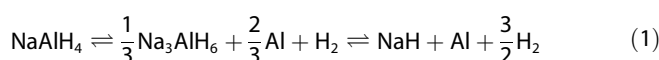


Improved Hydrogen Storage of TiF_3 -Doped NaAlH_4

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A key technical challenge in advancing "hydrogen economy" is to develop a hydrogen storage system that provides an on-board hydrogen source for fuel cell operations within combined constraints on weight/volume density, reversibility, efficiency, safety and costs.^[1–3] Among the various potential approaches, material-based hydrogen storage has been highly appreciated due to the significant advantage on safety, energy efficiency and operational convenience. However, decades of extensive efforts on metal/alloy hydrides and nanostructured carbon materials have led to no viable system that can meet the target of practical application. Most of the challenges come from the enormous gap between the practically attained hydrogen capacity and that required for feeding the full cell at commercial operation conditions.^[1–3]

In 1997, Bogdanović and Schwickardi reported their important finding that, upon doping with catalytic amount of transition metal catalysts, typically Ti species, NaAlH_4 underwent two-step reversible de-/hydrogenation reactions [according to Eq. (1)] with markedly enhanced kinetics:^[4]




This finding offers a clear potential of achieving >5 wt.% hydrogen capacity at a moderate temperature range, thus quickly sparking worldwide research activities that aimed at developing catalytically enhanced NaAlH_4 and related light-weight complex hydrides as practical hydrogen storage medium.^[5–26]

At a moderate temperature range, the reversible decomposition/reconstruction reactions of NaAlH_4 are dominated by the catalytic enhancement arising upon Ti-doping. Therefore, the exploitation of advanced dopant precursor and doping technology constitutes the center of research on the Ti– NaAlH_4 system.^[4–7, 11–15, 18–21, 24, 26–28] Currently, one popular choice for dopant precursor is titanium chloride. Its high activity on catalyzing reversible de-/hydrogenation of NaAlH_4 has been gener-

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ally recognized.^[4, 7, 11–15, 20, 21, 26] Whereas, the effectiveness of its analog TiF_3 acting as dopant precursor is a subject of great controversy. Majzoub et al.^[20] and Anton,^[21] respectively, reported that the catalytic activity of TiF_3 was similar to that of TiCl_3 . Bogdanović et al. claimed that TiF_3 was inferior to Ti chlorides as a dopant precursor.^[29] While a systematic comparative investigation on the systems doped with these two kinds of Ti-compounds, respectively, has led us to a contrary conclusion, that is, TiF_3 is superior to TiCl_3 as a dopant precursor in preparation of catalytically enhanced NaAlH_4 system for hydrogen storage.

Experimental Section

The starting materials NaH (95 %, ≈ 200 mesh), KH (30 wt.% dispersion in mineral oil), Al powder (99.95 + %, ≈ 200 mesh), and solid TiF_3 and TiCl_3 (99.999 %) powders were all purchased from Sigma-Aldrich Chemicals Inc. Except for KH, all other materials were used as received. The extraction of KH from the mineral oil was operated in an Ar-filled glove-box. The mixture was washed and filtered for several times by using pentane, followed by evaporation of the solvent.

The mixtures of NaH + Al + 4 mol% TiF_3 (TiCl_3), NaH + Al + 4 mol% TiF_3 + 4 mol% KH (with a typical mass around 0.5 g) were mechanically milled by using stainless steel pot (with a size of 51 cm³) and 8 balls (with a diameter of 8 mm) in a Fritsch 7 Planetary mill at 400 rpm. The milling was performed under Ar atmosphere, with an initial pressure of about 0.1 MPa. The ball-to-powder ratio was about 40:1. All the sample operations were performed in an Ar-filled glove box, in which the $\text{H}_2\text{O}/\text{O}_2$ levels are below 0.1 ppm.

Hydrogen absorption/desorption behaviors of the as-prepared materials were examined by using a carefully calibrated Sievert-type apparatus. Other than specified, a typical cyclic experiment entailed absorption at 120 °C and desorption at 150 °C with an initial pressure condition of ≈ 11 MPa and < 100 Pa, respectively. To minimize the $\text{H}_2\text{O}/\text{O}_2$ contamination, the high-purity hydrogen (with a purity of 99.999 %) was further purified by using a hydrogen storage alloy system. To allow a practical evaluation of the hydrogen storage properties of the materials, the weight of the dopant precursor was taken into account in the determination of H capacity.

