

Dehydrogenation properties of LaCl_3 catalyzed NaAlH_4 complex hydrides

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Abstract

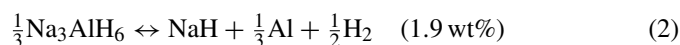
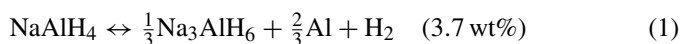
The effect of LaCl_3 dopant on the dehydrogenation properties of complex hydride NaAlH_4 has been investigated. The powder mixtures of NaAlH_4 and LaCl_3 were prepared by dry ball milling and the microstructure of powder mixture after milling and dehydrogenation were characterized by XRD and SEM. It was shown that the LaCl_3 dopants could markedly enhance the dehydriding kinetic performance of NaAlH_4 , especially the first decomposition reaction. The 5-h milled NaAlH_4 –2 mol% LaCl_3 mixture achieved 3.0 wt% hydrogen release in less than 2 h at a temperature of 120 °C.

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1. Introduction

Light metal complex hydrides, a new class of hydrogen storage materials, have drawn intensive research interest due to their high hydrogen content and moderate working temperature, which possibly meet the target established for the on-board hydrogen source for fuel cell. The typical complex hydride NaAlH_4 doped with the transition metal compounds, such as TiCl_3 and $\text{Ti}(\text{OBu}^n)_4$, firstly explored by Bogdanovic and Schwickardi [1,2] in the middle of 1990s, could release and readsorb about 5.6 wt% hydrogen in a two-step reversible chemical reaction (Eq. (1) and (2)) under mild condition. Before this breakthrough, the sodium alanate NaAlH_4 was considered



impossible to be rehydrogenated under practical conditions. Bogdanovic's finding has stimulated extensive investigations of NaAlH_4 and other alanates, and great effort has been aiming at searching for more efficient dopants and doping process. Considerable improvements in the kinetics and cycling perfor-

mances have been achieved in the past several years [3–14]. So far, doping NaAlH_4 with titanium-based compounds TiCl_3 by mechanical milling is considered as the most efficient approach [15]. Despite these improvements, there exist some unsolved scientific and engineering subjects for the commercial application of NaAlH_4 . For example, the nature and mechanism of catalytical species on the dehydrogenation and rehydrogenation reactions of NaAlH_4 are not well understood [7,16–18]. On the other hand, the high over pressure (not less than 10 MPa) and the sluggish rehydriding reaction kinetics are still two key technical challenges.

Rare earth compounds as catalyst have been greatly applied in various organic synthesis reactions because their specific electron structures, but the role of the rare earth compounds on the decomposition reactions of complex hydrides is rarely explored. Recently Bogdanovic's group reported the pronounced dehydrogenation and rehydrogenation properties of NaAlH_4 doped with rare earth chlorides CeCl_3 , SmCl_3 [19], but the nature of catalyst and the relevant catalytic mechanism is still unknown. The present work explores the structure and dehydrogenation properties of mechanical-milling prepared NaAlH_4 – LaCl_3 system.

2. Experimental details

NaAlH_4 (95%, 200 mesh) and LaCl_3 ($\text{La}_2\text{O}_3/\text{TREO} > 99.99\%$) were purchased from Sigma–Aldrich Co. and Rico National Engineering Research Center

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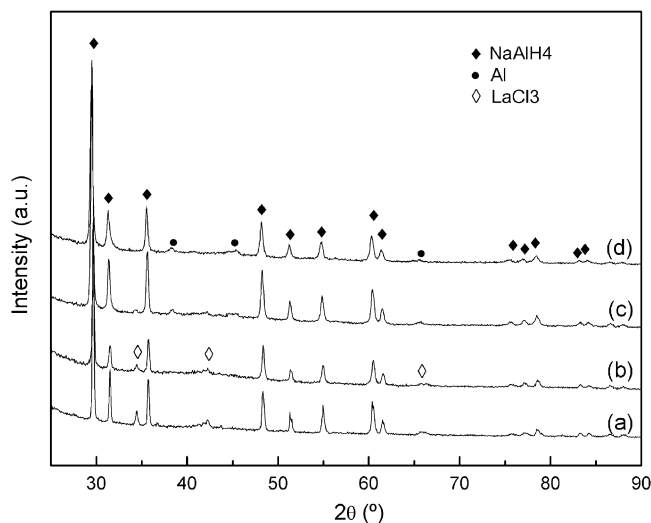


