Rare Metal Materials and Engineering
Volume 38, Issue 8, August 2009
Online English edition of the Chinese language journal

Cite this article as: Rare Metal Materials and Engineering, 2009, 38(8): 1328–1332.

ARTICLE

Effect of $LaCl_3$ and Ti on Hydrogen Storage Properties of $NaAlH_4$ and $LiAlH_4$

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Abstract: The effects of additives Ti and $LaCl_3$ on the hydrogen storage properties of $NaAlH_4$ and $LiAlH_4$ were investigated by the PCT (pressure-content-temperature) apparatus. $NaAlH_4$ doped with $LaCl_3$ and $LiAlH_4$ doped with $LaCl_3$ both show better capability of hydrogen release than the samples doped with Ti. The study on the first rehydrogenation cycle of $NaAlH_4$ doped with 3 mol% $LaCl_3$ finds that the dehydrogenation temperature has a marked decrease. In addition, the effect of $LaCl_3$ content on hydrogen release of $NaAlH_4$ is very obvious. The result indicates that the amount and rate of hydrogen release show the same change trends, increasing firstly and then decreasing with increasing of $LaCl_3$ content. The sample doped with 3 mol% $LaCl_3$ presents the best dehydrogenation properties in both the amount of hydrogen release and the desorption kinetics. The activation energy of the $NaAlH_4$ sample doped with 3 mol% $LaCl_3$ was measured to be 41.6 kJ/mol. This value is lower than that reported for the Ti-doped $NaAlH_4$.

Key words: $NaAlH_4$; $LiAlH_4$; hydrogen storage properties; additives

Hydrogen storage has been the subject of intensive research in recent years since hydrogen is pollution-free and can readily be produced from renewable energy resources[1,2]. Complex hydrides, such as $NaAlH_4$ and $LiAlH_4$, as hydrogen storage compounds are attractive due to their high hydrogen content and low mass. In 1997, Bogdanović and Schwickardi[3] demonstrated that the addition of Ti compounds and other transition metal compounds could enhance the desorption kinetics of $NaAlH_4$, and furthermore, that re-hydrogenation is possible under moderate conditions. This finding has created an entirely new prospect for complex hydrides based on Al as promising reversible hydrogen storage media. Theoretically, $NaAlH_4$ can reversibly store 5.6% (mass fraction, similarly hereinafter) H_2. The release of hydrogen occurs in consecutive steps, as depicted in reactions (1) and (2)[4-7]:

$$3NaAlH_4 \rightarrow Na_3AlH_6+2Al+3H_2 \quad (1)$$

$$2Na_3AlH_6 \rightarrow 6NaH+2Al+3H_2 \quad (2)$$

The first reaction releases 3.7% hydrogen, while the second reaction releases 1.9%. Recently, J. Wang et al[4,8] reported the systematic study on the dehydrogenation and hydrogenation kinetics of $NaAlH_4$ co-doped with $TiCl_3$, graphite, $FeCl_3$ and $ZrCl_4$. The results show that the samples of $NaAlH_4$ co-doped with binary and ternary combinations of Ti, Zr and Fe at 4 mol% total catalyst content exhibited synergistic behavior with respect to improving the dehydrogenation kinetics of the first decomposition reaction over that of the sample of $NaAlH_4$ doped with 4 mol% Ti or Zr as single catalysts. However, the effects of Ti, Zr and Fe as co-dopants on the second decomposition reaction were not as pronounced as their effects on the first reaction. Furthermore, the effect of the rare earth elements on the hydrogenation/ dehydrogenation behavior has been studied by D. Pukazhselvan et al recently[9]. Compared with catalyst Ti, mischmetal is a more effective catalyst for enhancing the desorption kinetics and rehydrogenation of $NaAlH_4$.

$LiAlH_4$ is another complex hydride. Compared with $NaAlH_4$, the theoretical capacity of $LiAlH_4$ is possessed of 7.9% hydrogen available below 200 °C. Hydrogen release occurs in three stages[10]:

$$3LiAlH_4 \rightarrow Li_3AlH_6+2Al+3H_2 \quad (5.3\%\ H_2) \quad (3)$$

Received date: September 22, 2008
Foundation item: Supported by the National Natural Science Foundation of China (50806007)

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$Li_3AlH_6 \rightarrow 3LiH+Al+3/2H_2$ (2.6% H_2) (4)

$3LiH+3Al \rightarrow 3LiAl+3/2H_2$ (2.6%H_2) (5)

