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Effect of K_2TiF_6 additive on the hydrogen storage properties of $4MgH_2-LiAlH_4$ destabilized system

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ABSTRACT

In this study, the hydrogen storage properties and reaction mechanism of $4MgH_2-LiAlH_4$ destabilized system with K_2TiF_6 additive were studied for the first time. It was found that the addition of K_2TiF_6 resulted in both decreased decomposition temperature, and enhanced sorption kinetics, compared to undoped $4MgH_2 + LiAlH_4$. The onset dehydrogenation temperature of the 10 wt% K_2TiF_6 -doped $4MgH_2 + LiAlH_4$ sample was reduced by about 50 °C compared to the as-milled undoped $4MgH_2 + LiAlH_4$, and the saturation of dehydrogenation process for the K_2TiF_6 -added $4MgH_2 + LiAlH_4$ sample was achieved within 25 min compared with 45 min for the undoped sample. From the Kissinger plot, the activation energy for the MgH_2 -relevant decomposition was reduced from 126 kJ/mol for $4MgH_2-LiAlH_4$ composite to 107 kJ/mol after addition of K_2TiF_6 . The differential scanning calorimetry measurements indicated that the enthalpy change in the $4MgH_2 + LiAlH_4$ composite system was unaffected by the addition of K_2TiF_6 . It was believed that the formation of Ti-containing and Al-containing species together with a small amount of Li-containing species during the ball milling or the dehydrogenation process might be actually responsible for the catalytic effects, and thus, further improved the dehydrogenation of the K_2TiF_6 -added $4MgH_2 + LiAlH_4$ composite system.

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Introduction

Being an environmental friendly energy carrier, numerous efforts have been made to realize the potential of hydrogen to become a major energy carrier, for both mobile and stationary applications. However, the storage of hydrogen is still a major problem. There are three main approaches to store hydrogen, including high pressure, cryogenics, and chemical compounds, which reversibly release H_2 upon heating (solid-state storage). Among them, solid-state storage offers several benefits over compressed and liquid hydrogen storages,

particularly in terms of safety, cost, and high volumetric and gravimetric densities. Among the solid-state hydrogen storage materials, MgH_2 has been widely studied as a potential material for solid-state hydrogen storage due its large hydrogen storage capacity (7.6 wt%), low cost, and good reversibility [1,2]. Nevertheless, the high thermodynamic stability and slow desorption kinetics [3,4] hampers the practical application of MgH_2 . Many studies have been conducted to overcome these problems, such as by preparing nanocrystalline Mg powder [5] and adding catalysts [6–12]. Besides the studies mentioned above, a “destabilization concept” was also introduced [13–15]. This approach is aimed at modifying the

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thermodynamics and kinetics of the hydrogen sorption reaction by mixing with additives that form a new compound during dehydrogenation. Many studies have shown that the dehydrogenation properties of MgH_2 were improved when it was mixed with other elements or compounds, such as Si [16], Ge [17], NaAlH_4 [18], LiAlH_4 [19], Li_3AlH_6 [20], and Na_3AlH_6 [21].

As one of an interesting destabilized system, the $\text{MgH}_2 + \text{LiAlH}_4$ system has been investigated by several groups [19,22–25]. Recently, Zhang et al. [19] showed that MgH_2 can be destabilized effectively by LiAlH_4 . They found that the reaction enthalpy of the MgH_2 -relevant decomposition in MgH_2 - LiAlH_4 composites (1: 1, 1: 2, and 4: 1 in mole ratio) was reduced by 31, 27.4, and 15 kJ/mol H_2 compared to as-milled pristine MgH_2 (76 kJ/mol H_2). Although the hydrogen storage properties of MgH_2 were improved after combination with LiAlH_4 , it still did not fulfil the requirements for practical application as a suitable hydrogen storage material. Therefore, it is important to find a catalyst or additive that can improve the hydrogen storage properties of the $\text{MgH}_2 + \text{LiAlH}_4$ composite system. To the best of the authors' knowledge, so far, there have only been a few reports on the effect of catalyst on the hydrogen storage properties of $\text{MgH}_2 + \text{LiAlH}_4$ [23,24,26,27]. So, it is of interest to further investigate the addition of a different type of catalyst and examine the difference in the way they take effect, and therefore, gain deeper understanding on the modification of dehydrogenation process of the $\text{MgH}_2 + \text{LiAlH}_4$ system.