Fig. 1. XRD patterns of NaAlH_4 -2 mol% LaCl_3 mixtures milled for different times: (a) 0 h, (b) 0.5 h, (c) 1 h and (d) 5 h.

of Rare-earth Metallurgy and Functional Materials (China), respectively. The mixture of NaAlH_4 -2 mol% LaCl_3 was prepared by vibratory mill at 1400 rpm using the stainless vial and balls. The milling was performed under the protection of pure argon (99.99%) with the ratio of ball to powder to be 40:1. The milling was stopped for 15 min after every 30 min of milling to avoid temperature rising during milling.

X-ray diffraction (XRD) analysis was performed with a Philips X'Pert X-ray (Cu $K\alpha$ radiation) diffractometer. The powder samples were mixed with liquid paraffin to protect it from atmosphere during XRD analysis. Isothermal dehydrogenation properties were examined in a gas reaction controller made by Advance Materials Corporation, the starting hydrogen pressure is 10 kPa. All the handlings of specimens were performed in the glove box under high pure argon atmosphere and with the content of water and oxygen less than 2 ppm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the NaAlH_4 -2 mol% LaCl_3 mixture milled for different duration. The diffraction peaks of NaAlH_4 and LaCl_3 are clearly observed for initial elemental powders. The peaks attributed to LaCl_3 gradually weakened and broadened with increasing the milling time. After 5 h of milling,

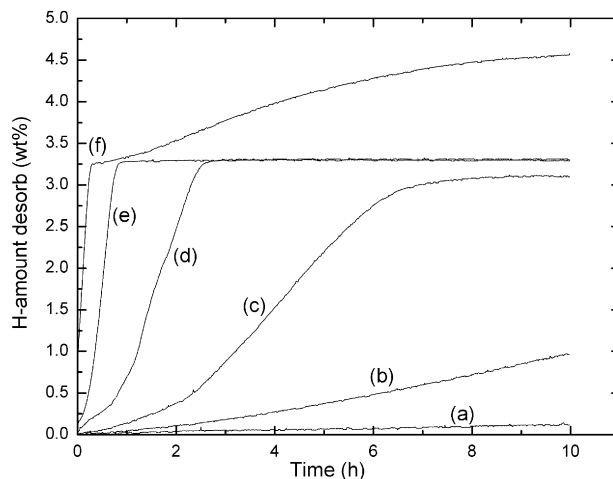


Fig. 3. Dehydrogenating curves of 1-h milled NaAlH_4 -2 mol% LaCl_3 mixtures at different temperatures: (a) 80 °C, (b) 100 °C, (c) 120 °C, (d) 140 °C, (e) 160 °C and (f) 180 °C.

the diffraction peaks of LaCl_3 completely disappear. This phenomenon is commonly explained by the refining of crystallite size and the introduction of internal strain caused by high-energy ball milling. It can be observed from the back scattering electron image of the 0.5-h/5-h milled NaAlH_4 -2 mol% LaCl_3 sample, as shown in Fig. 2, that LaCl_3 particle (bright particles) is homogeneously distributed in the NaAlH_4 matrix materials after longer milling time. Three new weak peaks corresponding to Al phase appear in the XRD profiles of samples milled for 1 h and 5 h, but not for 0.5 h. It is believed that the formation of Al is due to the first step decomposition reaction of NaAlH_4 (see Eq. (1)) during relatively long-term ball milling, not the reaction of NaAlH_4 and LaCl_3 (see Eq. (3)), because the diffraction peaks of NaCl are invisible. The absence of the diffraction peaks of the corresponding decomposition product— Na_3AlH_6 (see Eq. (1)) is probably due to its small amount and weak X-ray scattering intensity.