The decomposition temperatures are reported to be between 150-175 °C for the first stage and 180-220 °C for the second stage[11,12]. The last composition step occurs at 400 °C which is not considered to be supplied. The research for Li_3AlH_6 found that the addition of Ti as a catalyst made it possible to extract up to 2% reversibly from Li_3AlH_6 [12], but the same effect in $LiAlH_4$ was not found. In recent years, the focus has been on processing $LiAlH_4$ by ball-milling and adding catalysts. It has been proved that adding of catalysts can have a distinct effect on the decomposition of $LiAlH_4$. The principal catalysts studied were elemental titanium, $TiCl_4$, $TiCl_3$, $AlCl_3$, $FeCl_3$, elemental iron, elemental nickel, vanadium and carbon black[13-16]. Mirna Resan[13] reported that the addition of $TiCl_3$ and $TiCl_4$ to $LiAlH_4$ eliminated the first step of hydrogen evolution and significantly lowered the decomposition temperature of the second step. Doping with elemental iron caused only a slight decrease in the amount of hydrogen released and did not eliminate the first step of hydrogen evolution. The study by Blanchard[14] showed that ball-milling of $LiAlD_4$ and VCl_3 or $TiCl_3 \cdot 1/3AlCl_3$ reduced the thermal decomposition temperatures of the first stage by 50-60 °C.

In the current paper, a kind of new catalyst $LaCl_3$ was used. The effect of $LaCl_3$ and Ti catalysts on the hydrogen storage capability of $NaAlH_4$ and $LiAlH_4$ was analyzed.

1 Experimental

$NaAlH_4$, purity ≧93% (mass fraction) and $LiAlH_4$ were purchased from J&K Chemical Ltd and Tianjin Beidouxing Fine Chemical Co.,Ltd, respectively. Ti and $LaCl_3 \cdot 7H_2O$ were obtained from the Central Iron and Steel Research Institute. In this study, $NaAlH_4$, $LiAlH_4$ and Ti were used as the received with no additional purification in order to obtain a simple and economic process. Due to a mass of crystal water in $LaCl_3 \cdot 7H_2O$, dehydration was carried out before $NaAlH_4$ was mixed with $LaCl_3$ in order to prevent the effect of the crystal water on $NaAlH_4$. $LaCl_3 \cdot 7H_2O$ was heated to 150 °C and then kept at the temperature for 3 h. All operations of the samples were done under dry argon atmosphere in a glove box to prevent reaction with moisture and oxygen in air. $NaAlH_4$ or $LiAlH_4$, usually 1 g, was mixed with 3 mol% Ti and $LaCl_3$ by ball-milling for 10 min at a gyration rate of 200 r/min using a Spex mill. Three hardened steel vials sealed under argon with fourteen steel balls (1 g each) were used. Air-cooling of the vials was employed to prevent heating during the ball-milling process. The ball-milled samples were then transferred to 3 mL glass bottles in a glove box under dry argon atmosphere.

Hydrogen desorption experiments were carried out in pressure-composition-temperature (PCT) apparatus. This can be operated up to 10 MPa and at 400 °C. The pressure of hydrogen released in relation to volume was displayed by a pressure transducer. The experimental studies were done by a reactor. This consisted of two parts: heater and sample vessel. The former was used to connect with the pressure transducer and thermocouple. It had a 2.2 cm outer diameter (OD), 0.5 cm wall and 20 cm internal length. It was loaded with the sample vessel (1 cm OD, 0.1 cm wall and 5 cm internal length). The sample vessel was loaded with about 0.1 g of $NaAlH_4$ or 0.2 g of $LiAlH_4$. The reactor was heated with an air furnace. During heating, the hydrogen released overflowed from the sample vessel firstly into the heater and then into the transit pressure transducer. The value of hydrogen pressure can be clearly read. The samples doped with Ti and $LaCl_3$ were heated in a vacuum atmosphere at a heating rate of 2 °C/min. During the heating process, all pressure and temperature data were acquired and the dehydrogenation curves were drawn by special software.

2 Results and Discussion

2.1 Dehydrogenation/rehydrogenation of $LiAlH_4$

Theoretically, the thermal desorption is more thermodynamically favorable for $LiAlH_4$ than for $NaAlH_4$[17]. Evidently, lithium alanate is less stable than sodium alanate. Fig.1 shows the hydrogen desorption of the $LiAlH_4$ samples doped with 3 mol% Ti and 3 mol% $LaCl_3$, respectively. It can be seen that doping with $LaCl_3$ causes a lower dehydrogenation temperature than doping with Ti, which is the same to the effect of Ti and $LaCl_3$ on the hydrogen desorption of $NaAlH_4$. Differently, however, the dehydrogenation amount of the $LiAlH_4$ doped with Ti is lower than that of the $LiAlH_4$ doped with $LaCl_3$.

