

# A reality check on using NaAlH<sub>4</sub> as a hydrogen storage material

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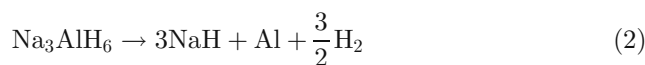
**Abstract** Sodium aluminum hydride or sodium alanate (NaAlH<sub>4</sub>) has been considered as a potential material for hydrogen storage. Although its theoretical hydrogen storage capacity is 5.5 wt.% at 250 °C, the material still has its drawback in the regeneration issue. With the use of certain catalysts, the regeneration problem can somewhat be alleviated with added benefits in the decrease in the hydrogen decomposition temperature and the increase in the decomposition rate. This work summarizes what we have learned from the decomposition of NaAlH<sub>4</sub> with/without catalysts and co-dopants. The decomposition was carried out using a thermovolumetric apparatus. For the tested catalysts—HfCl<sub>4</sub>, VCl<sub>3</sub>, TiO<sub>2</sub>, TiCl<sub>3</sub>, and Ti—the decomposition temperature of the hydride decreases; however, they affect the temperature in the subsequent cycles differently and TiO<sub>2</sub> appears to have the most positive effect on the temperature. Sample segregation and the morphological change are postulated to hinder the reversibility of the hydride. To prevent the problems, co-dopants—activated carbon, graphite, and MCM-41—were loaded. Results show that the hydrogen reabsorption capacity of HfCl<sub>4</sub>- and TiO<sub>2</sub>-doped NaAlH<sub>4</sub> added with

the co-dopants increases 10–50% compared with that without a co-dopant, and graphite is the best co-dopant in terms of reabsorption capacity. In addition, the decomposition temperature in the subsequent cycles of the co-dopant doped samples decreases about 10–15 °C as compared to the sample without a co-dopant. Porosity and large surface area of the co-dopant may decrease the segregation of bulk aluminum after the desorption and improve hydrogen diffusion in/out bulk of desorbed/reabsorbed samples.

**Keywords** Hydrogen storage · Co-dopants · NaAlH<sub>4</sub>

## Introduction

Sodium aluminum hydride or sodium alanate, NaAlH<sub>4</sub>, has been considered as a candidate medium for on-board hydrogen storage in fuel cell applications, in part, because of its high hydrogen content up to 5.6 wt.%. NaAlH<sub>4</sub> liberates hydrogen into two steps, as shown in Eqs. 1 and 2. The first step releases 3.7 wt.% hydrogen at 185 °C and the second one at 250 °C with 1.8 wt.% hydrogen [1, 2].



Although NaAlH<sub>4</sub> has favorable thermodynamics and hydrogen capacity for the fuel cell applications, the pristine NaAlH<sub>4</sub> cannot reabsorb hydrogen. It was not until 1997 that NaAlH<sub>4</sub> became even more attractive, thanks to the results from Bogdanovic and Schwickardi [3]. It was reported that NaAlH<sub>4</sub>, mixed with Ti(OBu<sup>n</sup>)<sub>4</sub>, can desorb 3.5–4 wt.% hydrogen and reabsorb hydrogen at 170 °C and

