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Catalytic effect of Al₃Ti on the reversible dehydrogenation of NaAlH₄

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Abstract

Al₃Ti was directly utilized as catalyst precursor to examine its catalytic activity in the reversible dehydrogenation of NaAlH₄. It was observed that Al₃Ti possessed considerable catalytic effect on the de-/hydriding reactions of NaAlH₄. The catalytic enhancement by Al₃Ti doping significantly increased with increasing ball-milling time. Moreover, it was noted that dehydriding kinetics and cycling performance of the Al₃Ti-doped NaAlH₄ were highly dependent on the starting material, 1:1 NaH/Al mixture or NaAlH₄. The combined property and phase examinations suggest that Al₃Ti may act as active species to catalyze the reversible de-/hydrogenation of NaAlH₄. © 2006 Published by Elsevier B.V.

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1. Introduction

Upon doping with a Ti-based catalyst, NaAlH₄ may undergo reversible dehydrogenation following Eq. (1) under moderate temperatures.

$$NaAlH_4 \iff 1/3Na_3AlH_6 + 2/3Al + H_2$$
$$\iff NaH + Al + 3/2H_2 \tag{1}$$

The two-step reversible reactions of NaAlH₄ yield a theoretical hydrogen capacity of 5.6 wt.%. The relatively high capacity, in combination with the moderate operation temperature and large reversibility, makes catalytically enhanced Ti–NaAlH₄ rather attractive as a potential hydrogen storage medium for onboard application [1–11].

While the catalytic enhancement arising upon doping NaAlH₄ with a Ti catalyst has been well established, the mechanism by which active Ti-species catalyze the dehydriding/rehydriding reaction of NaAlH₄ is still unclear. Even the nature of active Ti-species is still a subject of speculation and controversy. Several Ti-containing species, including zerovalent Ti [1,12–15], Al–Ti Alloy [9,16–23], Ti hydride(s) [23,24] and Ti cation with variable valances [25,26], have been sug-

0925-8388/\$ – see front matter © 2006 Published by Elsevier B.V. doi:10.1016/j.jallcom.2006.01.006 gested to act as active catalysts. Among them, Al₃Ti is the most thermodynamically stable phase ($\Delta G_{\rm f}^{\circ} = -136 \, \text{kJ/mol}$), followed by TiH₂ ($\Delta G_{\rm f}^{\circ} = -86$ kJ/mol) and AlTi alloy ($\Delta G_{\rm f}^{\circ} =$ -72 kJ/mol). The speculation that Al₃Ti acts as active species was also supported by theoretical calculation, X-ray absorption and electron-microscopy studies [19,21]. Actually, the formation of Al₃Ti has already been experimentally confirmed in the mechanically milled 4:1 LiAlH₄/TiCl₄ and 3:1 NaAlH₄/TiCl₃ mixtures. And the pronounced catalytic enhancement achieved in TiCl₄ or TiCl₃-doped hydrides has been partially attributed to the in situ formed nano/micro-crystalline Al₃Ti during milling [9,16]. At a typical doping level of $<5 \mod \%$, however, direct phase identification has provided no convincing evidence about the existence of crystalline Al₃Ti. Therefore, it was generally speculated that Al₃Ti presents in the hydride matrix in an X-ray amorphous state [1,12,17–19,23]. On the other hand, the hypothesis about Al₃Ti acting as active species was challenged by the property measurements. It was reported that direct doping the hydrides with Al₃Ti did not result in a considerable catalytic enhancement [16,29]. Therefore, whether Al₃Ti can explain the nature of active Ti-species is still an open question.

The present study aims at clarification of the catalytic effect of Al₃Ti on the reversible dehydrogenation reactions of NaAlH₄. For this purpose, Al₃Ti was prepared and directly utilized as a dopant precursor to prepare doped NaAlH₄, and

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the property and structure of the Al_3Ti -doped $NaAlH_4$ were investigated.