The as-prepared materials were characterized by powder X-ray diffraction (XRD, Rigaku D/MAX-2500, $\text{CuK}\alpha$ radiation). The sample preparation was operated in the glove box. To minimize the $\text{H}_2\text{O}/\text{O}_2$ contamination during the sample transferring and measurement, small amount of grease was used to cover the surface of the samples.

Results and Discussion

The hydrogen storage performance of the mechanically doped Ti– NaAlH_4 systems is highly dependent on the preparation conditions. In this regard, a systematic investigation has established an optimized doping condition for preparing Ti halide– NaAlH_4 systems: mechanical milling of a 1:1 NaH/Al powder mixture with Ti halides under inert atmosphere for about 0.5 h. Herein, this condition was applied in the preparation of all samples.

Figures 1 and 2 give the cycling hydriding/dehydriding profiles of the material doped with 4 mol% TiF_3 at moderate tem-

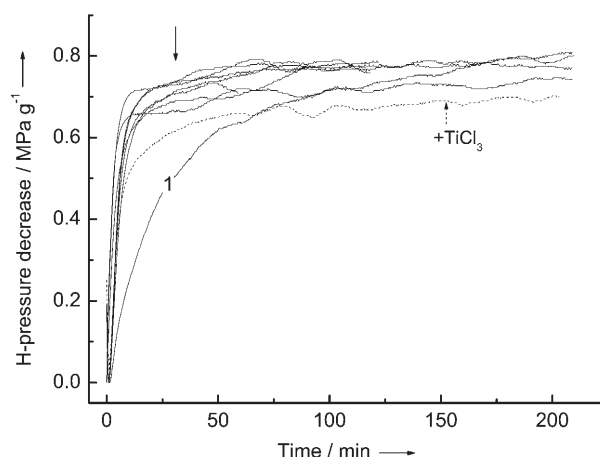


Figure 1. Comparison of the rehydriding performance between the samples doped with TiF_3 (the first 10 cycles, —) and TiCl_3 (----), respectively. Both samples were prepared by milling 1:1 NaH/Al mixture with 4 mol% dopant precursors under Ar atmosphere for 0.5 h, and measured at 120 °C with an initial hydrogen pressure of about 11 MPa.

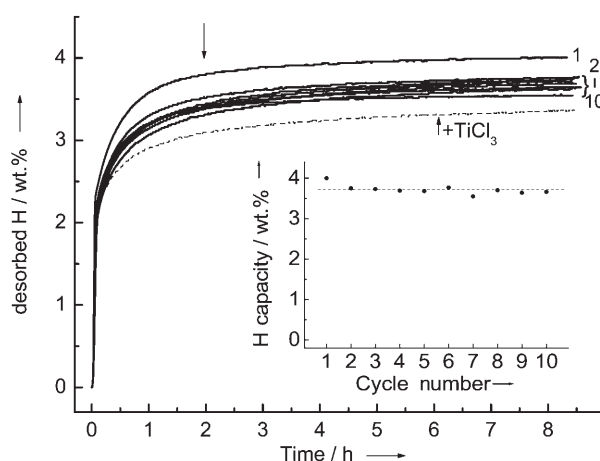


Figure 2. Dehydriding profiles (at 150 °C) of the first 10 cycles of NaH + Al + 4 mol% TiF_3 milled under Ar atmosphere for 0.5 h. (----): A typical profile of NaH + Al + 4 mol% TiCl_3 prepared and measured under identical conditions. The inset gives the cycling hydrogen capacity of the TiF_3 -doped sample.

perature, respectively. For comparison purpose, the typical profiles of the TiCl_3 -doped sample that were prepared under identical conditions were also included. It was found that the utilization of TiF_3 as dopant precursor has led to an increased hydrogen capacity together with slightly improved de-/hydriding kinetics, in comparison with TiCl_3 -doped hydrides. As shown in the inset of Figure 2, the cycling hydrogen capacity of the hydride, doped with TiF_3 stabilized at about 3.7 wt.%, is about 10% higher than that of the TiCl_3 -doped sample. Here, the increased hydrogen capacity should be partially ascribed to the lighter molecular mass of TiF_3 than TiCl_3 . At a typical doping level of 4 mol%, the usage of TiF_3 instead of TiCl_3 leads to an increase of about 3.5% in the theoretical capacity. At typical cyclic conditions, hydrogenation at 120 °C and dehydrogenation at 150 °C of the TiF_3 -doped hydride can almost be completed within about 0.5 and 2 h (as specified by the solid

arrows in Figures 1 and 2), respectively. Moreover, the kinetic enhancement arising upon doping with TiF_3 persists in the de-/hydriding cycles. Here, it was noticed that the TiF_3 -doped material exhibited a substantially different de-/hydrogenation behavior in the first cycle compared to the the following ones, more exactly, a markedly lowered rehydriding kinetics and a considerable increase in the desorbed H-amount. In our opinion, such variation on the hydrogen storage performance should be related to the relaxation of the defectively doped structure that was produced during the milling process.

