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Synergistic hydrogen desorption properties of the $4LiAlH_4 + Mg_2NiH_4$ composite

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ABSTRACT

Mg_2NiH_4 was prepared by hydriding combustion synthesis (HCS) method firstly. Then, the as prepared Mg_2NiH_4 was mechanically milled with $LiAlH_4$ to form a novel composite of $4LiAlH_4 + Mg_2NiH_4$. Hydrogen storage properties and reaction mechanism of the $4LiAlH_4 + Mg_2NiH_4$ composite during hydrogenation/dehydrogenation have been investigated systematically by pressure-composition-temperature (PCT), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements. The microstructure of the composite has been investigated by scanning electron microscopy (SEM). The experimental results show that there is a mutual destabilization effect between Mg_2NiH_4 and $LiAlH_4$ during hydrogen desorption. Mg_2NiH_4 can promote the decomposition of $LiAlH_4$ in both of the ball milling process and the thermal desorption process. Conversely, the in situ formed Al from the decomposition of $LiAlH_4$ can destabilize Mg_2NiH_4 via a new reaction pathway with lower activation energy. Moreover, the $4LiAlH_4 + Mg_2NiH_4$ composite shows ultrafast re-hydrogenation kinetics, and the re-hydrogenation mechanism has been revealed.

1. Introduction

The drastic energy crisis and environment pollution due to the excessive usage of finite fossil fuels have made hydrogen an ideal energy carrier for transportation application [1,2]. The hydrogen storage technology is one of major challenges and also a bottleneck for the wide use of hydrogen [3–6]. Complex hydrides of light metals, like $LiAlH_4$, have low decomposition temperature and high theoretical hydrogen capacity [7–9]. $LiAlH_4$ can release about 10.5 wt% of hydrogen by the following reactions [10]:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \text{ (5.3 wt\%, 423–448 K)} \tag{1}$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \text{ (2.6 wt\%, 453–493 K)} \tag{2}$$

$$LiH + Al \rightarrow LiAl + 1/2H_2 \text{ (2.6 wt\%, >673 K)} \tag{3}$$

However, unfavorable thermodynamics and sluggish hydrogen desorption kinetics restrict its application [11,12]. To overcome these obstacles, several approaches have been used to improve $LiAlH_4$ for hydrogen storage, including combining with other complex/metal hydrides [13–15] and doping with different catalysts [16–19].

A destabilized system, with excellent hydrogen storage properties, can be developed by the combination of $LiAlH_4$ with MgH_2 [20–23]. Zhang et al. [20] firstly reported that MgH_2 can effectively destabilize $LiAlH_4$. Ismail et al. [21] found that the dehydrogenation process of the MgH_2-$LiAlH_4$ composite consists of two stages: the first stage is the two-step decomposition of $LiAlH_4$ and the second stage is that the yielded Al and LiH phases disintegrate MgH_2 to form $Al_{12}Mg_{17}$ and $Li_{0.92}Mg_{4.08}$ phases along with the self-decomposition of the excessive MgH_2. In our previous work, the unique microstructure of MgH_2 prepared by hydriding combustion synthesis (HCS) is beneficial to its reaction with in situ formed Al from $LiAlH_4$, which not only destabilizes MgH_2, but also promotes the decomposition of Li_3AlH_6 [22]. Furthermore, the $MgH_2 + LiAlH_4$

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composite can be partially re-hydrogenated reversibly [23].

To the authors' certain knowledge, the study on the combination of $LiAlH_4$ with Mg_2NiH_4 for hydrogen storage has never been reported. Based on our previous study, the process of HCS can make for the high activity of Mg_2NiH_4 decided by its pure composition, loose and porous morphology, a large number of microfissures and crystal defects [24]. Compared with MgH_2 which is featured by the sluggish sorption kinetics and high thermal stability [25,26], sorption kinetics of Mg_2NiH_4 is distinctly enhanced with high reaction rate without any activation treatment in the first hydriding/dehydriding process [24]. Moreover, the dehydrogenation enthalpy of Mg_2NiH_4 (64 kJ/mol H_2) is lower than that of MgH_2 (75 kJ/mol H_2), suggesting the lower thermal stability of Mg_2NiH_4 [27]. Therefore, it is of importance to develop a $LiAlH_4$-Mg_2NiH_4 composite and reveal the hydrogen sorption mechanism of the composite.

In this paper, $LiAlH_4$ was milled with Mg_2NiH_4 prepared by HCS. The reaction pathway and the mechanism during the de/rehydrogenation process of $4LiAlH_4 + Mg_2NiH_4$ composite have been investigated in detail.

2. Experimental details

2.1. Materials and methods

$LiAlH_4$ (97 wt%) was purchased from Alfa-Aesar. Mg powder (99.72 wt%) and Ni powder (99.9 wt%) were purchased from TangShan WeiHao Magnesium Powder Co., Ltd. and JiangYou Hei-Bao Nanomaterial Co., Ltd., respectively.