2. Experimental section

The starting materials NaH (95%, 200 mesh, <74 μ m), Al powder (99.95+%, 200 mesh, <74 μ m) were all purchased from Sigma–Aldrich Corp. and used as received. Raw NaAlH₄ was purchased from Albemarle Corp. and purified following a procedure as described in [27] before usage. Al₃Ti was prepared by arc-melting stoichiometric mixtures of pure Al (99.9%) and Ti (99.8%) metals under Ar atmosphere in a water-cooled copper hearth. To ensure composition homogeneity, the alloy ingot was turned over and re-melted for three times during arc-melting. The as-prepared Al₃Ti(D0₂₂) ingot was smashed and then mechanically milled for 10 h under Ar atmosphere by using a high-energy SPEX 8000 mill to prepare a metastable Al₃Ti(L1₂) dopant precursor.

The powder mixtures of NaH + Al + 4 mol% Al₃Ti and NaAlH₄ + 4 mol% Al₃Ti were mechanically milled under Ar atmosphere by using a Fritsch 7 Planetary mill at 400 rpm in a vial together with eight balls (10 mm in diameter) made of stainless steel. The ball-to-powder weight ratio was around 40:1. All sample operations were performed in an Ar-filled glove box equipped with a recirculation system to keep the H₂O and O₂ levels < 1 ppm.

Hydriding/dehydriding behaviors of the samples were examined by using a carefully calibrated Sievert's type apparatus. A typical cyclic experiment entailed absorption at 120 °C and desorption at 150 °C with an initial pressure condition about 11 MPa and <100 Pa, respectively. To minimize H_2O/O_2 contamination, the high-purity hydrogen gas (with 99.999%) was further purified using a hydrogen storage alloy system. Hydrogen capacity was determined with respect to the total sample weight, including the catalyst.

The samples were characterized by powder X-ray diffraction (XRD, Rigaku D/MAX-2500, Cu K α radiation) and scanning electron microscope (SEM, LEO Supra 35) equipped with an energy dispersive X-ray (EDX) analysis unit (Oxford). All the sample preparation was operated in the Ar-filled glove-box. To minimize the H₂O/O₂ contamination during the XRD measurement, small amount of grease was used to cover the surface of the samples. The SEM samples were prepared by spreading the dry powder on conducting tape supported on a copper pole. The subsequent sample transferring into SEM equipment was performed in a specially designed Ar-filled device.

3. Results and discussion

Al₃Ti has two types of crystal structure. Upon mechanical milling, Al₃Ti may undergo polymorphic modification from tetragonal $D0_{22}$ - to metastable cubic $L1_2$ -structure [9]. In view of that mechanical milling has been generally adopted as a predominant technique in preparation of doped hydrides, we selected cubic L12-type Al3Ti as dopant to prepare doped NaAlH₄. Metastable cubic L1₂-Al₃Ti was prepared by mechanically milling the arc-melted Al₃Ti under Ar atmosphere by using a high-energy SPEX 8000 mill. As shown in Fig. 1, a complete transformation from tetragonal D0₂₂- to cubic L1₂phase had been achieved after 10h milling. The XRD pattern of this metastable phase is characterized by low-intensity and wide diffraction peaks, indicating the grain pulverization and the introduction of micro-strain during milling process. According to Scherrer equation, the grain size of L1₂-Al₃Ti after 10 h milling was estimated to be about 5 nm.

Nanocrystalline Al₃Ti was found to possess catalytic function on the de-/hydriding reactions of NaAlH₄. Moreover, the catalytic enhancement by Al₃Ti doping becomes more pronounced with increasing milling time. Fig. 2 gives the XRD patterns of the samples prepared by mechanical milling 1:1 NaH/Al mixture with 4 mol% Al₃Ti under Ar atmosphere for 1, 5, and

(i) Al₃Ti, as prepared (D0₂₂) (a) Al₃Ti, as prepared (D0₂₂) (b) Al₃Ti, ball-milled for 10h (L1₂) (c) Al₃Ti, ball-milled for 10h (L1₂) 20 30 40 50 60 70 80 20 (deg.)

Fig. 1. XRD patterns of the conventionally prepared Al_3Ti (D0₂₂) (a) and the metastable Al_3Ti (L1₂) formed after ball-milling for 10 h (b).