The advantage of TiF_3 over TiCl_3 as a dopant precursor in NaAlH_4 systems becomes more pronounced at reduced operational temperatures. Figure 3 gives the rehydriding profiles of

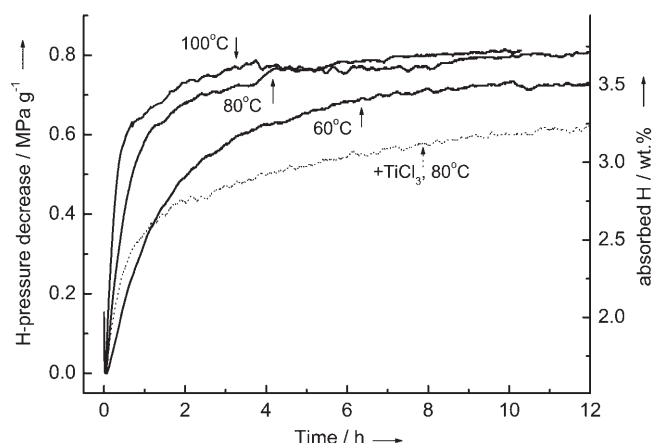


Figure 3. Rehydriding profiles of the TiF_3 -doped sample in the temperature range: 60–100 °C, with an initial hydrogen pressure of about 11 MPa. The amount of absorbed H (in wt.%) is determined in the following dehydrogenation. The rehydriding profile (at 80 °C) of the TiCl_3 -doped sample (----) is also included.

the TiF_3 -doped hydride that were measured at 60–100 °C with an initial hydrogen pressure of ≈ 11 MPa. It was observed that even at a temperature as low as 60 °C, the material could restore 3.4 wt.% hydrogen in about 6 h. With increasing the temperature to 80–100 °C, the time required for recharging about 3.7 wt.% hydrogen decreased to 3–4 h. While for the TiCl_3 -doped hydride, it takes over 10 h to restore a hydrogen amount of 3.2 wt.%. The hydrogenation-pressure dependence of the TiF_3 -doped hydride was further investigated at 80 °C, and the results are shown in Figure 4. It was observed that the decrease on the initial hydrogen pressure, especially in the range of 6–9 MPa, produced slightly negative influence on rehydriding kinetics and the restored hydrogen amount. Clearly, the considerably reduced temperature and pressure conditions for recharging the materials imply practical advantages in operational convenience, safety and costs.

The thermal decomposition of Na_3AlH_6 at moderate temperatures has been a key challenge in developing Ti– NaAlH_4 as viable hydrogen storage system. As reported, Na_3AlH_6 needs to be heated up to above 110 °C to attain a dissociation pressure of 1 bar.^[7,12,13] To achieve the two-step decomposition at a reasonable rate, the dehydriding temperature of the NaAlH_4

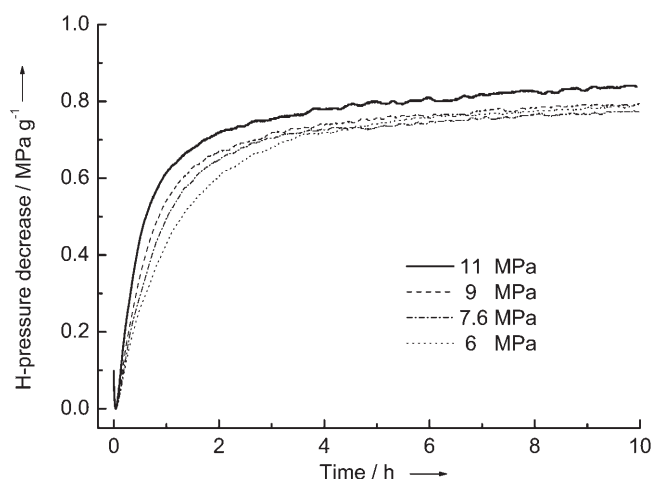


Figure 4. Rehydrogenation-pressure dependence (at 80 °C) of the TiF_3 -doped sample.