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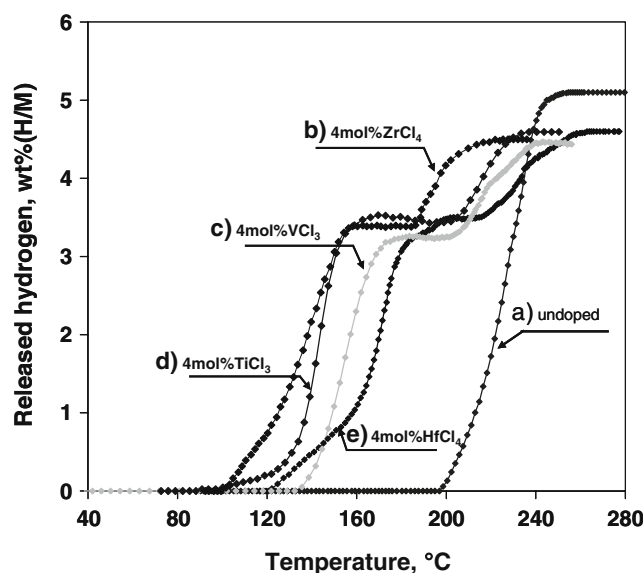
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150 bar. After this breakthrough, attempts have been made to develop and modify hydrogen desorption/absorption of  $\text{NaAlH}_4$  in terms of its kinetics, capacity, and reversibility [4–9]. A metal dopant and doping method significantly affect the reversibility of  $\text{NaAlH}_4$ . So far, Ti-catalysts seem to be the best catalyst for the reaction. The reported maximum reversible hydrogen capacity of Ti-catalyzed  $\text{NaAlH}_4$  is around 5% [10], which is still lower than the U.S. Department of Energy goal (6.0 wt.% hydrogen for 2010) [11]. An understanding of the hydrogen desorption/absorption of  $\text{NaAlH}_4$  doped with a transition metal is still unclear. The questions are: How do metal dopants activate the hydrogen desorption/reabsorption in  $\text{NaAlH}_4$ ?; What is the state of metal species after doping?; and Why does a Ti dopant show higher potential than other metal dopants in the hydrogen desorption/reabsorption in  $\text{NaAlH}_4$ ?

In this short review, we reported what we have learned from the improvement of the hydrogen desorption/absorption of  $\text{NaAlH}_4$ . In addition, this work also includes information reported by other research groups. We believe that the understanding of the  $\text{NaAlH}_4$  system would be a basis for further development of other hydride systems, such as  $\text{Mg}(\text{AlH}_4)_2$  9.27 wt.% and  $\text{Ca}(\text{AlH}_4)_2$  7.84 wt.% [12], and propel the quest for hydrogen storage materials towards reality.

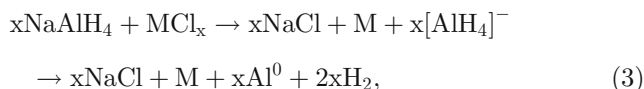
### Effect of dopant on the hydrogen desorption/absorption of $\text{NaAlH}_4$

After the discovery that doping Ti substantially improves the desorption kinetics and hydrogen reversibility of  $\text{NaAlH}_4$ , other metal transitions, particularly transition metals in the same group with Ti (Zr, Hf, and V), have been used as a catalyst for hydrogen desorption/absorption of  $\text{NaAlH}_4$ . In addition, Anton has reported that almost all transition metals improve the reversibility of  $\text{NaAlH}_4$  but with a difference extend depending on the nature of each metal [6]. Besides a metal catalyst, a method to load a transition metal is also equally important if not more.  $\text{NaAlH}_4$  was first doped with  $\text{Ti}(\text{O}i\text{Bu})_4$  by co-precipitation or wet method [3, 7]. The drawback is the inherited complicated preparation technique and organic contamination in the product [13]. Then, the ball milling method was introduced to mix  $\text{Ti}(\text{O}i\text{Bu})_4$  with  $\text{NaAlH}_4$ . It was found that the material prepared by the ball milling method shows better kinetic hydrogen desorption than that prepared by the wet method [1]. However, to avoid the contamination of organic compounds from the decomposition of  $\text{Ti}(\text{O}i\text{Bu})_4$ ,  $\text{TiCl}_3$ , and other Ti-based inorganic materials were used instead. As shown in Fig. 1, we reported the temperature program desorption from the first hydrogen desorption of milled  $\text{NaAlH}_4$ ,  $\text{NaAlH}_4$  doped with 4 mol%  $\text{HfCl}_4$



**Fig. 1** Correlation between temperature and hydrogen capacity, during the first hydrogen desorption on  $\text{NaAlH}_4$ : a undoped  $\text{NaAlH}_4$ ; b 4%  $\text{ZrCl}_4$ - $\text{NaAlH}_4$ ; c  $\text{VCl}_3$ - $\text{NaAlH}_4$ ; d 4%  $\text{TiCl}_3$ - $\text{NaAlH}_4$ , and e 4%  $\text{HfCl}_4$ - $\text{NaAlH}_4$