To our knowledge, no studies have been reported on $\text{MgH}_2 + \text{LiAlH}_4$ system doped with K_2TiF_6 for solid state hydrogen storage. Li et al. [28] reported that the K_2TiF_6 is a promising additive that can remarkably improve the dehydrogenation performance of LiAlH_4 . From the XRD results, they suggested that TiH_2 , Al_3Ti , LiF , and KH were in situ formed, which were responsible for the improved dehydrogenation properties of LiAlH_4 . More recently, we have demonstrated that the hydrogen storage properties of MgH_2 were improved after doping with K_2TiF_6 [29]. It is believed that the K_2TiF_6 additive doped with MgH_2 played a catalytic role through the formation of active species of KH , TiH_2 , MgF_2 and Ti during the ball milling or heating process. Thus, it is reasonable to believe that K_2TiF_6 would show great potential as a suitable catalyst to improve the hydrogen storage properties of the $\text{MgH}_2 + \text{LiAlH}_4$ composite system.

In the present paper, we investigated the effect of K_2TiF_6 on the hydrogen storage properties of $\text{MgH}_2 + \text{LiAlH}_4$ system. The possible mechanism behind the catalytic effect of K_2TiF_6 in the MgH_2 - LiAlH_4 composite is discussed herein.

Experimental details

MgH_2 (hydrogen storage grade) and LiAlH_4 ($\geq 95\%$) were purchased from Sigma Aldrich. K_2TiF_6 (97%) was obtained from Alfa Aesar. All the materials were used as received with no further purification. Ball milling (BM) of MgH_2 and LiAlH_4 powders in the mole ratio of 4: 1 was performed in a planetary ball mill (NQM-0.4) for 1 h at the rate of 400 rpm. Handling of the samples was conducted in an MBraun Unilab

glove box filled with high purity Ar atmosphere. The samples were put into a sealed stainless steel vial, together with hardened stainless steel balls. The ratio of the weight of balls to the weight of powder was 30: 1.10 wt% of K_2TiF_6 was mixed with $\text{MgH}_2 + \text{LiAlH}_4$ under the same conditions to investigate the catalytic effects. Pure MgH_2 and LiAlH_4 were also prepared under the same conditions for comparison purposes.

The temperature programmed desorption (TPD) and re/dehydrogenation kinetics experiments were performed in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. As for the TPD experiment, all the samples were heated in a vacuum chamber, and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the TPD experiment was 5 °C/min, and the samples were heated from room temperature to 450 °C. The re/dehydrogenation kinetics measurements were performed at the desired temperature with initial hydrogen pressures of 3.0 MPa and 0.1 MPa, respectively.

The phase structures of the samples before and after desorption, as well as after rehydrogenation, were determined by X-ray diffraction (Rigaku MiniFlex X-ray diffractometer with Cu K α radiation). Before measurement, a small amount of the sample was spread uniformly on the sample holder and was wrapped with a plastic wrap to prevent oxidation. $\theta - 2\theta$ scans were carried out over diffraction angles from 25° to 80° with the speed of 2.00°/min.

Thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) of the dehydrogenation process was carried out on a Mettler Toledo TGA/DSC 1. The sample was loaded into an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove box to the TGA/DSC apparatus. An empty alumina crucible was used for reference. The samples were heated from room temperature to 500 °C under an argon flow of 30 ml/min, and different heating rates were used.

Result and discussion

Dehydrogenation temperature

Fig. 1 displays the TPD curves of the as-milled MgH_2 , the as-milled LiAlH_4 , and the $4\text{MgH}_2 + \text{LiAlH}_4$ composite with and without K_2TiF_6 . The as-milled MgH_2 started to release hydrogen at about 330 °C and desorbed about 7.1 wt% H_2 after 420 °C. Meanwhile, the as-milled LiAlH_4 released about 7.5 wt% hydrogen in the dehydrogenation temperature range between 180 °C and 230 °C. As for the $4\text{MgH}_2 + \text{LiAlH}_4$ composite with and without K_2TiF_6 , it was believed that two significant stages of dehydrogenation occurred during the heating process. The two stages of dehydrogenation process were of the same order as reported by Zhang et al. [19] and Chen et al. [22]. As for the 4MgH_2 - LiAlH_4 without K_2TiF_6 , the first stage, which took place within the temperature range from 130 to 250 °C, was attributed to the two-step decomposition of LiAlH_4 , as shown in Eqs. (1) and (2).

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