To date, few studies have been done to show whether Eq.3 is reversible when doped with Ti. However, the research for Li_3AlH_6 found that the addition of Ti as a catalyst made it possible to extract up to 2% reversibly from Li_3AlH_6[12]. Therefore, the rehydrogenation studies of Li_3AlH_6 doped with $LaCl_3$ and Ti were carried out. After the first complete dehydrogenation (first two reactions), the samples were kept at 180 °C at 8 MPa hydrogen pressure for 2 h. The result found that the Li_3AlH_6 samples doped with 3 mol% $LaCl_3$ and 3 mol% Ti present a very poor hydrogen absorption capacity in the whole

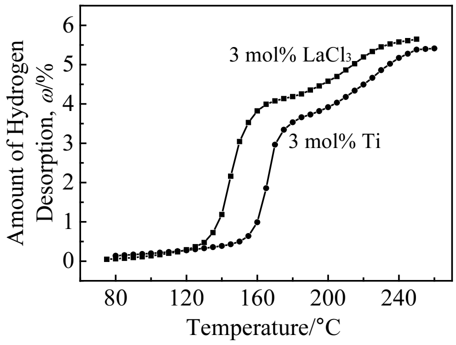

Fig.1 Thermal desorption of $LiAlH_4$ doped with 3 mol% Ti and 3 mol% $LaCl_3$

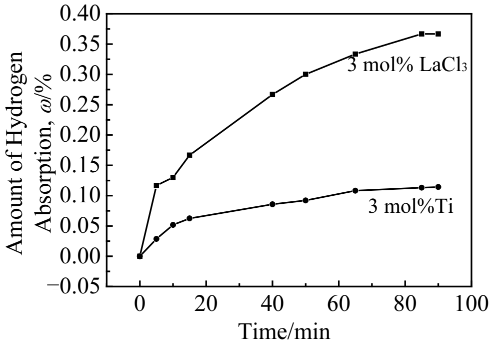

Fig.2 The hydrogen absorption amount of the Li_3AlH_6 samples doped with 3 mol% $LaCl_3$ and Ti at 180 °C under 8 MPa hydrogen pressure

rehydrogenation process (Fig.2). Particularly, the hydrogen absorption amount of the sample doped with Ti is only about 0.11%.

2.2 Dehydrogenation /rehydrogenation of $NaAlH_4$

Since the initial discovery that Ti catalyzes the dehydrogenation, more metals and compounds have also been proven to be effective catalysts for the hydrogen storage capacity of $NaAlH_4$. In this study, we analyzed the effect of the catalysts Ti and $LaCl_3$ on the two-step dehydrogenation process of $NaAlH_4$.

In the present work, commercial $NaAlH_4$ was used as the received in order to obtain a simple and economic process. Fig.3 gives the two-step decomposition results of the $NaAlH_4$ samples doped with 3 mol% Ti and doped with 3 mol% $LaCl_3$, respectively. It can be seen that the dehydrogenation of these two samples both shows two obvious region which correspond to Eq. 1 and Eq. 2, respectively. However, within the examined temperature range, hydrogen is desorbed from these two samples with different behavior. In the case of the sample doped with 3 mol% Ti, the obvious desorption of hydrogen started at about 200 °C and ended at 250 °C. In the case of the sample doped with 3 mol% $LaCl_3$, the starting temperature of hydrogen desorption is around 150 °C, and ended at about 220 °C, and the whole hydride decomposition shifts by about 35-50 °C. Significantly, a slow desorption of about 0.8% is observed between 60-150 °C, indicating that doping with $LaCl_3$ make $NaAlH_4$ decomposition much more easily.