10 h, respectively, followed by hydrogenation with an initial Hpressure of about 11 MPa for over 10 h. For the 1 h sample, the long period of hydrogen exposure only resulted in a partial restoration of Na₃AlH₆. While for the sample milled for 10 h, a largely complete restoration of NaAlH₄ from the NaH/Al mixture has been achieved in the hydriding process.

The increased hydrogenation level with increasing the milling time was further quantified by dehydriding measurements. As seen in Fig. 3, the sample milled for 1 h only released about 0.6 wt.% hydrogen after being kept at $150 \degree \text{C}$ for over 10 h. When the milling time was increased to 10 h, the sample was observed to release 4.0 wt.% hydrogen within about 10 h. This value corresponds to about 80% of the theoretical hydrogen capacity of the doped sample containing $4 \mod \%$ Al₃Ti dopant. Here, it should be noted that the increasingly favorable de-/hydriding performance arising upon increasing the milling time



Fig. 2. The XRD patterns of the samples prepared by mechanically milling NaH+Al+4 mol% Al₃Ti under Ar atmosphere for (a) 1 h; (b) 5 h; (c) 10 h. The inset gives the magnified patterns of the marked region in Fig. 2 and the corresponding multi-peaks lines fitted by Lorentz function.



Fig. 3. The typically dehydriding profiles at $150 \,^{\circ}$ C of NaH + Al + 4 mol% Al₃Ti mixtures milled under Ar atmosphere for 1, 5 and 10h, respectively.

were also observed in our studies on the metallic Ti-doped NaAlH₄ [27,28].

Al₃Ti is highly stable according to thermodynamic consideration. It was therefore highly expected that Al₃Ti retained its phase stability during milling process. However, definite identification of Al₃Ti in doped samples by XRD is difficult due to the combined effects of co-existence of large amount of Al, the close peak position of Al₃Ti to that of Al and the nanostructure of Al₃Ti. To minimize the interference of Al phase, we examined the samples in the hydrogenated state, as given in Fig. 2. Even in this case, the diffraction signal of Al₃Ti only appears as a weak and broad peak at the higher angle side of Al peaks (at $2\theta = 39.3^{\circ}$). In addition, no reaction between NaH/Al mixture (or sodium aluminum hydride) and nanocrystalline Al₃Ti is expected to occur during the milling process. Therefore, the improved catalytic enhancement arising upon increasing milling time should be correlated to the increasingly favorable dispersion of Al₃Ti in the hydride matrix. This was evidenced by the SEM morphology observation combined with EDX analyses. As seen in Fig. 4, a more homogeneous distribution of the Ticontaining particles (bright ones) in the NaH/Al matrix has been achieved after increasing the milling time from 1 to 10 h. EDX analyses confirm that the Al/Ti atomic ratio in the bright particles is close to 3:1. Recently, there have been several experimental efforts to clarify the catalytic activity of Al₃Ti in the reversible dehydrogenation of NaAlH₄, but with no positive results and conclusions being reported [16,29]. This is in great contrast to our findings. One possible reason is that the applied milling time in the literatures, typically around 1 h, was insufficient to achieve a favorable distribution of Al₃Ti phase in the hydride matrix.

We further examined the sample prepared by milling 1:1 NaH/Al with Al₃Ti under Ar atmosphere for 10 h, and found that its cycling performance was highly stable. As shown in Fig. 5, other than a slightly decreased H-capacity from the NaAlH₄/Na₃AlH₆ + Al decomposition step in the first cycle, the dehydriding profiles of the following cycles are almost identical. The samples after the first and 5 cycles, both in the hydrogenated state, were examined by XRD. It was observed from Fig. 6 that the phase stability of Al₃Ti was well maintained in



Fig. 4. Back scattering electron (BSE) images of NaH + Al + 4 mol% Al₃Ti mechanically milled under Ar atmosphere for 1 h (top, left), 10 h (top, right), and the representative EDX results. It should be noted that, despite the special caution taken, a significant amount of oxygen contamination has been introduced into the samples during sample transfer.