(4%  $\text{HfCl}_4$ - $\text{NaAlH}_4$ ),  $\text{NaAlH}_4$  doped with 4 mol%  $\text{TiCl}_3$  (4%  $\text{TiCl}_3$ - $\text{NaAlH}_4$ ),  $\text{NaAlH}_4$  doped with 4 mol%  $\text{ZrCl}_4$  (4%  $\text{ZrCl}_4$ - $\text{NaAlH}_4$ ), and  $\text{NaAlH}_4$  doped with 4 mol%  $\text{VCl}_3$  (4%  $\text{VCl}_3$ - $\text{NaAlH}_4$ ). In addition, the reversibility of each sample is shown in Fig. 2. Both figures indicate that all tested transition metals catalyze the hydrogen desorption of  $\text{NaAlH}_4$  by lowering the desorption temperature and contribute to the reversibility of  $\text{NaAlH}_4$ . About 30–75% of their original hydrogen capacities can be recovered.  $\text{NaAlH}_4$  doped with  $\text{TiCl}_3$  has the highest reversible hydrogen capacity. It can reabsorb hydrogen up to 3.85 wt.% (H/M), while the reversible hydrogen capacities of  $\text{HfCl}_4$ - $\text{NaAlH}_4$ ,  $\text{ZrCl}_4$ - $\text{NaAlH}_4$ , and  $\text{VCl}_3$ - $\text{NaAlH}_4$  are about 2.75 wt.% (H/M), 2.5 wt.% (H/M), and 1.5 wt.% (H/M), respectively. A possible reason why a transition metal chloride can reduce the desorption temperature of  $\text{NaAlH}_4$  is because of the reaction between  $\text{NaAlH}_4$  and the metal chloride forming  $\text{NaCl}$  and facilitating the decomposition of Al-H bond as shown in Eq. 3.



where  $M$  is donated the transition metal, and  $x$  is the stoichiometric number. Although the formation of  $\text{NaCl}$  accelerates the decomposition of  $\text{NaAlH}_4$ , it also lowers the hydrogen capacity of  $\text{NaAlH}_4$  as  $\text{NaCl}$  is a non-reducible species. In other words, doping a metal chloride in the hydride system poses the formation of  $\text{NaCl}$ , which consumes active Na in the hydride system and may be one of the reasons for the low reversible hydrogen capacity of