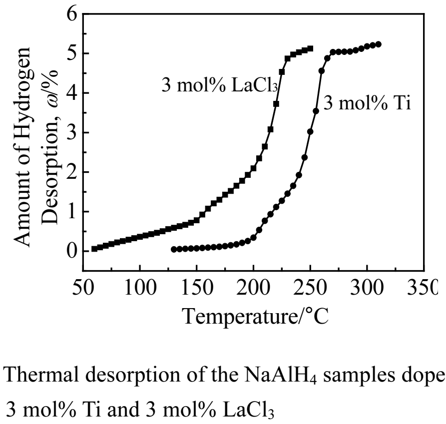

Fig.3 Thermal desorption of the $NaAlH_4$ samples doped with 3 mol% Ti and 3 mol% $LaCl_3$

Fig.4 shows the desorption kinetics of $NaAlH_4$ catalyzed by 3 mol% Ti and 3 mol% $LaCl_3$ catalysts. As can be seen, a clear difference exists between these two curves. For the case of Ti, the desorption at the temperature 150 °C finally yields the storage capacity of 0.5%. However, for the same concentration and temperature, the $LaCl_3$ catalyst finally yields the storage capacity of about 3.2%. This result indicates that $LaCl_3$ is a better catalyst in regard to both the desorption to reach higher storage capacity at lower temperature and also faster desorption kinetics.

The study on the first rehydrogenation cycle was carried out in PCT at 150 °C under 8 MPa. After the desorption, the $NaAlH_4$ sample doped with 3 mol% $LaCl_3$ reabsorbed hydrogen, and then it was desorbed to determine the amount of reversible hydrogen absorption. The result found that the two-step dehydrogenation process of subsequent desorption is very obvious compared with the first dehydrogenation (Fig.5). In addition, the dehydrogenation temperature of the subsequent desorption presents a marked decrease, while the amount of hydrogen release also presents a sharp decrease.

2.3 Dehydrogenation kinetics of $NaAlH_4$

It is important to study the effect of the catalyst concentration on the dehydrogenation kinetics. Fig.6 gives 150 °C dehydriding curves for all the catalyzed samples studied (1 mol%-6 mol% $LaCl_3$ precursor). For each series, the test

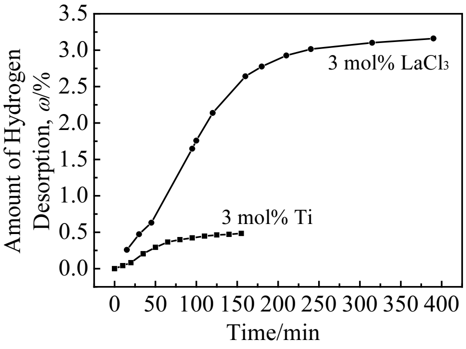

Fig.4 Dehydrogenation of the $NaAlH_4$ samples doped with 3mol% Ti and 3mol% $LaCl_3$ at 150 °C

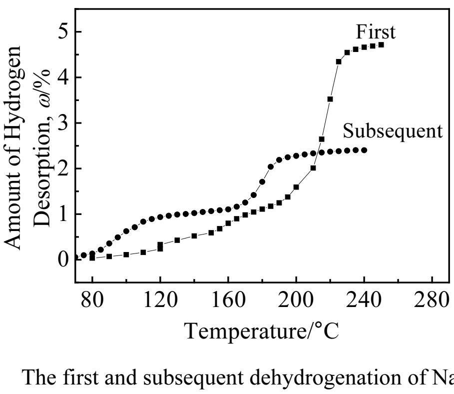

Fig.5 The first and subsequent dehydrogenation of $NaAlH_4$ doped with 3 mol% $LaCl_3$

conditions were held as closely as possible. Increasing of the $LaCl_3$ content from 1 mol% to 6 mol% caused such marked changes in behavior that the total amount and the rate of hydrogen release increased first and then decreased. The sample doped with 3 mol% $LaCl_3$ presents the largest amount of hydrogen release about 3.2% and the fastest dehydrogenation rate, while the sample doped with 1mol% $LaCl_3$ has the least amount of hydrogen release about 0.4% and the slowest dehydrogenation rate.

Fig.7 shows the hydrogen desorption rates at different temperatures of 110, 130, 150 and 180 °C for the 3 mol% $LaCl_3$-doped $NaAlH_4$. The desorption rates present a great difference at the different heating temperatures. Increasing of the heating temperature induces an obvious increase in the desorption rate. The temperature dependence of desorption rate (V) can be correlated by the Arrhenius equation:

$$V=k\exp(-Q/RT) \tag{6}$$

where k is the rate constant, Q is the thermal activation energy, R is the gas constant (8.32 J/mol·K) and T is absolute temperature (K). The decomposition rates of $NaAlH_4$ doped with 3 mol% $LaCl_3$ are plotted in Arrhenius form (lg$V$ versus 1/T), shown in Fig.8. The activation energy was measured to be 41.6 kJ/mol and coefficient k is 3.8×10^7 ω%/h. These values are lower than that reported for the Ti-doped $NaAlH_4$[3]. Thus the Arrhenius equation for the decomposition reaction can be written as follows:

$$V_{(NaAlH_4)}=3.8\times10^7\exp(-5000/T) \tag{7}$$

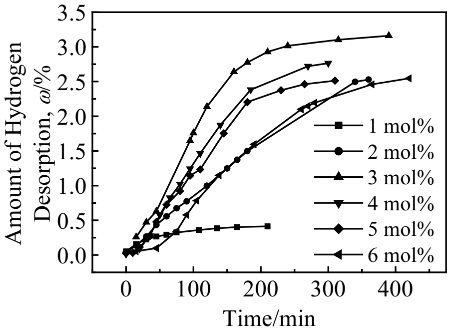

Fig.6 Effect of different contents of $LaCl_3$ on dehydrogenation amount of $NaAlH_4$ at 150 °C

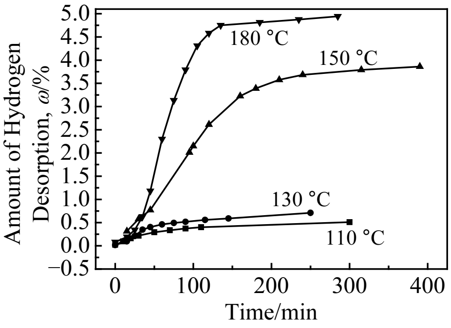

Fig.7 Constant temperature desorption curves of the $NaAlH_4$ sample doped with 3 mol% $LaCl_3$ at 110, 130, 150 and 180 °C

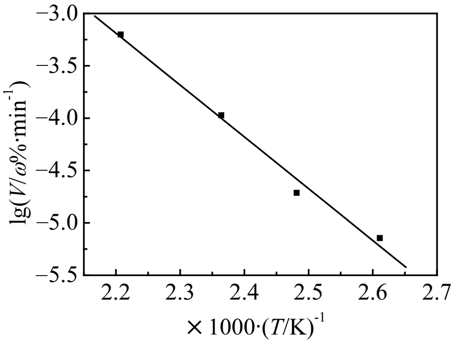

Fig.8 Arrhenius dots of the $NaAlH_4$ doped with $LaCl_3$

3 Conclusions

1) Doping with $LaCl_3$ induces a lower dehydrogenation temperature of $NaAlH_4$ and $LiAlH_4$ than doping with Ti. Under the condition of the subsequent desorption of $NaAlH_4$ doped with 3 mol% $LaCl_3$ the dehydrogenation temperature and amount in the subsequent desorption are obviously lower than that in the first dehydrogenation. Comparatively, the rehydrogenation capability of Li_3AlH_6 is very poor.

2) Increasing of $LaCl_3$ content from 1 mol% to 6 mol% will cause such marked changes in behavior that the total amount and the rate of hydrogen release increase first and then decrease. The $NaAlH_4$ sample doped with 3 mol% $LaCl_3$ presents the largest amount of hydrogen release about 3.2% and the fastest dehydrogenation rate.

3) Doping with $LaCl_3$ will cause a significant decrease in the thermal activation energy. The thermal activation energy of the $LaCl_3$-doped $NaAlH_4$ is 41.6 kJ/mol.

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$LaCl_3$和 Ti 对氢化铝钠（$NaAlH_4$）和氢化铝锂（$LiAlH_4$）储氢性能的影响

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摘 要：通过 PCT(pressure-content-temperature)设备研究催化剂 Ti 和 $LaCl_3$对 $NaAlH_4$和 $LiAlH_4$储氢性能的影响。$NaAlH_4$和 $LiAlH_4$掺杂 $LaCl_3$比掺杂 Ti 的放氢性能有明显提高。在吸氢性能的研究中发现，在第 1 个吸氢循环中，掺杂 3 mol% $LaCl_3$的 $NaAlH_4$试样的放氢温度明显降低。此外，$LaCl_3$的摩尔含量对 $NaAlH_4$的放氢性能的影响是非常明显的。研究结果显示，随着 $LaCl_3$含量的增加，$NaAlH_4$的放氢量和放氢速率显示出相同的变化趋势，即先增加后减少。其中掺杂 3 mol% $LaCl_3$的 $NaAlH_4$试样的放氢量最大并且放氢动力学性能最好，其激活能为 41.6 kJ/mol，这个值低于所报道的掺杂 Ti 的 $NaAlH_4$的激活能。

关键词：$NaAlH_4$；$LiAlH_4$；储氢性能；催化剂

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