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Synthesis and dehydrogenation of CeAl₄-doped calcium alanate

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1. Introduction

Hydrogen is considered as an environmental friendly energy carrier because the produces almost zero pollution emitted from hydrogen fuel equipments. The lack of suitable high density storage hydrogen material remains one of the important problems for the development of hydrogen energy utilization [1]. Complex metal hydrides show much promise, but their hydriding/dehydriding kinetics need to be improved under moderate temperature and pressure [2,3]. Since the breakthrough work by Bogdanović and Schwickardi who showed that NaAlH₄ doped with Ti alkoxides or chlorides could reversibly desorb and absorb hydrogen below 150°C, sodium alanate has been investigated intensively [4–6]. However, utilization of such Ti-compounds as dopants generally gives birth to nonvolatile byproduct (sodium-chloride) that occupies a significant weight percentage [4,5]. Recently, our investigations found that directly doping catalytic active species (CeAl₄) instead of catalytic precursor (CeCl₃) into NaAlH₄ can enhance its kinetics without decrease of hydrogen capacity [7]. It is believed that CeAl₄ may also have similar catalyzing effects on other complex aluminum hydrides (such as Li AlH₄, Ca(AlH₄)₂).

So far the hydrogen storage capacity of catalyzed NaAlH₄ system was difficult to break through 5.5 wt.%. Besides NaAlH₄, other alkaline complex aluminum hydrides with higher mass and volume densities of hydrogen have also attracted attention in the past few years [8–10]. Among these, Ca(AlH₄)₂ has a total hydro-

ABSTRACT

CeAl₄-doped Ca(AlH₄)₂ was synthesized by reactive ball-milling NaH/Al and CaCl₂ with a few moles of CeAl₄ catalyst under hydrogen atmosphere. Its synthesis mechanism and dehydriding behavior were systematically investigated by XRD, FTIR, TG/DSC and TPD analyses. These results show that the synthetic process of Ca(AlH₄)₂ can be divided into two steps: the first step is ball-milling NaH/Al with CeAl₄ under hydrogen atmosphere to form CeAl₄-doped NaAlH₄, the second step is ball-milling the as-synthesized CeAl₄-doped NaAlH₄ and CaCl₂ to form CeAl₄-doped Ca(AlH₄)₂. The CeAl₄-doped Ca(AlH₄)₂ can desorb more than 5.5 wt.% hydrogen below 200 °C with an acceptable reaction kinetics, and shows attractive dehydriding behavior better than that of Ca(AlH₄)₂ directly prepared by primary NaAlH₄ and CaCl₂. © 2010 Elsevier B.V. All rights reserved.

> gen capacity of 7.8 wt.%. The decomposition of Ca(AlH₄)₂ can mainly divided into four steps [9], the first two decomposition steps (Ca(AlH₄)₂ first decomposes into CaAlH₅, Al and H₂; and then $CaAlH_5$ decomposes into CaH_2 , Al and H_2) release 5.9 wt.% H₂, which could be considered for practical applications. Currently, investigations about Ca(AlH₄)₂ were mainly concentrated on the synthetic method and theoretical calculation [10-13]. It was reported that the Ca(AlH₄)₂ and CaAlH₅ can be synthesized using AlH₃ and CaH₂ as primary material [14,15]. CaAlH₅ can hydrogenate/dehydrogenate reversibly by the DSC measurement and DFT calculation [11,16]. However, the rehydrogenation of CaAlH₅ to form Ca(AlH₄)₂ is the endothermic reaction, indicating the Ca(AlH₄)₂ system is a non-reversible hydrogen storage material. It is well known that the metal element contents of earth crust are 7.73 wt.% for Al, 3.45 wt.% for Ca and 2.74 wt.% for Na, respectively. So it seems that $Ca(AIH_4)_2$ is the promising off-board hydrogen storage candidate. It was ever reported that the decompositions of Ca(AlH₄)₂ and CaAlH₅ are kinetically stabilized with rather high activation energy [14], resulting in slow dehydrogenation process. The catalytic modification and dehydriding performance of $Ca(AlH_4)_2$ system were studied much less than those of NaAlH₄ system.

> In this work, we synthesized CeAl₄-doped Ca(AlH₄)₂ by reactive ball-milling NaH/Al and CaCl₂ with a few moles of CeAl₄ catalyst. The synthesis mechanism of CeAl₄-doped Ca(AlH₄)₂ was investigated. Moreover, for comparison, the dehydrogenation processes of synthesized Ca(AlH₄)₂ doped with and without CeAl₄ catalyst were characterized and compared by simultaneous thermogravimetry, differential scanning calorimetry. The CeAl₄-doped Ca(AlH₄)₂ can desorb more than 5.5 wt.% hydrogen below 200 °C.

