text{ °C}$  for 3 h. These curves clearly show the reversible hydrogen absorption of the partial dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite: under the pressure of 3.2 MPa  $\text{H}_2$ , a hydrogenation capacity of 1.59 wt% can be achieved at  $420\text{ °C}$  for 8 h, while it can absorb 1.28 wt% at  $400\text{ °C}$  and 1.19 wt% at  $380\text{ °C}$ , respectively. By contrast, under 3.5 MPa hydrogen pressure, pure  $\text{NaBH}_4$  shows no hydrogen absorption at  $400\text{ °C}$ .<sup>36</sup>

The hydrogenation activation energy ( $E_{ab}$ ) is generally utilized to discriminate kinetics of absorption, by analyzing the entire energy barriers of hydrogen absorption process. Based on the Johanson–Mehl–Avrami (JMA) model, the following equation can be used to evaluate absorption kinetics:<sup>48</sup>

$$\ln[-\ln(1 - \alpha_A)] = \eta \ln k + \eta \ln t \quad (7)$$

where  $\alpha(t)$  is a function of time  $t$ ,  $k$  is a parameter describing kinetic,  $\eta$  is the Avrami exponent which matches transformation mechanism. Then, the following Arrhenius equation is used to calculate  $E_{ab}$ :

$$k = A \exp\left(-\frac{E_{ab}}{RT}\right) \quad (8)$$

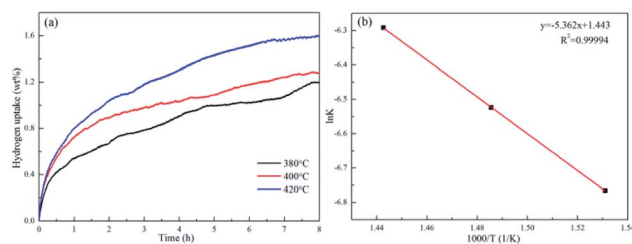


Fig. 5 Isothermal hydrogen absorption curves for the partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite sample at temperatures of  $380\text{ °C}$ ,  $400\text{ °C}$  and  $420\text{ °C}$  (a) and the  $\ln k-1000/T$  fitting plot (b).





where  $A$  represents temperature-independent constant,  $R$  represents universal gas constant, and  $T$  represents the absolute temperature. The scheme of  $\ln k$  versus  $1000/T$ , which is shown in Fig. 5, displays a good linear relationship. Therefore, the  $E_{ab}$  value obtained from the slope is therefore estimated to be  $44.58 \text{ kJ mol}^{-1} \text{ H}_2$  for the partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite.

To elucidate the mechanism of hydrogen absorption in the partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite, XRD analysis is carried out on the rehydrogenated sample and the result is shown in Fig. 6. The  $3\text{NaBH}_4/\text{ScF}_3$  sample was dehydrided at  $420^\circ\text{C}$  for 3 h in vacuum and then rehydrogenated at  $420^\circ\text{C}$  for 10 h under the pressure of  $3.2 \text{ MPa H}_2$ . In Fig. 6, the diffraction peaks from  $\text{NaBF}_4$  and  $\text{ScB}_2$  phases became weaker and even disappeared along with the increment in peak intensities of  $\text{NaBH}_4$  and  $\text{ScF}_3$  as compared to those in Fig. 3c. Therefore, the hydrogen absorption in the partial dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite follows exactly the reverse reaction path of the second step dehydrogenation. That is, the rehydrogenation consumes  $\text{Na}_3\text{ScF}_6$ ,  $\text{NaBF}_4$  and  $\text{ScB}_2$ , accompanied with the regeneration of  $\text{NaBH}_4$  and  $\text{ScF}_3$ . Compared to the completely dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite, the partially dehydrogenated composite contains  $\text{Na}_3\text{ScF}_6$  and  $\text{NaBF}_4$  phases, indicating that these two phases play the key role for the rehydrogenation.

The results of FTIR analyses for the ball-milled  $3\text{NaBH}_4/\text{ScF}_3$  sample, sample dehydrogenated at  $420^\circ\text{C}$  for 3 h and corresponding products rehydrogenated at  $400^\circ\text{C}$  for 3 h can be found in Fig. 7. In Fig. 7a, the FTIR spectrum of sample after ball milling has the signatures of B–H stretching band in the position of  $2226 \text{ cm}^{-1}$ ,  $2306 \text{ cm}^{-1}$  and  $2366 \text{ cm}^{-1}$ , and B–H bending band peak at  $1119 \text{ cm}^{-1}$ , all of which are supposed to be originated from borohydride. These peaks are considered to be from  $\text{NaBH}_4$ .<sup>19</sup> However, it should be noted that, the height of those peaks, which represent the intensity of B–H bonds vibration from the  $[\text{BH}_4]^-$  group, gradually become weaker as dehydrogenation reaction proceeds, indicating the decomposition of  $\text{NaBH}_4$ , as seen at  $1121 \text{ cm}^{-1}$ ,  $2221 \text{ cm}^{-1}$ ,  $2338 \text{ cm}^{-1}$  and  $2369 \text{ cm}^{-1}$  in Fig. 7b. According to the work of D. Syamala,<sup>44</sup> peak located at  $1065 \text{ cm}^{-1}$  can be marked as  $[\text{BF}_4]^-$  asymmetric stretching, indicating the formation of  $\text{NaBF}_4$  after the second step