Isothermal dehydrogenation curves of the 1-h milled NaAlH_4 -2 mol% LaCl_3 mixture at different temperatures are shown in Fig. 3. It shows that the dehydrogenating kinetics of NaAlH_4

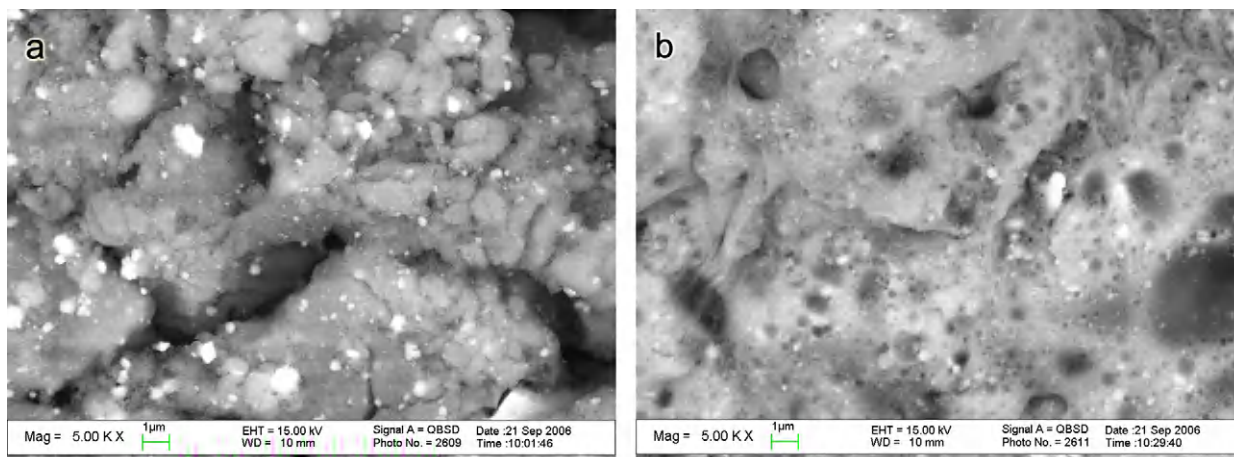


Fig. 2. Back scattering electron image of NaAlH_4 -2 mol% LaCl_3 mixture, the bright particles are LaCl_3 : (a) 1-h milled sample and (b) 5-h milled sample.

is improved with the increasing of dehydrating temperature. When temperature was raised to 120 °C, the dehydrating curve firstly presented a fast hydrogen desorption stage and then a maximum H₂ desorption amount corresponding to 3.0 wt%. At temperature ranging from 140 °C to 160 °C, the maximum H₂ desorption amount was around 3.2 wt%. At 180 °C, the dehydrating curve successively mounts up after a short plateau and finally overall hydrogen desorption capacity of 4.5 wt% is achieved. This capacity is much lower than the theoretical level (5.6 wt%), which is associated with the impurity in the original NaAlH₄ powder, the amount of LaCl₃ dopants and the above-mentioned partial decomposition of NaAlH₄ during milling. It can be found from Fig. 3 that the dehydrating curves of NaAlH₄ at temperature ranging from 120 °C to 160 °C reveal almost the same plateau capacity. The dehydrating kinetics of NaAlH₄ measured below 120 °C is greatly slow and the hydrogen desorption capacity is also dramatically lowered.

Fig. 4 shows the XRD patterns of above samples after dehydrogenation at different temperatures. The strong diffraction peaks of NaAlH₄ in the diffractogram: (a) reveals that most NaAlH₄ could not decompose at 100 °C, whereas the weak diffraction peaks of NaAlH₄ in the diffractogram (b) suggests that only small amount of NaAlH₄ is remained after dehydrogenation at 120 °C. The diffractogram (c) and (d) are very similar with the absence of NaAlH₄ and NaH Bragg peaks and the appearance of Na₃AlH₆ Bragg peaks, which indicates that only the first step decomposition reaction of NaAlH₄ was completed at 140 °C and 160 °C. The increasement of peak intensity of Na₃AlH₆ and Al from diffractogram (b) to (d) shows that the decomposition amount of NaAlH₄ increased with the increasement of temperature. And this result can partly explains the relatively lower maximum H₂ desorption amount at 120 °C than that at 140 °C and 160 °C. When dehydrogenated at 180 °C, the disappearance of the diffraction peaks of Na₃AlH₆ and NaAlH₄ implies the full decomposition of NaAlH₄ and Na₃AlH₆, which also explains the highest hydrogen desorption content as shown