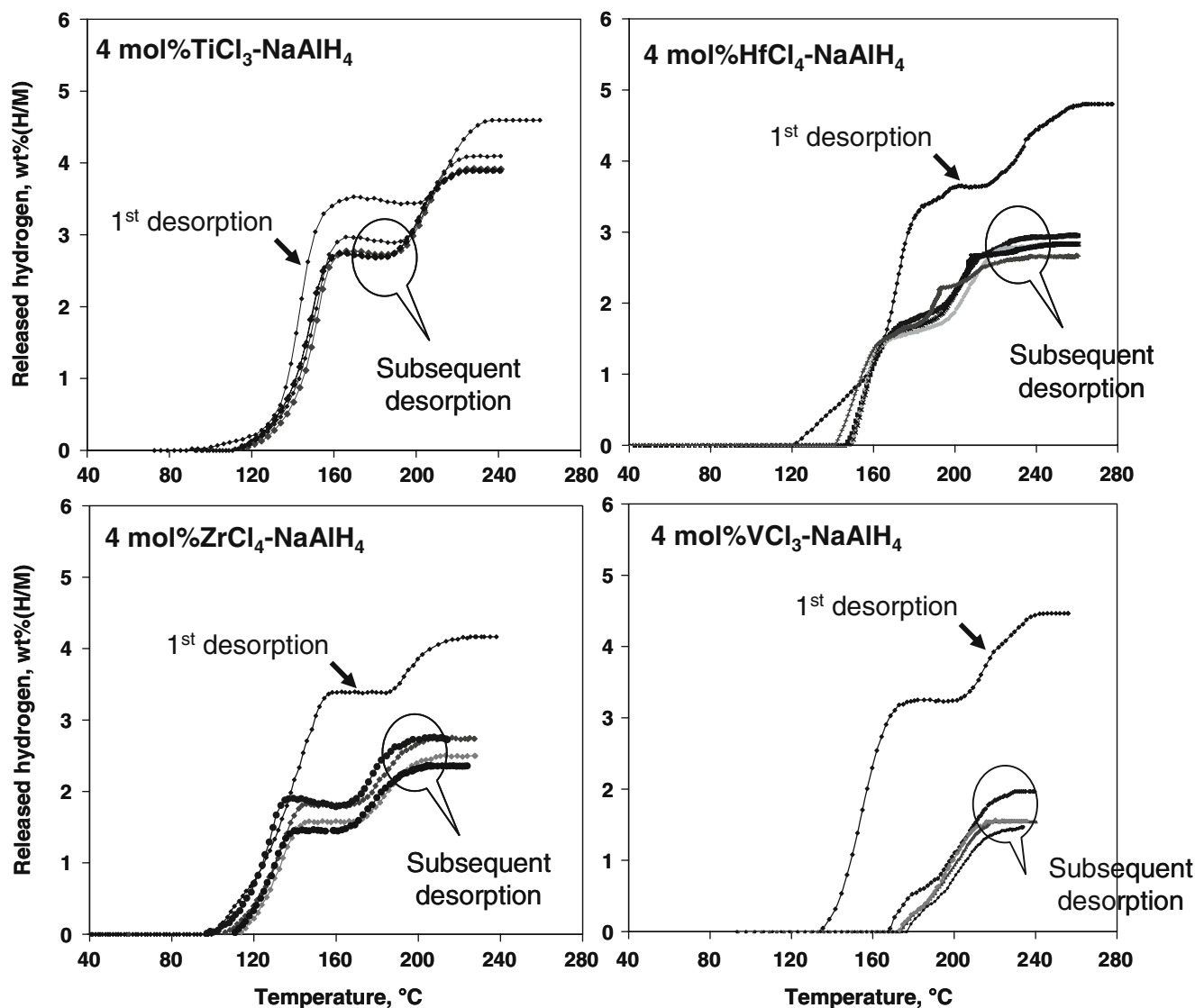
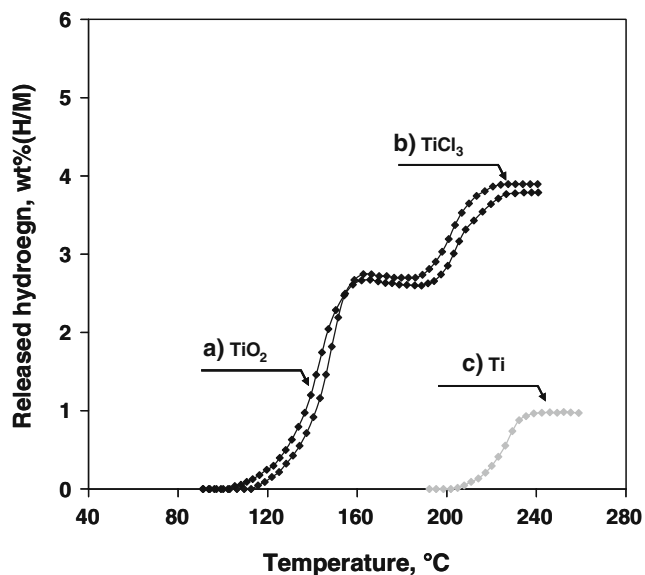


Fig. 2 Reversibility of: 4%TiCl<sub>3</sub>-NaAlH<sub>4</sub>, 4%ZrCl<sub>4</sub>-NaAlH<sub>4</sub>, 4%HfCl<sub>4</sub>-NaAlH<sub>4</sub>, and VCl<sub>3</sub>-NaAlH<sub>4</sub>

NaAlH<sub>4</sub>. In addition, it was found that the undoped hydride sinters and totally changes its morphology after the thermal hydrogen desorption. However, the addition of one of the metal catalysts decreases the extent to which the morphology of the desorbed product changes. In other words, it prevents the segregation and agglomeration of NaH and Al after heating [14, 15]. The effect of the catalyst nevertheless diminishes with the increase in the hydrogen desorption/absorption cycle [16].