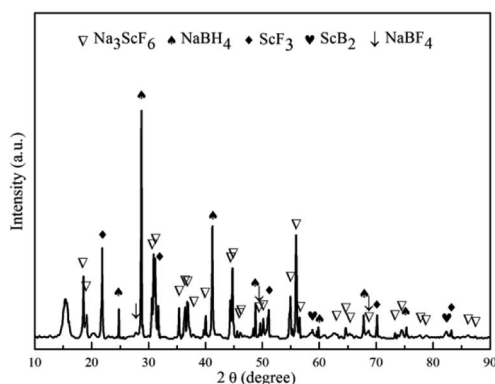


Fig. 6 XRD pattern of the partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite sample after rehydrogenation.

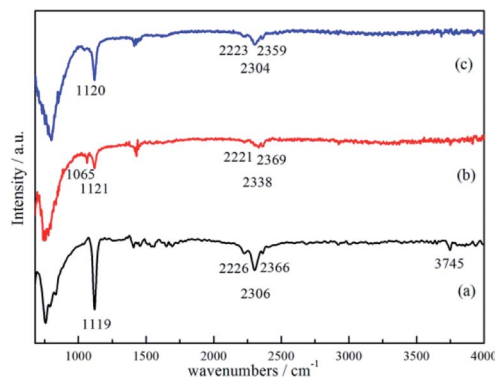


Fig. 7 FTIR spectra of the  $3\text{NaBH}_4/\text{ScF}_3$  composite after ball-milling (a), half dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  sample (b), rehydrogenation of partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  sample (c).

dehydrogenation, which is in good agreement with the XRD results (Fig. 3c). In Fig. 7c, the signatures of  $[\text{BH}_4]^-$  bending at  $1120 \text{ cm}^{-1}$  and  $[\text{BH}_4]^-$  stretching at  $2223 \text{ cm}^{-1}$ ,  $2304 \text{ cm}^{-1}$  and  $2359 \text{ cm}^{-1}$  were clearly revealed for the rehydrogenated sample and the intensity of these peaks increased, indicating the regeneration of  $\text{NaBH}_4$ .<sup>49</sup> Meantime, the peak from  $[\text{BF}_4]^-$  asymmetric stretching disappeared after rehydrogenation, showing the consumption of  $\text{NaBF}_4$  along with rehydrogenation. Peaks at wave numbers between  $1330 \text{ cm}^{-1}$  and  $1800 \text{ cm}^{-1}$  (Fig. 7a) were subtracted from the unavoidable moisture absorption and atmospheric humidity absorbed by the sample during measurement, while peak located at around  $3745 \text{ cm}^{-1}$  was identified as stretching band vibration of O–H.<sup>50</sup>

### 3.3 Mechanisms of hydrogenation in $3\text{NaBH}_4/\text{ScF}_3$ composite

It is shown in the present work that the hydrogen storage performance of  $\text{NaBH}_4$  can be effectively improved by introducing  $\text{ScF}_3$  as a reagent. In particular, rehydrogenation can be achieved in the partially dehydrogenated  $3\text{NaBH}_4/\text{ScF}_3$  composite. Analyses revealed that both  $\text{Sc}^{3+}$  cation and  $\text{F}^-$  anion show irreplaceable importance during the re/dehydrogenation processes of the composite. Firstly,  $\text{F}^-$  anion can replace  $\text{H}^-$  anion in the initial process of dehydrogenation, from  $\text{NaBH}_4$  to form  $\text{NaBH}_x\text{F}_{4-x}$ . Then,  $\text{Sc}$  cation loses electron to form  $\text{ScB}_2$ , in which  $\text{Sc}$  cation has the calculated valence of  $+4.08$ ,<sup>51</sup> rather than served as a three-valent cation. This is accompanied with the formation of hydrogen gas. Meanwhile, during the second dehydrogenation step, a portion of  $\text{F}^-$  anions from  $\text{ScF}_3$  incorporate into  $\text{Na}_3\text{ScF}_6$  crystallites, which might serve as the nucleation center for the growth of other products.