Fig. 5. The cyclic stability of the NaH + Al + $4 \mod \%$ Al₃Ti mixture milled under Ar atmosphere for 10 h.

the de-/hydriding cycles. This is consistent with the recent studies using X-ray absorption spectroscopy [14,19,21].

These results suggest that Al₃Ti may act as active species and catalyze the reversible de-/hydriding reactions of NaAlH₄, thus providing evidence to support the previous speculation about the catalytic function of Al₃Ti. However, before this finding could be generalized to account for the nature of active Ti-species in the Ti–NaAlH₄ system, further investigations are still required to achieve a comprehensive understanding of the following experimental findings:

 Catalytic effect of Al₃Ti was significantly weaker than that of Ti(III) or Ti(IV) dopants on the sorption properties of NaAlH₄. As seen in Fig. 5, the Al₃Ti-doped hydrides take about 1 h to fulfill the first dehydriding step, and another 10 h to complete the second step at 150 °C. While for the



Fig. 6. The XRD patterns of the NaH + Al + 4 mol% Al₃Ti mixture milled under Ar atmosphere for 10 h. (a) in the hydrogenated state in the first cycle; (b) in the hydrogenated state in the sixth cycle. The inset gives the magnified patterns of the marked region in Fig. 6 and the corresponding multi-peaks lines fitted by Lorentz function.



Fig. 7. The cyclic stability of $NaAlH_4 + 4 \mod 8 Al_3Ti$ mechanically milled under Ar atmosphere for 10 h.

 $TiF_3/TiCl_3$ -doped samples, the typical dehydriding periods for fulfilling the two steps are within 10 min and 2–3 h, respectively.

- (2) The variation of starting materials for Al₃Ti doping leads to substantially different hydrogen storage performance. In great contrast to the highly stable cycling performance of the 1:1 NaH/Al mixture doped with Al₃Ti (as seen in Fig. 5), the sample prepared by milling NaAlH₄ with Al₃Ti was observed to undergo serious capacity degradation during the first several cycles. As shown in Fig. 7, the H-capacity decreased from the initial 3.2 to about 2.0 wt.% after four cycles, especially with a degradation of ~0.8 wt.% in the first two cycles. In addition, the dehydriding kinetics of the sample doped from NaAlH₄ was found to be significantly lower than that of the sample doped from the 1:1 NaH/Al mixture.
- (3) Recently, we have found that mechanical milling the 1:1 NaH/Al mixture (or NaAlH₄) together with metallic Ti powder resulted in the in situ formation of nanocrystalline Ti hydride, which might act as active species to enhance the reversible dehydrogenation of NaAlH₄ [30]. This finding further complicated the situation of the Ti–NaAlH₄ system. In view of thermodynamic consideration, both Al₃Ti and TiH₂ are more stable than zerovalent Ti. Experimentally, the phase stability of both phases in the de-/hydriding cycles was evidenced by the XRD examinations [30]. Therefore, it is hard to generalize a common active Ti-species originated from different Ti-sources. Rather these findings suggest a possibility that there exist different active Ti-species that can catalyze the reversible de-/hydriding reactions of NaAlH₄.

Further research efforts to answer these "puzzling" questions may provide valuable hints for understanding the key aspects of the catalytically enhanced Ti–NaAlH₄ system, including the effect of distribution of catalyst particles, the nucleation/growth processes of the parent hydride with the presence of catalyst particles, and the catalysis mechanism.

4. Conclusions

Directly doping the hydride with Al₃Ti through long period of mechanical milling results in a considerable catalytic enhancement on the reversible dehydrogenation of NaAlH₄. This finding supports the previous hypothesis about the catalytic function of Al₃Ti. However, the catalytic effect from Al₃Ti doping was substantially weaker than from Ti-halide doping. In addition, dehydriding kinetics and cycling performance of the Al₃Ti-doped hydrides was found to be highly dependent on the starting material, 1:1 NaH/Al mixture or NaAlH₄. Therefore, further investigations on distribution of the catalyst particles and its influence on the H-storage performance of the material, and the nucleation/growth processes involved in de-/hydriding reactions of NaAlH₄ are still required to firmly establish the catalytic mechanism of Al₃Ti in the reversible dehydrogenation of NaAlH₄.

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