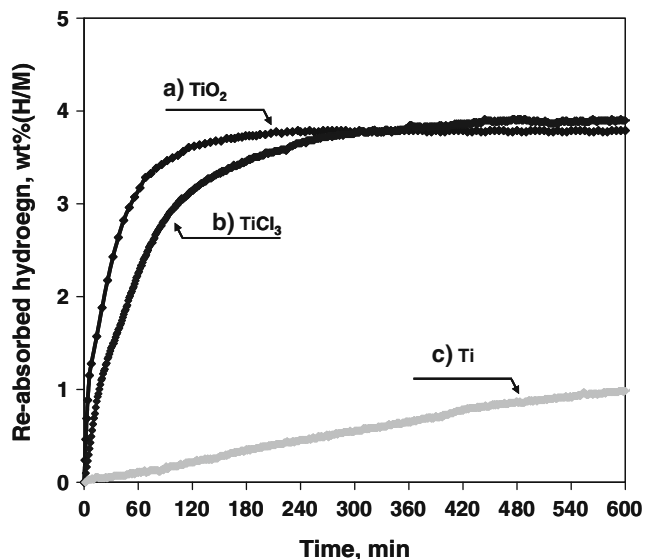
To avoid the NaCl formation problem as a by-product, the effects of using other Ti precursors (metal Ti microparticle and TiO<sub>2</sub>) as a catalyst were investigated. We found that NaAlH<sub>4</sub> doped with TiO<sub>2</sub> (TiO<sub>2</sub>-NaAlH<sub>4</sub>) exhibits the similar behavior as that doped with TiCl<sub>3</sub> with the reversible hydrogen capacity about 3.8 wt.% (H/M). In contrast, the hydrogen capacity of NaAlH<sub>4</sub> doped with Ti (Ti-NaAlH<sub>4</sub>) is around 1 wt.% (H/M) as shown in Fig. 3.

Unexpectedly, the hydrogen reabsorption of TiO<sub>2</sub>-NaAlH<sub>4</sub> is superior to that of TiCl<sub>3</sub>-NaAlH<sub>4</sub> (Fig. 4). From the BET surface area result, the sample doped with TiO<sub>2</sub> has a higher surface area than the one doped with TiCl<sub>3</sub>. This may elucidate that adding TiO<sub>2</sub> increases the surface area of the hydride because the porous structure of TiO<sub>2</sub> increases the grain boundary, prevents the agglomeration, and maintains the small grain size of the desorbed sample (Suttisawat et al., submitted). These facilitate the hydrogen diffusion into the system and lead to better hydrogen reabsorption of the TiO<sub>2</sub>-NaAlH<sub>4</sub> sample. This reveals that TiO<sub>2</sub> not only acts as a catalyst but also as a grain refiner for the hydride. However, some TiO<sub>2</sub> is reduced by NaAlH<sub>4</sub> and produces sodium oxide and hydroxide as by-products. This may be a reason why the reversible hydrogen capacity of TiO<sub>2</sub>-NaAlH<sub>4</sub> is not different from that of TiCl<sub>3</sub>-NaAlH<sub>4</sub>. Surprisingly, Ti-NaAlH<sub>4</sub> shows inferior hydrogen desorption/reabsorption.

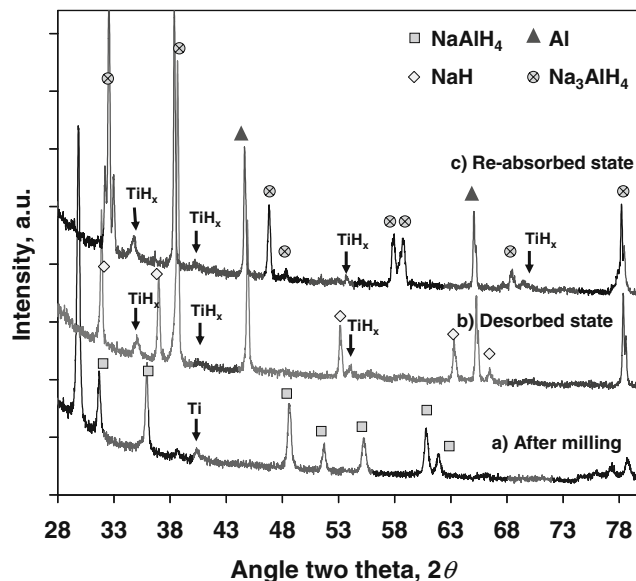


**Fig. 3** Comparison of the hydrogen desorption in the seventh desorption of *a* TiO<sub>2</sub>-NaAlH<sub>4</sub>, *b* TiCl<sub>3</sub>-NaAlH<sub>4</sub>, and *c* Ti-NaAlH<sub>4</sub>