system is therefore generally controlled at over 150 °C, which is beyond the acceptable level for practical onboard application. Of particular interest, the present study found that upon doping with TiF_3 , the $\text{Na}_3\text{AlH}_6 \rightarrow \text{NaH} + \text{Al}$ dehydriding process could be substantially improved. As shown in Figure 5, the ma-

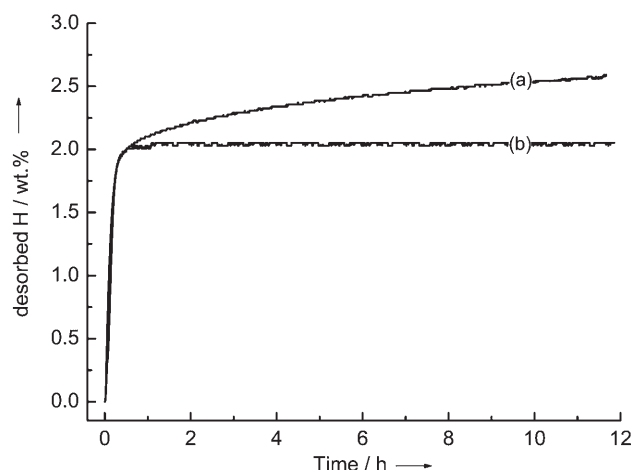


Figure 5. Comparison of the dehydriding performance at 120 °C between the samples doped with 4 mol % a) TiF_3 and b) TiCl_3 .

terial doped with TiF_3 undergoes substantial dehydrogenation up to the $\text{NaH} + \text{Al}$ stage at 120 °C. This is in great contrast to the case of TiCl_3 -doped sample, in which no appreciable H desorption from the second decomposition step was observed within the examined period. In principle, the possible reason for the pronounced property improvement may involve favorable thermodynamic adjustment (increased dissociation plateau pressure), kinetic enhancement or combined mechanisms. In all cases, it seems likely that the substantial differences on the two-step dehydriding behavior, as well as on the rehydriding performance at relatively low temperatures, originate from the variation of the halide anions. This is rather unexpected according to the current understanding of the catalytic mecha-

nism. It is generally believed that only the Ti species are responsible for the catalytic enhancement, while the simultaneously incorporated anions produce no positive influence but generating inactive by-products.^[7, 10, 15–19, 24–26, 30] These results lead us to a speculation that the F[−] anion is substantially incorporated into the doped structure, and in some way contributes to the catalytic enhancement on the reversible dehydrogenation of NaAlH₄. This speculation was partially supported by the X-ray diffraction examination (see Supporting Information). In great contrast to the well-established formation of NaCl^[12, 13, 16, 23] in the hydrides doped with Ti chloride, the counterpart NaF has not been definitely identified in our XRD examination of the TiF₃-doped materials. This finding is consistent with the results of Brinks et al.^[23, 31] Clearly, it is a subject of significance to firmly establish the status and possible role of F[−] ions played in reversible dehydrogenation of NaAlH₄. It may pave a new way for pursuing further improved hydrogen storage performance of NaAlH₄ and other related complex hydrides. In this regard, our further structure–property investigations are underway. Additionally, it was noticed that the hydrogen capacity obtained from the first dehydriding step at 120 °C was only about 2.0 wt.%, far below the theoretical value. This is mainly ascribed to the incomplete transformation from Na₃AlH₆ to NaAlH₄ in the hydrogenation process (see Supporting Information).

While the utilization of TiF₃ has led to further improved hydrogen storage performance in comparison with TiCl₃-doped hydrides, the system still suffers from low cycling capacity. We have found that this problem could be partially alleviated by co-doping the hydride with catalytic amounts of KH together with TiF₃ (see Supporting Information). However, even in this case, there is still a long way to go before alanate systems can be accepted as viable hydrogen storage medium due to the concerns about its safety in practical operation and industrial-scale production.

In summary, TiF₃ is superior to TiCl₃ as a dopant precursor in preparation of catalytically enhanced NaAlH₄ for reversible hydrogen storage. The hydrogen storage performances of the doped hydride, on both the hydrogen capacity and de-/hydriding kinetics, have been further improved upon changing the dopant precursor from popular TiCl₃ to TiF₃. In particular, the pronounced catalytic activity of TiF₃ allows de-/hydrogenation of NaAlH₄ to be performed at a considerably reduced temperature and/or pressure conditions. In view of the analogy between these two Ti compounds, these findings challenge the traditional beliefs that the anions in the dopant precursors contribute nothing but to generate inactive by-products. Further investigation into the nature of this modification may promote the development of new mechanisms, and thus lead to further improved hydrogen storage performance of alanate systems.

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