HCS Mg_2NiH_4 was prepared by hydriding combustion synthesis method. Firstly, the commercial Mg powder and Ni powder were well mixed in a molar ratio of 2.1:1 by an ultrasonic homogenizer in acetone for 1 h. Secondly, after being completely dried in air, the well-mixed powder was directly placed into the synthesis reactor without any compressive treatment. Thirdly, the powder mixture was heated to 853 K at the rate of 7 K/min and held for 1 h, and subsequently cooled down to 613 K and held for 2 h under 2.0 MPa hydrogen atmosphere. Finally, the powder mixture was cooled down to room temperature under hydrogen atmosphere and the HCS Mg_2NiH_4 was obtained. Chourashiya et al. [28] synthesized the Mg-Ni-C sample by HCS process, in which the technological conditions are different from our study. In their work, the powder mixture under an initial pressure of 2 MPa H_2 was heated to 863 K and held for 1 h. Then the powder mixture was cooled down to 673 K and held for 4 h. Finally, the powder mixture was cooled down to room temperature and the Mg-Ni-C sample was obtained. During the HCS process, the hydrogen pressure was varying with temperature change instead of keeping constant in our experiment.

$LiAlH_4$ and HCS Mg_2NiH_4 with mole ratio of 4:1 were mechanically milled for 3 h with 2 wt% graphite as grinding aid. To prevent reaction with moisture and oxygen, all handling of the samples were performed in an Ar-filled glove box with low concentration of O_2 (<1 ppm) and H_2O (<1 ppm). Then the ball mill jar filled with the powder mixture and stainless steel balls under 0.1 MPa argon atmosphere was taken out of the glove box for mechanical milling. The milling treatment was performed on a QM-3SP2 planetary ball mill at 400 rpm, with ball to powder ratio of 40:1.

2.2. Sample characterization

The dehydrogenation and re-hydrogenation properties of the samples were measured using a Sievert's-type apparatus made by Advanced Materials Corporation (AMC, No. 0360Q). The phase composition of the sample was determined by XRD measurement, which was performed on an ARLX'TRA diffractometer using Cu Kα radiation at 45 kV and 35 mA. Sample was mounted in an Ar-filled sample holder in order to avoid oxidation during the XRD measurement. The surface morphology of the sample was observed by a JSM-6510 SEM. DSC analysis of the sample was carried out on a NETZSCH DSC 200 F3. During the DSC test, about 8 mg of sample was loaded into a ceramic crucible and then heated to 773 K under argon atmosphere with 40 ml/min flow rate and different heating rates.

3. Results and discussion

3.1. Mutual destabilization between $LiAlH_4$ and Mg_2NiH_4

Fig. 1 exhibits the thermal dehydrogenation performances of $4LiAlH_4 + Mg_2NiH_4$ composite. The TPD curves of as-milled $LiAlH_4$ and HCS Mg_2NiH_4 after mechanical milling (HCS + MM Mg_2NiH_4) are also collected for comparison. The milling time is 3 h. It can be noticed that the as-milled $LiAlH_4$ desorbs hydrogen through the two-step decomposition as shown in Eqs. (1) and (2) in the temperature ranges of 373–468 K and 468–546 K, respectively. After combining with HCS Mg_2NiH_4, a faster kinetics in the first step dehydrogenation can be observed, which is completed at 433 K, 35 K lower than that of the as-milled $LiAlH_4$ sample. Further heating leads to the second step decomposition, which is finished at 495 K, 51 K lower than that of the as-milled $LiAlH_4$. It can be seen that HCS + MM Mg_2NiH_4 starts to desorb hydrogen at about 453 K, which is in the second-step decomposition range of $4LiAlH_4 + Mg_2NiH_4$ system, indicating that the hydrogen released in the second step partly comes from Mg_2NiH_4. The total dehydrogenation capacity of the composite is 5.13 wt%, which is lower than the theoretical calculation value. The phenomenon can be attributed to the part decomposition of $LiAlH_4$ during the milling process, which will be discussed in the following.

To further analyse the mutual destabilization between Mg_2NiH_4 and $LiAlH_4$, the thermal decomposition behaviour of $4LiAlH_4 + Mg_2NiH_4$ composite, as well as the milled $LiAlH_4$ and HCS + MM Mg_2NiH_4, has been investigated by DSC as represented in Fig. 2. As-milled $LiAlH_4$ displays one exothermic peak at 421 K and one endothermic peak at 513 K, corresponding to the two-step decomposition of $LiAlH_4$ [18]. HCS + MM Mg_2NiH_4 shows three endothermic peaks. The first peak at 520 K results from the phase transformation of Mg_2NiH_4 (low-temperature (LT) monoclinic phase → high-temperature (HT) cubic phase). The second peak at

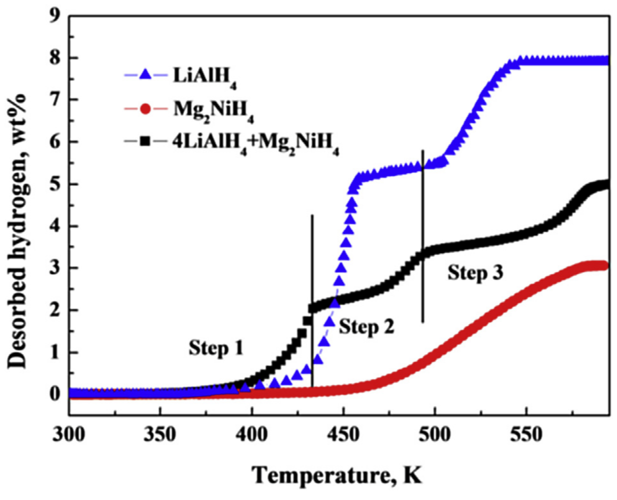

Fig. 1. Thermal desorption curves for as-milled $LiAlH_4$, HCS + MM Mg_2NiH_4 and $4LiAlH_4 + Mg_2NiH_4$ composite. The heating rate is 10 K/min.