It has been established that the regeneration of  $\text{NaBH}_4$  in the  $\text{NaBH}_4\text{-MF}_x$  systems is associated with electronegativity ( $\chi_p$ ) of the metal cations.<sup>52</sup> Previous works have shown that after adding transition metal fluorides into  $\text{NaBH}_4$  based composites, when the Pauling's electronegativity of the transition metal lies in around between  $1.23\text{--}1.54$ , hydrogen sorption reversibility has larger thermodynamic tendency to occur.<sup>52</sup> The  $\chi_p$  value of  $\text{Sc}^{3+}$  is  $1.415$ , which lies in such specific range, thus the



regeneration of NaBH<sub>4</sub> in the dehydrided 3NaBH<sub>4</sub>/ScF<sub>3</sub> system is favorable.<sup>53</sup>

Using a database of density functional theory,<sup>54–56</sup> the enthalpies of desorption reactions are calculated to be 41.01 kJ mol<sup>-1</sup> H<sub>2</sub> for the second dehydriding step, and 43.31 kJ mol<sup>-1</sup> H<sub>2</sub> for the final step. These values are comparably higher than the values obtained from DSC/TG analyses, but significant lower than that of pristine NaBH<sub>4</sub> (108 ± 3 kJ mol<sup>-1</sup> of H<sub>2</sub>).<sup>57</sup> The differences between the calculated and measured enthalpies can be explained by fact that H<sup>-</sup> was partially substituted by F<sup>-</sup> in NaBH<sub>4</sub>, which is also observed in other NaBH<sub>4</sub> based systems containing fluorides.<sup>58</sup> However, the enthalpy for complete dehydrogenation is still fairly high, about 56.97 kJ mol<sup>-1</sup> H<sub>2</sub> calculated from DSC analyses. Consequently, the rehydrogenation of the complete dehydrided 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite is difficult from the thermodynamic point of view.<sup>52</sup>

During the rehydrogenation process, the experimental results show that only partial dehydrogenated products (NaBF<sub>4</sub> + ScB<sub>2</sub> + Na<sub>3</sub>ScF<sub>6</sub>) have reversibility, while the final dehydriding products (NaF + ScB<sub>2</sub> + B) cannot be rehydrogenated. Apart from the thermodynamic factors, this might also be understood from structural similarity between [BF<sub>4</sub>]<sup>-</sup> in NaBF<sub>4</sub> and [BH<sub>4</sub>]<sup>-</sup> in NaBH<sub>4</sub>, which may facilitate the regeneration of NaBH<sub>4</sub> through the exchange between H<sup>-</sup> and F<sup>-</sup>. The structural similarity was also observed between dehydrogenated and rehydrogenated products in the 3NaBH<sub>4</sub>/LnF<sub>3</sub> systems, which led to the improved rehydrogenation kinetics in these systems.<sup>25</sup> Researchers have also found that substitution reaction could be well understood from the hydride–fluoride isostructure, which has been proposed and confirmed in various hydrides–fluorides compounds having different stoichiometries.<sup>59–61</sup>

## 4 Conclusions

In this study, the 3NaBH<sub>4</sub>/ScF<sub>3</sub> composite was prepared through mechanical milling. The behaviors and mechanisms of hydrogen de/absorption of the composite were explained by using TPD, DSC/TG, XRD and FTIR techniques. Following are the summarized results:

(1) TPD and DSC analyses confirmed that NaBH<sub>x</sub>F<sub>4-x</sub> compound formed at the early dehydriding stage due to the partial substitution of H<sup>-</sup> anion by F<sup>-</sup> anion in NaBH<sub>4</sub>, releasing about 0.19 wt% of hydrogen. When temperature further increases, Na<sub>3</sub>ScF<sub>6</sub>, NaBF<sub>4</sub> and ScB<sub>2</sub> formed through the reaction between NaBH<sub>4</sub> and ScF<sub>3</sub> with 2.52 wt% of hydrogen released. Finally, the reaction of residual NaBH<sub>4</sub> with Na<sub>3</sub>ScF<sub>6</sub> produces NaF, B and ScB<sub>2</sub>, releasing about 2.83 wt% of hydrogen.

(2) The partially dehydrogenated products, Na<sub>3</sub>ScF<sub>6</sub>, ScB<sub>2</sub> and NaBF<sub>4</sub>, can be rehydrogenated to generate NaBH<sub>4</sub> with an activation energy of 44.58 kJ mol<sup>-1</sup> H<sub>2</sub>. In contrast, the fully dehydrogenated products, NaF + ScB<sub>2</sub> + B, cannot be hydroge-nated. The hydrogen sorption reversibility of the partially dehydrogenated composite can be understood through thermodynamic point of view and the structural similarity between [BF<sub>4</sub>]<sup>-</sup> in NaBF<sub>4</sub> and [BH<sub>4</sub>]<sup>-</sup> in NaBH<sub>4</sub>.

## Conflicts of interest

There are no conflicts to declare.

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