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Fig. 1. XRD patterns of NaH/Al + $0.02CeAl_4$ samples ball-milled for (a) 0 h; (b) 30 h; (c) 60 h; (d) 90 h; and the mixture of $0.02CeAl_4$ -doped NaAlH₄ and CaCl₂ (NaAlH₄ and CaCl₂ with a mole ratio of 2:1) ball-milled for (e) 5 h; (f) 10 h; (g) 20 h.

2. Experimental

The starting materials of NaH powder (purity 95%), Al powder (purity 99%), NaAlH₄ (purity >95%) and CaCl₂ (purity \ge 96%) which purchased from Sigma–Aldrich Corp. were used as received. CeAl₄ catalyst (purity 99%) was prepared by induction melting stoichiometric mixtures of pure Ce (purity 99%) and Al (purity 99.%) metals, which detail can be found in our previous paper [7]. The samples were handled and stored in a glove box with a dry argon atmosphere to prevent any contact with oxygen or moisture. The CeAl₄-doped Ca(AlH₄)₂ was synthesized by two-step process. First, about 2.5 g mixture of NaH, Al and CeAl₄ in a mole ratio of 1:1:0.02 was milled in the Planetary mill for 0–90 h under a hydrogen pressure of 3 MPa. The CeAl₄-doped NaAlH₄ was synthesized when the milling time increases to 90 h. Second, mixture of CeAl₄-doped NaAlH₄ and CaCl₂ (NaAlH₄ and CaCl₂ with a mole ratio of 2:1) according to the reaction: 2NaAlH₄ + CaCl₂ \rightarrow Ca(AlH₄)₂ + 2NaCl with a total amount of 2.08 g was milled in the Planetary mill for 0–20 h under a hydrogen pressure of 2 MPa.

The structural characteristics of the as-synthesized samples were determined by means of by X-ray diffractometer (XRD, X'Pert Pro) with Cu K α radiation at 40 kV and 40 mA. A special plastic tape was used to prevent the XRD sample from contacting with water air and moisture. A–H vibrations in the samples were identified using a Fourier infrared spectrometer (FTIR, Bruker Tensor27). The powder sample was mixed uniformly with KBr powder at a weight ratio of about 1:30 and then the mixture was cold pressed into a pellet of 13 mm diameter for testing. The heat decomposition features of samples were also measured by a synchronous thermal analyses thermogravimetry and differential scanning calorimetry (TG/DSC, Netzsch STA 449F3). The heating rate was 3–10 °C/min and the flow rate of argon protective gas was 40 ml/min. Thermal programmed desorption (TPD) of CeAl₄-doped Ca(AlH₄)₂ sample was carried out on a Sievert's type apparatus and heated to the assigned temperature at a rate of 2 °C/min. The hydrogen capacity was calculated in weight percent and normalized to the weight of Ca(AlH₄)₂ with CeAl₄ catalyst, but the weight of NaCl was excluded.

3. Results and discussions

Ca(AlH₄)₂ was generally synthesized by a metathesis reaction of NaAlH₄ and CaCl₂ [12,17]. However, as a raw material of hydride, NaH and Al are cheap than NaAlH₄. So we chose NaH/Al and CaCl₂ instead of NaAlH₄ and CaCl₂ as raw materials to synthesize Ca(AlH₄)₂. To investigate the mechanics of synthesis, the XRD patterns of NaH/Al + 0.02 CeAl₄ ball-milled under 3.0 MPa initial hydrogen pressure for different milling-times are shown in Fig. 1. It can be found that the NaH and Al diffraction peaks become weaker and broader when milling-time increases to 30 h, indicating the average crystallite size is strongly reduced. At the same time, the Na₃AlH₆ diffraction peaks are detected in Fig. 1(b). After ball-milled for 60 h, some Na₃AlH₆ and broader Al diffraction peaks together with NaAlH₄ diffraction peaks can be detected in Fig. 1(c), indicat-



Fig. 2. FTIR spectra of (a) as-synthesized 0.02CeAl₄-doped NaAlH₄; (b) assynthesized 0.04CeAl₄-doped Ca(AlH₄)₂.