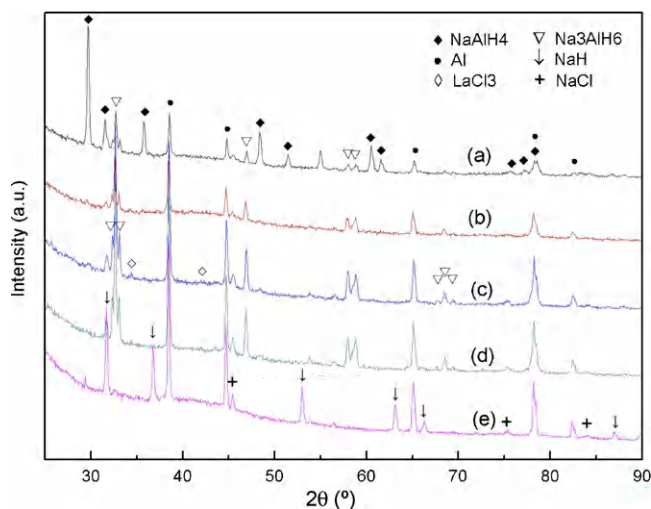


Fig. 4. XRD patterns of 1-h milled NaAlH₄-2 mol% LaCl₃ mixture after dehydrogenation at different temperatures: (a) 100 °C, (b) 120 °C, (c) 140 °C, (d) 160 °C and (e) 180 °C.

in Fig. 3. It is also observed that the weak diffraction peaks of NaCl occur in those five diffractogram. The formation of NaCl should arise from some chemical reaction taking place between NaAlH₄ and LaCl₃ at elevated temperature. Sandrock et al. once reported a similar situation in the mechanically milled NaAlH₄-TiCl₃ system [20]. In this experiment, the reaction formula can be referred as follows:



From the five XRD profiles, it is observed that the intensity of NaCl Bragg peaks increase with the dehydrogenation temperature, which indicates that this reaction is temperature dependant. This situation should be avoided because it causes the consumption of NaAlH₄ and the catalytical species, and thereby the loss of capacity in the NaAlH₄-LaCl₃ mixture.

Fig. 5 gives the comparison of dehydrating curves (120 °C) of NaAlH₄ milled for different times. It is clearly seen that the dehydrogenation kinetics is milling-time dependant. The 5-h milled NaAlH₄-LaCl₃ mixture demonstrated fastest hydrogen desorption rate and desorbed 3.0 wt% hydrogen in 2 h. The sample milled for 3 h exhibits highest hydrogen desorption content. As above explained, longer time of ball milling leads to slight decomposition of NaAlH₄ and thereby the loss of hydrogen desorption capacity. At the same time, sufficient ball milling also results in fine grain size of LaCl₃ and its homogenous distribution on the surface of NaAlH₄ particles, and thus enhances both the hydrogen desorption rate and the complete decomposition of NaAlH₄ in less time. Consequently, the 3-h milled NaAlH₄-LaCl₃ powder mixture exhibits better comprehensive dehydrogenation properties. We also compared the different catalytic effect of TiCl₃ and LaCl₃ using the same doping process. From Fig. 5, it is seen that the catalytical effectiveness of LaCl₃ is a little inferior than that of TiCl₃. Comparing with NaAlH₄ doped with titanium-based compounds by other groups [9,11,20,21], the 5-h milled NaAlH₄-2 mol% LaCl₃ mixture exhibits the similar kinetic performances, but its hydrogen capacity is a little bit lower.

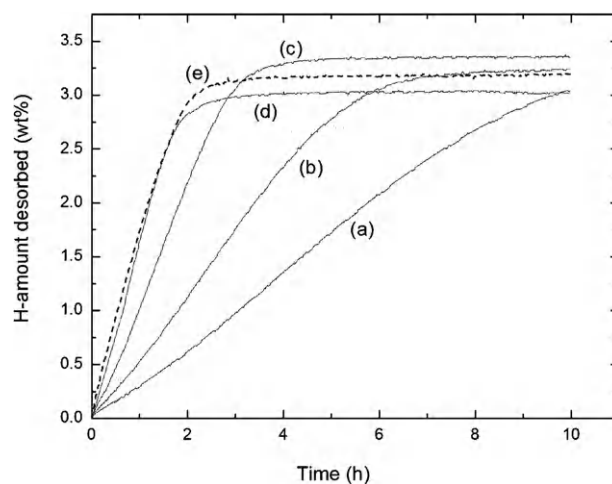


Fig. 5. Dehydrating curves at 120 °C of NaAlH₄-2 mol% LaCl₃ mixture (solid lines) milled for different times: (a) 0.5 h, (b) 1 h, (c) 3 h, (d) 5 h, (e) NaAlH₄-2 mol% TiCl₃ mixture (dashed line) milled for 3 h.