Its hydrogen reversible capacity is around 1 wt.% (H/M). The formation of TiH<sub>x</sub>(1x2) was detected by XRD in the sample after hydrogen desorption/reabsorption, Fig. 5. This may be attributed to the formation of TiH<sub>x</sub> that decreases the activity of hydrogen dissociation in the desorbed sample. However, nanosized Ti was reported to show the most positive effect on the hydrogen desorption/absorption of NaAlH<sub>4</sub> with respect to other metal precursors [10, 17]. In addition, Lee et al. also reported the effect of TiAl<sub>3</sub> with various particle sizes on the hydrogen desorption of NaAlH<sub>4</sub> [18]. However, recently many research groups claimed the catalytic effect of Ce, Sc, and Pr on the



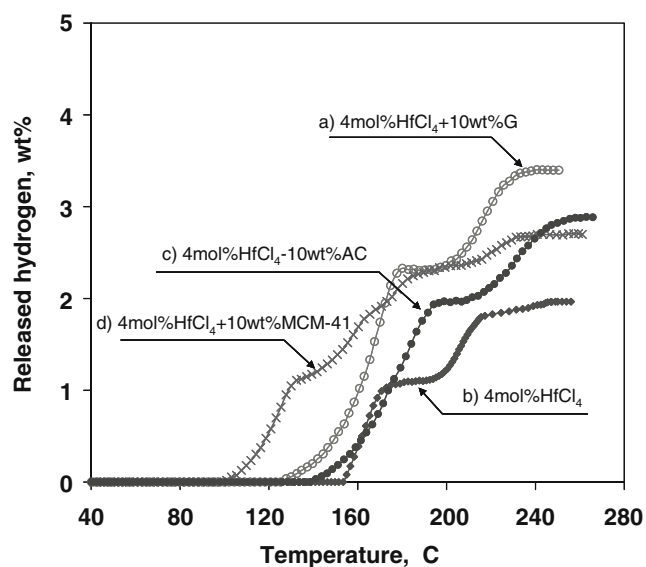
**Fig. 4** Hydrogen reabsorption rate of *a* TiO<sub>2</sub>-NaAlH<sub>4</sub>, *b* TiCl<sub>3</sub>-NaAlH<sub>4</sub>, and *c* Ti-NaAlH<sub>4</sub>



**Fig. 5** XRD patterns of 4 mol% Ti-NaAlH<sub>4</sub>: *a* after milling, *b* after the hydrogen desorption, and *c* after hydrogen reabsorption

reversible hydrogen capacity of NaAlH<sub>4</sub> is superior to that of Ti after several cycles [19–21]. Therefore, it can be concluded that a type of metal, particle size, and doping technique all play important roles on the activity of catalyst of the hydrogen desorption/absorption of NaAlH<sub>4</sub>.