ing that NaH and Al are completely hydrogenated to form Na₃AlH₆, and some Na₃AlH₆ and Al are further hydrogenated to form NaAlH₄. When the milling-time increases to 90 h, Na₃AlH₆ and Al diffraction peaks are almost disappeared, suggesting they completely transform to the NaAlH₄ in Fig. 1(d). The above results indicate that the NaAlH₄ can be synthesized according to reactions (1) and (2) [6,7]. Moreover, it is remarkable to note that the CeAl₄ diffraction peaks remain unchanged in the whole ball-milling process. Here, the CeAl₄ catalyst plays a critical role in the formation of NaAlH₄ from NaH and Al [7].

$$3NaH + Al + 1.5H_2 \leftrightarrow Na_3AlH_6$$
 (1)

$$Na_{3}AlH_{6} + 2Al + 3H_{2} \leftrightarrow 3NaAlH_{4}$$
(2)

The XRD patterns of mixtures of as-synthesized CeAl₄-doped NaAlH₄ and CaCl₂ (NaAlH₄ and CaCl₂ with a mole ratio of 2:1) ball-milled for different milling-times under 2.0 MPa initial hydrogen pressure are also shown in Fig. 1. After ball-milled for 5 h, the sample consists of NaAlH₄ and CaCl₂ main phases together with CeAl₄ minor phase. Except the CaCl₂·(H₂O)₄ comes from the impure phase of CaCl₂ reactant, no new phase has been found in Fig. 1(e). Some NaAlH₄ and CaCl₂ diffraction peaks are disappeared as the milling-time increases to 10 h, while the Ca(AlH₄)₂ and NaCl diffraction peaks are present in the sample. When the milling-time increases to 20 h, the NaAlH₄ and CaCl₂ phases are disappeared completely, and the Ca(AlH₄)₂ phase can be detected obviously in Fig. 1(g). The CeAl₄ phase is almost unchanged in the whole synthetic process. These results suggest that the Ca(AlH₄)₂ can be synthesized according to reaction (3) [12,17]:

$$+ \operatorname{CaCl}_2 \rightarrow 0.04 \operatorname{CeAl}_4 \operatorname{-doped} \operatorname{Ca}(\operatorname{AlH}_4)2 + 2\operatorname{NaCl}$$
(3)

The synthetic process of $Ca(AlH_4)_2$ can be mainly divided into two steps: the first step was ball milling NaH/Al with CeAl₄ under hydrogen to form CeAl₄-doped NaAlH₄, and the second step was ball milling the as-synthesized CeAl₄-NaAlH₄ and CaCl₂ to form CeAl₄-doped Ca(AlH₄)₂.

To further identify the chemical reactions occurring during the ball milling process, the FTIR spectra of the as-synthesized CeAl₄-doped NaAlH₄ and Ca(AlH₄)₂ are shown in Fig. 2. It is well known that the characteristic band of Al–H bond changes with different chemical environment. The as-synthesized 0.02CeAl₄-doped NaAlH₄ exhibits two infrared active vibration peaks in 1640 and



Fig. 3. TG/DSC profiles of dehydrogenation from (a) as-synthesized $0.02CeAl_4$ -doped NaAlH₄; (b) primary Ca(AlH₄)₂; (c) as-synthesized $0.04CeAl_4$ -doped Ca(AlH₄)₂ (heating rate is 5 °C/min).

1675 cm⁻¹, the as-synthesized 0.04CeAl₄-doped Ca(AlH₄)₂ also exhibits two vibration peaks in 1640 and 1797 cm⁻¹. The vibration peak at 1640 cm⁻¹ can be associated to water bending vibration visible [18], it may be due to the moisture present in test system during the characterization of the as-synthesized samples. It can be found that, the band at 1675 cm⁻¹ corresponds to a Al–H stretching vibration for NaAlH₄, and the band at 1797 cm⁻¹ corresponds to a Al–H stretching vibration for Ca(AlH₄)₂ [19]. This result suggests further that the as-synthesized NaAlH₄ and CaCl₂ have transformed completely to Ca(AlH₄)₂ according to reaction (3).

