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A novel catalyst precursor K_2TiF_6 with remarkable synergetic effects of K, Ti and F together on reversible hydrogen storage of NaAlH₄†‡

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A synergetic effect of K, Ti and F together on improving the reversible hydrogen storage properties of NaAlH₄ is found by intruding K_2TiF_6 as catalyst precursor. Around 4.4 wt% of hydrogen can be released from the NaAlH₄–0.025 K_2TiF_6 sample within 40 min at 140 °C.

Complex hydrides of light metals, such as alanates, borohydrides and amides, have attracted considerable attention as potential hydrogen storage media due to their high gravimetric and volumetric hydrogen capacities.¹ NaAlH₄ is regarded as the most promising one of them for practical applications since Bogdanović and Schwickardi found that it could reversibly store 3–4 wt% hydrogen under moderate conditions by introducing a small amount of Ti-based additive.² It is well known that NaAlH₄ decomposes to release hydrogen in three steps according to the following reactions:

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

$$Na_{3}AlH_{6} \rightleftharpoons 3NaH + Al + \frac{3}{2}H_{2}$$
(2)

$$NaH \rightleftharpoons Na + \frac{1}{2}H_2$$
 (3)

The stepwise reaction liberates about 3.7, 1.9 and 1.9 wt% hydrogen, respectively. However, only the first two steps are utilized for technical applications since the decomposition of NaH occurs at high temperatures (> 400 °C). So, the amount of hydrogen practically available is ~ 5.6 wt%, which is close to the new 2010 target (4.5 wt% for system) set by the US DOE in 2009.3 Recent investigations on NaAlH₄ were mainly focused on understanding the roles played by Ti-based additives and exploring novel high-performance catalysts.4-8 Various hypotheses have been proposed to explain the catalytic nature of the active Ti species, including the formation of catalytic $Al_x Ti_v$ complexes,⁴ the substitution of Ti for Na or Al,⁵ and the presence of Na and/or Al vacancy.⁶ It was also found that the F⁻ anion plays an important role in improving the de-/hydriding performances of NaAlH₄ as TiF₃ exhibits a superior catalytic effect over TiCl₃ owing to the favorable thermodynamic modification caused by the substitution of H⁻ by F⁻.⁷ Moreover, introducing KH into NaAlH₄ pronouncedly enhances the dehydrogenation performances as well, especially for the decomposition of Na₃AlH₆ (reaction (2)).⁸ In spite of these intense research efforts, a complete understanding of the roles played by the catalysts is still lacking, and further improvements in the de-/hydriding thermodynamics and kinetics of NaAlH₄ are highly desirable. Here, we are reporting a novel additive, K₂TiF₆, which provides the synergetic catalytic effects of Ti, F and K together for NaAlH₄.

Five samples of NaAlH₄ with no and different amounts of K_2TiF_6 introduced were prepared by ball milling as described in the ESI.[‡] After 36 h of milling, pressure increases were detected inside the milling jars with K₂TiF₆ as additives while no pressure change was observed for the jar with pure NaAlH₄ (Table S1, ESI[‡]). Since NaAlH₄ is quite stable when ball milled alone, the hydrogen generated from the samples with catalyst should come from the chemical reaction between NaAlH₄ and K₂TiF₆. As shown in Table S1 (ESI[‡]), ca. 0.12 atoms of H are liberated from NaAlH₄-0.01 K₂TiF₆, and the hydrogen release amounts to 0.36 atoms for NaAlH₄-0.03 K₂TiF₆. A proportional increase in the dehydrogenation amount with respect to the addition of K₂TiF₆ is disclosed. To understand the mechanochemical reaction between NaAlH₄ and K₂TiF₆, XRD analysis was carried out on the post-36 h milled NaAlH₄-0.03 K₂TiF₆ sample (Fig. 1a). Obviously, the NaAlH₄ phase dominates in the XRD profile. In the meantime, the characteristic peaks of Na₃AlH₆, KAlH₄, KH, Al, NaF and TiF₃ can all be identified on referring to the PDF-2 database of the JCPDS-ICDD. Thus, the chemical reaction between NaAlH₄ and K₂TiF₆ during ball milling can be expressed as follows:

$$6\text{NaAlH}_4 + \text{K}_2\text{TiF}_6 \xrightarrow{\text{BM}} \text{Na}_3\text{AlH}_6 + \text{KAlH}_4 + \text{KH} + 3\text{NaF} + 4\text{Al} + \text{TiF}_3 + \frac{13}{2}\text{H}_2$$
(4)