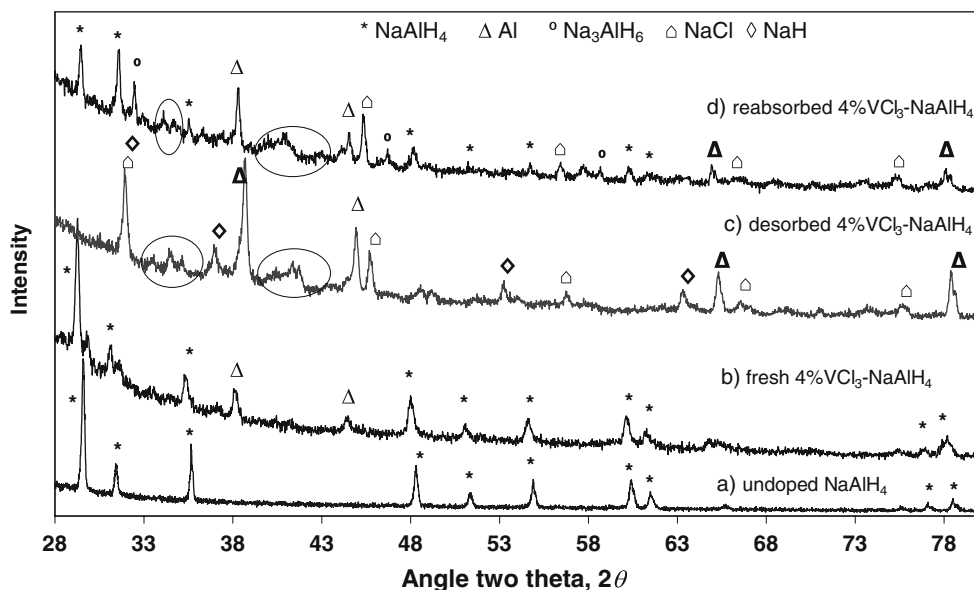
As mentioned above that the increase in the surface area or grain boundary of the hydride system from the addition of TiO<sub>2</sub> leads to the faster hydrogen reabsorption, interests were then shifted to the effects of adding porous and high surface materials or co-dopant, together with transition metal catalysts in order to prevent the agglomeration and increase the surface area of the hydride system. Figure 6 shows the reversible hydrogen capacity of NaAlH<sub>4</sub> doped with 4 mol% HfCl<sub>4</sub> together with 10 wt.% co-dopant (graphite, activated carbon, CMC-41). To better reflect the effect of the co-dopant, the reported hydrogen capacity was calculated based on the total weight of sample (NaAlH<sub>4</sub> plus dopant). The results reveal that all co-dopants increase the amount of the reabsorbed hydrogen and decrease the desorption temperature in the subsequent cycles compared to NaAlH<sub>4</sub> doped with only HfCl<sub>4</sub>. An increase of about 40–50% in the reabsorbed hydrogen amount from the sample without any co-dopant can be observed. Among the studied co-dopants, graphite exhibits the best activity for the hydrogen desorption/reabsorption of NaAlH<sub>4</sub> with the transition metal catalysts. The hydrogen capacity of NaAlH<sub>4</sub> doped with TiO<sub>2</sub> and graphite (3.7 wt.%) is increased around 10% as compared with the sample without graphite [22]. This may be because of the unique properties of graphite as a mixing agent manifested through lubrication phenomena and as a micro-grinding agent manifested through the formation of carbide species, which is known



**Fig. 6** Correlation between temperature and hydrogen released during the seventh hydrogen desorption cycle of doped NaAlH<sub>4</sub>: *a* 4 mol% HfCl<sub>4</sub> + 10 wt.% graphite, *b* 4 mol% HfCl<sub>4</sub>, *c* 4 mol% HfCl<sub>4</sub> + 10 wt.% activated carbon, and *d* 4 mol% HfCl<sub>4</sub> + 10 wt.% MCM-41 [31]

as the hardest materials. Moreover, it was reported that graphite might be imparting an electron contribution to transition metal catalysts through a hydrogen spillover mechanism [20–26]. Some research works reported that the hydrogen capacity of NaAlH<sub>4</sub> doped with Ti and single-walled carbon nanotube (SWNT) can uptake hydrogen more than 4 wt.% and increase the hydrogen absorption rate more than twofolds as compared with the one without SWNT [27, 28]. One possible reason for the improvement of the hydrogen desorption/reabsorption of NaAlH<sub>4</sub> with the co-dopants could be the role of their physical properties (porosity and high surface area) as it is these properties that

**Fig. 7** XRD patterns of *a* as-received NaAlH<sub>4</sub>, *b* 4%VCl<sub>3</sub>-NaAlH<sub>4</sub>, *c* 4%VCl<sub>3</sub>-NaAlH<sub>4</sub>-after subsequent desorption, and *d* 4%VCl<sub>3</sub>-NaAlH<sub>4</sub>-after reabsorption (Suttisawat et al., submitted)



may help in increasing the hydrogen transfer in and out from the bulk sample by decreasing the grain aggregation of the desorbed NaAlH<sub>4</sub> as reported by Cento et al. [29]. Moreover, the co-dopants could facilitate the mixing during the sample preparation and increase the dispersion of the metal catalysts in the sample. Recently, Berseth et al. reported the fundamental electronic effect of carbon materials on the catalyzed decomposition of NaAlH<sub>4</sub> that the electronegative carbon substrate induces the electron from Na of NaAlH<sub>4</sub> leading to the weakened AlH<sub>4</sub><sup>-</sup> bond [30]. It was found that the larger curvature of carbon substrate, the higher electron affinity of carbon substrate leading to the lower H-removal energy. C<sub>60</sub> shows better electron affinity than graphite and CNT.