Fig. 3 presents the TG/DSC profiles of the as-synthesized 0.02CeAl₄-doped NaAlH₄, primary Ca(AlH₄)₂ and as-synthesized 0.04CeAl₄-doped Ca(AlH₄)₂. The primary Ca(AlH₄)₂ was directly synthesized from primary NaAlH₄ and CaCl₂ without doping catalyst. It can be found that two weight loss signals about 2.56 wt.% at the first endothermic peak of 172 °C, and 1.68 wt.% at the second endothermic peak of 200 °C appear in the TG curve of 0.02CeAl₄doped NaAlH₄, which are in agreement with previous reports [6]. Moreover, 0.04CeAl₄-doped Ca(AlH₄)₂ desorbs 2.46 wt.% hydrogen at the first exothermic peak of 76.9°C, and desorbs 2.36 wt.% hydrogen at the second endothermic peak of around 205 °C, which total dehydriding capacities in first two stages are high than that of 0.02CeAl₄-doped NaAlH₄. This result indicates that Ca(AlH₄)₂ system is a potential candidate for off-board hydrogen storage material with large capacity. Moreover, although the 0.04CeAl₄doped Ca(AlH₄)₂ shows a slight decrease of dehydriding capacity,



Fig. 4. DSC curves and Kissinger plots of as-synthesized 0.04CeAl₄-doped Ca(AlH₄)₂ at different heating rates: (a) DSC curves; (b) Kissinger plots.

compared to that of primary $Ca(AlH_4)_2$. The dehydriding temperature of $CeAl_4$ -doped $Ca(AlH_4)_2$ is much lower than that of primary $Ca(AlH_4)_2$. It indicates that the $CeAl_4$ catalyst can improve the dehydrogenation performance of $Ca(AlH_4)_2$ effectively, which catalysis may be similar to that in the NaAlH₄ system [7].

In order to gain the insight of the improved dehydrogenation of CeAl₄-doped Ca(AlH₄)₂, the reaction kinetics parameters (activation energy E_a and pre-exponential factor A) were measured by the Kissinger relation of reaction (4) [14,20]:

$$\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{RT_p} + \ln\left(\frac{AR}{E_a}\right) \tag{4}$$

where β is the heating rate, T_p is the transformation peak temperature that changed with different heating rate, E_a is the activation energy, *R* is the gas constant, and *A* is the pre-exponential factor. A series of DSC measurements were conducted at different heating rates of 3, 5, 8 and 10°C/min for the as-synthesized 0.04CeAl₄doped Ca(AlH₄)₂ in Fig. 4(a). With increasing the heating rate, T_p shifts towards the higher temperature side [14]. It is important to note that, the first weak exothermic peak between 72 and 96°C can be attributed to the decomposition of $Ca(AlH_4)_2$ into $CaAlH_5$, Al and H₂, the second endothermic peak between 198 and 217 °C can be attributed to the decomposition of CaAlH₅ into CaH₂, Al and H₂ [9]. The relation of $\ln(\beta/T_p^2)$ vs. $1/T_p$ was plotted in Fig. 4(b), the activation energy E_a and pre-exponential factor A can be calculated from the slope $-E_a/R$ and the intercept $\ln(AR/E_a)$ according to reaction (4). The values of E_a and A of the primary Ca(AlH₄)₂ were also determined and compared in Table 1 for comparison. It is found that the E_a values of Ca(AlH₄)₂ and CaAlH₅ are reduced, and their A values are enhanced obviously after doped with CeAl₄ catalyst. The changes of E_a and A also agree with the TG/DSC results in Fig. 3. The reduction of activation energy is associated with the change in the rate-limiting step [21], which finally improves the dehydriding kinetics of CeAl₄-doped Ca(AlH₄)₂. However, further investigation on the reaction path of dehydrogenation and its rate-

Table 1
Activation energy (E_a) and pre-exponential factor (A) calculated from Kissinger rela-
tion for the decompositions of Ca(AlH ₄) ₂ and CaAlH ₅ .

Complex hydride		E _a (kJ/mol)	$A(\min^{-1})$
Primary sample	Ca(AlH ₄) ₂ CaAlH ₅	62.8 154.9	$\begin{array}{c} 4.58 \times 10^5 \\ 1.64 \times 10^{14} \end{array}$
CeAl ₄ -doped sample	Ca(AlH ₄) ₂ CaAlH ₅	43.7 136.1	$\begin{array}{c} 6.32 \times 10^5 \\ 2.68 \times 10^{14} \end{array}$



Fig. 5. TPD curve of as-synthesized 0.04CeAl_4-doped Ca(AlH_4)_2 (heating rate is 2 $^\circ C/min).$

limiting step in $CeAl_4$ -doped $Ca(AlH_4)_2$ system are needed in the future.

Fig. 5 is the TPD curve of as-synthesized 0.04CeAl₄-doped Ca(AlH₄)₂. The sample was heated from 30 to 200 °C with a heating rate of 2 °C/min. Hydrogen desorption starts at about 70 °C, and increases noticeably with increasing the temperature from 100 to 200 °C. In the temperature ranges of 70–140 °C and 140–200 °C, two dehydrogenation steps take place one after the other to desorb 2.74 and 2.79 wt.% hydrogen (equivalent to about 1.5 and 1.5 mol H atoms *vs.* Ca(AlH₄)₂). It is important to point out that the CeAl₄-doped Ca(AlH₄)₂ can desorb more than 5.5 wt.% H₂ below 200 °C with acceptable dehydriding kinetics.