According to reaction (4), 0.03 mol of $K_2 TiF_6$ reacts with 0.18 mol of NaAlH₄ to liberate 0.195 mol of H₂, which is in good agreement with the experimental result shown in Table S1 (0.36 H atoms, ESI‡). Similar solid-state transformation of [AlH₄] into [AlH₆] has also been found for TiCl₄-doped LiAlH₄.⁹

As compared to the pristine sample, dramatic shifts towards lower temperatures are observed for the first two peaks of dehydrogenation of K_2TiF_6 -added samples by TPD testing while the position of the third peak remains almost unchanged (Fig. S1, ESI‡). It suggests that K_2TiF_6 works as an effective catalyst only for the decomposition of [AlH₄] and [AlH₆]

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[‡] Electronic supplementary information (ESI) available: Material preparation and characterization; amount of hydrogen released during milling; TPD curves of NaAlH₄ with K₂TiF₆; dehydrogenation curves of NaAlH₄ with different additives; dehydrogenation curves of NaAlH₄–0.025 K₂TiF₆ and NaAlH₄–0.025 TiF₃–0.025 KH–0.075 NaF; dehydrogenation curves of NaAlH₄–0.025 K₂TiF₆ at different heating rates; hydrogenation curves of dehydrogenated NaAlH₄–0.025 K₂TiF₆. See DOI: 10.1039/c0cc03264f



Fig. 1 XRD patterns of the post-36 h milled NaAlH₄–0.03 K₂TiF₆ sample (a) and the dehydrogenated NaAlH₄–0.025 K₂TiF₆ samples at different stages.

groups. Hence, quantitative measurements were focused only on the first two steps of dehydrogenation reaction. Fig. 2 shows the hydrogen desorption curves of NaAlH₄ with and without K_2TiF_6 . As expected, the operating temperatures for hydrogen desorption of NaAlH₄ are all significantly lowered after adding K_2TiF_6 . Regretfully, the hydrogen capacities are also decreased due to the dead weight of additives which do not contain hydrogen. Taking into account the operating temperature and the hydrogen capacity, 0.025 mol should be the optimal concentration for adding K_2TiF_6 into NaAlH₄ in the present study. Approximately 4.4 wt% of hydrogen or 2.64 atoms of H is released from NaAlH₄–0.025 K_2TiF_6 milled for 36 h in the temperature range of 75–175 °C. Inspiringly, a 110 °C reduction in the end temperature for the second step of dehydrogenation is attained relative to the pure NaAlH₄.

For unveiling the chemical process which occurred in the dehydrogenation process, $NaAlH_4$ –0.025 K_2TiF_6 samples at different dehydrogenation stages were collected for XRD examination. As shown in Fig. 1b, the $NaAlH_4$ –0.025 K_2TiF_6 sample milled for 36 h is comprised of $NaAlH_4$, Na_3AlH_6 , KAlH₄, KH, NaF, Al and TiF₃. After dehydrogenation at 135 °C, the intensity of diffraction peaks of $NaAlH_4$ is



Fig. 2 Dehydrogenation curves of NaAlH₄ with and without K_2TiF_6 with temperatures.

distinctly weakened, and correspondingly peaks of Na₃AlH₆ and Al are enhanced. Meanwhile, Al₃Ti can be identified from the shoulder on the high-angle side of the strongest Al reflection with the disappearance of TiF₃. As the temperature is elevated to 160 °C, NaAlH₄ is almost not detectable, and a new product of NaH is observed with the growth of diffraction peaks of Al. In addition, K₂NaAlH₆ is also discernible with relatively weak diffraction peaks. At 200 °C, the dehydrogenated product contains NaH, Al, NaF, K₂NaAlH₆ and Al₃Ti. From the above changes, we are trying to present a full picture of the chemical process for dehydrogenation of K₂TiF₆-added NaAlH₄ with temperatures.

Below 135 °C, NaAlH₄ first reacts with TiF₃ to yield NaF, Al₃Ti and H₂.

$$3NaAlH_4 + TiF_3 \rightarrow NaF + Al_3Ti + 6H_2$$
 (5)

With catalysis of Al₃Ti and NaF, the self-decomposition of NaAlH₄ occurs simultaneously according to reaction (1). As the temperature is increased to 200 °C, Na₃AlH₆ decomposes to release hydrogen and convert to NaH and Al (reaction (2)). Moreover, part of the newly developed NaH may further react with KH and KAlH₄ to convert to K₂NaAlH₆ as a side reaction caused by a favorable thermodynamic condition since the decomposition of Ti-doped KAlH₄ occurs at above 200 °C.¹⁰

$$KAlH_4 + KH + NaH \rightarrow K_2NaAlH_6$$
(6)

Based on the above reactions, the theoretical dehydrogenation capacity is calculated to be about 4.5 wt% (2.7 H atoms) for the NaAlH₄–0.025 K₂TiF₆ sample milled for 36 h, which is consistent with the experimental results shown in Fig. 2.