### State of metal catalyst and action on the reaction of NaAlH<sub>4</sub>

So far, Ti-dopants seem to be the best catalyst on the hydrogen desorption/absorption of NaAlH<sub>4</sub>. The reversible hydrogen capacities of NaAlH<sub>4</sub> doped with Ti-catalysts were reported in the range of 3.5–5 wt.% depending on a type of Ti, purity of NaAlH<sub>4</sub>, and a doping method [10, 11, 31]. However, the hidden roles of a metal catalyst on the hydrogen desorption/absorption of NaAlH<sub>4</sub> have been argued. Sun et al. suggested that a Ti dopant might catalyze the reaction by the substitution of the dopant in the lattice of NaAlH<sub>4</sub> then affecting the activation and involving the lattice distortions [32]. In the mechanism, Ti is believed to substitute Na<sup>+</sup> and form Ti<sup>4+</sup> resulting in the lattice distortions, vacancy formation, and enhancement of hydrogen desorption kinetics when less than 2 mol% of Ti (OBU<sup>n</sup>)<sub>4</sub> is doped into NaAlH<sub>4</sub>. However, it was also found

that the doped metal catalyst with NaAlH<sub>4</sub> was reduced to zerovalent state and form alloy with Al [33]. Graetz et al. reported the result from Ti K-edge X-ray absorption near-edge spectroscopy showing that Ti does not substitute in the bulk lattice nor form the Ti metal, but it is present on the Al surface in the highly dispersed form of amorphous TiAl<sub>3</sub>, so that is why the Ti-catalyst phase is not visible by the X-ray diffraction analysis at room temperature [34, 35]. In the case of VCl<sub>3</sub>-, ZrCl<sub>4</sub>-, and HfCl<sub>4</sub>-dopants after doping with NaAlH<sub>4</sub>, they also form alloy with Al presenting in the crystal phase, which can be detected by XRD (Fig. 7) [31, 36]. The different forms of the metal catalysts in the hydride system may indicate the different ability on dispersion, hence, the catalyst activity [33]. Chaudhuri et al. reported the step of hydrogen storage in NaAlH<sub>4</sub> catalyzed by Ti using a computational approach that Ti atoms act as a catalyst in the hydrogen dissociation and decrease the energy barrier in the hydrogen absorption on the Al surface. In addition, they proposed that the formation of AlH<sub>3</sub> or alane is a mobile species, which reacts with NaH to form Na<sub>3</sub>AlH<sub>6</sub>, and then NaAlH<sub>4</sub> [37, 38].

## Conclusions

The above discussion is the improvement of hydrogen desorption/absorption of NaAlH<sub>4</sub>. So far, the reversible hydrogen capacity of NaAlH<sub>4</sub> catalyzed by a metal dopant does not exceed 5 wt.%. Although the NaAlH<sub>4</sub> system probably does not have a sufficiently high enough hydrogen storage capacity for transportation (6 wt.%), the information gained from the investigation of this system can be applied with other hydrides.

- Structure defect and destabilization

Mechanical ball milling can decrease the particle size of a hydride and introduce a crystal lattice defect in the material. The destabilization of Al-H bond leads to the lower temperature of hydrogen desorption.

- Action of a catalyst

A transition metal, particularly Ti, catalyzes the decomposition of hydride and facilitates the dissociation of hydrogen into the hydride system. Moreover, a metal catalyst decreases the barrier energy of the hydrogen absorption on the Al surface. Alane (AlH<sub>3</sub>) is the mobile species to react with NaH, and then form as Na<sub>3</sub>AlH<sub>6</sub> and NaAlH<sub>4</sub>.

- Increasing surface area

Adding carbon materials in a hydride system can decrease the segregation of the hydride components and maintain the small grain size of the desorbed sample, which

reduces the diffusion pathway of hydrogen. This can improve the rate of hydrogen absorption of the hydride. In addition, electronegative carbon substrate destabilizes the AlH<sub>4</sub><sup>-</sup> bond leading to lower the hydrogen desorption temperature.

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