4. Conclusion

As a summary, the CeAl₄-doped Ca(AlH₄)₂ was successfully synthesized by ball-milling NaH/Al and CaCl₂ instead of NaAlH₄ and CaCl₂. Introducing a few moles of CeAl₄ catalyst can accelerate the synthetic process of Ca(AlH₄)₂ and improve its dehydrogenation performance. The activation energies of Ca(AlH₄)₂ and CaAlH₅ are reduced after doped with CeAl₄ catalyst, resulting in the enhancement of dehydriding kinetics of calcium alanate hydride. The dehydrogenation of CeAl₄-doped Ca(AlH₄)₂ starts at 77 °C, and desorb more than 5.5 wt.% H₂ below 200 °C.

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References

- [1] L. Schlapbach, A. Züttel, Nature 414 (2001) 353-358.
- [2] J. Yang, S. Hirano, Adv. Mater. 21 (2009) 3023-3028.
- [3] B. Bogdanović, U. Eberle, M. Felderhoff, F. Schüth, Scripta Mater. 56 (2007) 813–816.
- [4] B. Bogdanović, M. Schwickardi, J. Alloys Compd. 253-254 (1997) 1-9.
- [5] B. Bogdanović, R.A. Brand, A. Marjanovic, M. Schwickardi, J. Tölle, J. Alloys Compd. 302 (2000) 36–58.
- [6] X.Z. Xiao, L.X. Chen, X.L. Fan, X.H. Wang, C.P. Chen, Y.Q. Lei, Q.D. Wang, Appl. Phys. Lett. 94 (2009) 041907-1-041907-3.
- [7] X.L. Fan, X.Z. Xiao, L.X. Chen, K.R. Yu, Z. Wu, S.Q. Li, Q.D. Wang, Chem. Commun. 44 (2009) 6857–6859.
- [8] Q.A. Zhang, Y. Nakamura, K. Oikawa, T. Kamiyama, E. Akiba, Inorg. Chem. 41 (2002) 6547–6549.
- [9] M. Mamatha, C. Weidenthaler, A. Pommerin, M. Felderhoff, F. Schüth, J. Alloys Compd. 416 (1–2) (2006) 303–314.
- [10] A. Marashdeh, T.J. Frankcombe, J. Chem. Phys. 128 (23) (2008) 234505-1–234505-5.
- [11] C. Wolverton, V. Ozolins, Phys. Rev. B 75 (6) (2007) 064101-064115.
- [12] K. Komiya, N. Morisaku, Y. Shinzato, K. Ikeda, S. Orimo, Y. Ohki, K. Tatsumi, H. Yukawa, M. Morinaga, J. Alloys Compd. 446 (2007) 237– 241.
- [13] T. Sato, M.H. Sorby, K. Ikeda, S. Sato, B.C. Hauback, S. Orimo, J. Alloys Compd. 487 (1-2) (2009) 472-478.
- [14] V. Iosub, T. Matsunaga, K. Tange, M. Ishikiriyama, Int. J. Hydrogen Energy 34 (2) (2009) 906–912.
- [15] H. Kabbour, C.C. Ahn, S.J. Hwang, R.C. Bowman Jr., J. Graetz, J. Alloys Compd. 446 (2007) 264–266.
- [16] A. Mamatha, B. Bogdanović, M. Felderhoff, A. Pommerin, W. Schmidt, F. Schüth, C. Weidenthaler, J. Alloys Compd. 407 (1-2) (2006) 78-86.
- [17] T.N. Dymova, M. Mukhidin, N.G. Eliseeva, Zh. Neorg. Khim. 15 (9) (1970) 2318–2320.
- [18] K. Bukka, J.D. Miller, J. Shabtai, Clay Clay Miner. 40 (1) (1992) 92-102.
- [19] M. Fichtner, C. Frommen, O. Fuhr, Inorg. Chem. 44 (10) (2005) 3479– 3484.
- [20] H.E. Kissenger, Anal. Chem. 29 (1957) 1702-1706.
- [21] X.B. Yu, Y.H. Guo, H. Yang, Z. Wu, D.M. Grant, G.S. Walker, J. Phys. Chem. C 113 (13) (2009) 5324–5328.