A comparative evaluation on the isothermal dehydrogenation kinetics of NaAlH₄ and NaAlH₄-0.025 K₂TiF₆ was performed (Fig. 3). It is seen that the isothermal dehydrogenation kinetics of NaAlH₄ is dramatically enhanced by adding 0.025 mol of K₂TiF₆. For the pure NaAlH₄, no appreciable hydrogen desorption is detected within 300 min at 140 °C. However, the NaAlH₄-0.025 K_2TiF_6 sample releases ~4.4 wt% of hydrogen, almost all hydrogen in the post-milled sample in 40 min at the same temperature. Even at a temperature as low as 100 °C, it also liberates ~ 2.6 wt% of hydrogen in 90 min. More interestingly, isothermal desorption kinetics of the K2TiF6-added NaAlH4 is much faster than that of TiF₃ or KH-doped samples.^{7,8} This phenomenon indicates that a synergistic catalysis from the active species Ti, F and K is existing for NaAlH₄. As mentioned above, TiF₃, KH and NaF are involved in the post-36 h milled NaAlH₄-0.025 K₂TiF₆ sample. Among these catalysts, TiF₃ first reacts with NaAlH₄ in the heating process to form Al₃Ti which facilitates specifically the catalytic dissociation and recombination of hydrogen molecules on its surface.⁴ It is also reported that NaF particles work as nucleation centers for the formation of NaH due to their identical crystallographic structure and comparable lattice parameter, which promotes nucleation and growth of NaH in the dehydrogenation process.¹¹ On the other hand, the Al-H bonds in [AlH₄] and [AlH₆] groups are weakened by the substitution of F⁻ anion for H⁻, resulting in the decrease of the stability of the Al-H group.⁷ Moreover, recent studies reveal



Fig. 3 Isothermal dehydrogenation curves of NaAlH₄ and NaAlH₄–0.025 K_2 TiF₆.

that the addition of KH substantially decreases the enthalpy change for the decomposition of Na₃AlH₆, and consequently lowers the operating temperature for hydrogen desorption.⁸ Thus, we believe that in the present study, the *in situ* developed Al₃Ti, NaF and KH by reacting K₂TiF₆ with NaAlH₄ are working together to improve remarkably the dehydrogenation kinetics of NaAlH₄. Significantly, it exhibits a much superior catalytic performance over the addition of TiF₃, KH or NaF alone as seen in Fig. S2 (ESI‡). A strong synergetic catalysis of Ti, K and F is the result, which is further supported by the fact that co-adding TiF₃, KH and NaF gives similar effects on the dehydrogenation of NaAlH₄ (Fig. S3, ESI‡). More excitingly, the synergetic catalytic effects exhibit good cycling stability (Fig. S4, ESI‡), which is meritorious for practical applications.

Fig. 4 shows the Kissinger plots of the first- and second-step dehydrogenation of NaAlH₄–0.025 K₂TiF₆. T_m was extracted here by differentiating the non-isothermal dehydrogenation curves as shown in Fig. S5 (ESI^{\ddagger}). The activation energy (E_a) is calculated to be 99.8 and 88.0 kJ mol⁻¹ for the first and second dehydrogenation, a 15% and 27% reduction relative to the pristine sample,¹² respectively. Interestingly, a bigger reduction in E_a is achieved for the second dehydrogenation, viz., the decomposition of Na₃AlH₆. It indicates that the synergetic catalysis of Ti, F and K is more effective for decomposition of [AlH₆] group than that of [AlH₄] group in this case. The rehydrogenation experiment (Fig. S6, ESI[‡]) shows that under an initial hydrogen pressure of 105 atm, the dehydrogenated NaAlH₄-0.025 K₂TiF₆ sample starts to absorb hydrogen at about 45 °C, a rather low hydrogenation temperature for alanates. As the temperature is elevated to 120 °C, ~4.3 wt% of hydrogen is recharged, exhibiting a good reversibility for hydrogen storage.

In summary, we have found a remarkable improvement in hydrogen storage performances of NaAlH₄ by introducing K_2TiF_6 as a catalyst precursor. It is found that K_2TiF_6 reacts with NaAlH₄ to convert into Al₃Ti, KH and NaF during ball milling and subsequent heating. The newly developed Al₃Ti, KH and NaF work together as active species for improving hydrogen storage in NaAlH₄ with a synergetic catalysis. This finding opens up a feasible way for



Fig. 4 Kissinger plots for the first- and second-step dehydrogenation of $NaAlH_4$ -0.025 K₂TiF₆.

further improving hydrogen storage performances of alanates *via* the finding and design of novel high-performance catalysts.

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