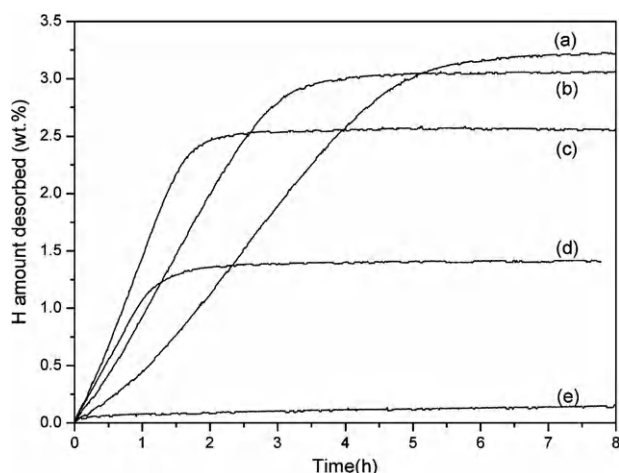


Fig. 6. Dehydrogenation curves (120 °C) of 3-h milled NaAlH₄-LaCl₃ mixtures with different doping amount of LaCl₃: (a) 1 mol%, (b) 2 mol%, (c) 4 mol%, (d) 10 mol% and (e) 5-h milled pure NaAlH₄ sample.

The effect of the doping amount of LaCl₃ on the dehydrogenation of NaAlH₄ is shown in Fig. 6. It is clearly observed that the increasing of LaCl₃ doping amount is favorable for the dehydrogenation rate of NaAlH₄, but with the cost of much more loss of hydrogen release content. It is worth to be mentioned that both as-received and 5-h milled pure NaAlH₄ powders without doping LaCl₃ desorbs no hydrogen at temperatures below 140 °C. It is consequently believed that the markedly improvement on the dehydrogenation properties of NaAlH₄ is attributed to the catalytical effect of LaCl₃, rather than the ball milling process that may reduce the structural stability of NaAlH₄.

Bogdanovic et al. firstly explored the catalytical effect of some rare earth compounds in Ref. [2], their latest work shows that the rare earth chlorides, such as CeCl₃ and SmCl₃, has pronounced catalytical effect on the dehydrogenation and rehydrogenation reactions of NaAlH₄ [19], much better than TiCl₃. In the present work, it seems that only the first step dehydrogenation reaction of NaAlH₄ is markedly enhanced at medium temperature and the low hydrogen desorption capacity mainly arises from the incomplete decomposition of Na₃AlH₆. However, it was found that the decomposition reaction of Na₃AlH₆ could proceed when the pressure of reacting chamber is lowered to a level of 10 kPa, but the dehydrogenation rate is very slow. This result is due to the lower equilibrium pressure of Eq. (2) compared with that of Eq. (1) as well as indicates the catalytical selectivity of LaCl₃. The work on the catalytical effect of other rare earth chlorides dopants on the dehydrogenation/rehydrogenation reaction of NaAlH₄ and the underlying mechanism are undergoing.

4. Conclusions

Rare earth metal compound LaCl₃ was introduced by dry mechanical milling and could remarkably improves the dehydrogenation

properties of NaAlH₄. The milling time and doping amount of LaCl₃ have important influences on the dehydrogenation properties of NaAlH₄. After 5 h of milling, the NaAlH₄-2 mol% LaCl₃ mixture achieves a hydrogen desorption content of 3.0 wt% in less than 2 h at a temperature of 120 °C, and the 3-h milled NaAlH₄-2 mol% LaCl₃ better comprehensive dehydrogenation properties. The incomplete second decomposition reaction of NaAlH₄-LaCl₃ mixture at temperatures below 180 °C indicates that LaCl₃ has better catalytical effect for the first decomposition into the Na₃AlH₆ of NaAlH₄.

Acknowledgements

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