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Enhancement of hydrogen sorption properties of MgH_2 with a MgF_2 catalyst

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ABSTRACT

Effect of a MgF_2 catalyst, prepared by ball-milling, on the hydrogen desorption ability of commercial MgH_2 was investigated. When MgH_2 was catalyzed with a MgF_2 composite, it exhibited good cyclability and sharp faceting, with a small grain size (around 10 nm), which differs from those of pure MgH_2. The addition of the MgF_2 catalyst suggests that the F anion could significantly contribute to the cyclability of Mg particles and aid in the inhibition of MgH_2 grain growth.

Introduction

The interest in using hydrogen as an alternative fuel has increased for many applications over the past decade, from mobile electronics to aerospace industries [1–3]. Solid storage of hydrogen using a reversible metal hydride is one of the most promising methods for hydrogen storage [3–5]. Advantages of using reversible metal hydrides include improved safety, reduced environmental impact, and high hydrogen storage capacity. The high temperature required for the formation of metal hydrides with acceptable hydrogen uptake and release kinetics, however, is an important limitation that makes the process expensive [3,6,7].

Magnesium-based hydrides, with a reversible hydrogen capacity of up to 7.6 wt% for on-board applications, are promising for hydrogen storage [8–10]. Magnesium hydride, MgH_2, has the highest energy density (9 MJ/kg Mg) of all of the reversible hydrides used for hydrogen storage. MgH_2 has a high H_2 capacity of 7.7 wt%, and is low cost, using readily available magnesium that has good reversibility [8,9]. However, the main disadvantages of using MgH_2-based hydrogen storage include the high temperature of hydrogen desorption (>673 K) and its high reactivity in air and oxygen [8,9]. Technologies currently under research for improving the hydrogen storage of MgH_2/Mg can be classified into four categories: alloying, nanoscaling, nanoconfinement, and additive-

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addition [11,12]. Ball milling/mechanical milling, a current technology, can be used for improving the surface and kinetic properties of MgH_2/Mg, due to changes caused by structural defects, phase change, and crystallinity [8–13].

Several experiments have been conducted for improving kinetics through ball milling of the bulk of magnesium metal, alloying with transition metal oxides or transition metal fluoride catalysts (such as TiF_3, NbF_5, and NiF_2), and destabilizing the magnesium-transition metal-hydrogen matrix [14–20]. MgH_2 could react with metal fluoride (TiF_3, NbF_5, etc.) and form MgF_2 during the milling and hydrogenation/dehydrogenation processes [15,20]. Liu and Susa [21] reported the formation of a MgF_2 layer on a Mg_2Ni particle, which suggests that MgF_2 has a high affinity to hydrogen with a rapid initial activation. Jian et al. [22] reported the effect of MgF_2 on the hydrogenation properties of MgH_2, and found that adsorption at a low temperature could be possible, since MgF_2 was evenly distributed within the MgH_2 powder. They also reported that the presence of chemically stable MgF_2 during hydrogen cycling affected the improvement of sorption ability; however, the actual role of MgF_2 on the dehydrogenation/hydrogenation of MgH_2 powder has not yet been systematically understood. The main objectives of this study were to investigate how the addition of MgF_2 catalyst enhanced the kinetics of the hydrogen desorption mechanism of metal hydride.

Experimental method

The methodology used for sample preparation and elements of the hydrogenation system have been described in depth in a previous study [23]. Therefore, only the experimental conditions are outlined here. MgH_2 particles (nominally 90% pure, with most of the remainder being Mg) were ball milled with 1, 3, and 10 mol% MgF_2 at 400 rpm for 60 min. Hydrogen absorption was measured using a PCT pro 2000 instrument (Hy-Energy, CA). Two conventional transmission electron microscopes (TEM, Zeiss Libra 200 FEG and CM 200 FEG, 200 kV accelerating voltage) were used for electron energy loss spectroscopy (EELS) and high-resolution imaging, respectively. MgH_2 powder was dispersed in hexane to minimize any possible exposure to air [24], and a drop of the suspension was deposited onto a Cu TEM grid in an argon glove box directly before the TEM session. The EELS technique was used to map the fluorine distribution of MgH_2–MgF_2 composites. The x-ray diffraction patterns of MgH_2–MgF_2 composites (as-synthesized, and after 3rd and 6th desorption of MgH_2–MgF_2) were identified with reference to the diffraction patterns of hexagonal Mg (JCPDS 04-0770), tetragonal MgH_2 (JCPDS 12-0697), and tetragonal MgF_2 (JCPDS 38-0882), respectively.

Result and discussion

Determination of optimal MgF_2 loading conditions

Distribution and dispersion of the catalyst over the surface of magnesium particles are critical in determining hydrogen absorption and desorption kinetics. The effect of MgF_2 loading was evaluated using 1, 3, and 10 mol% MgF_2 (Fig. 1).

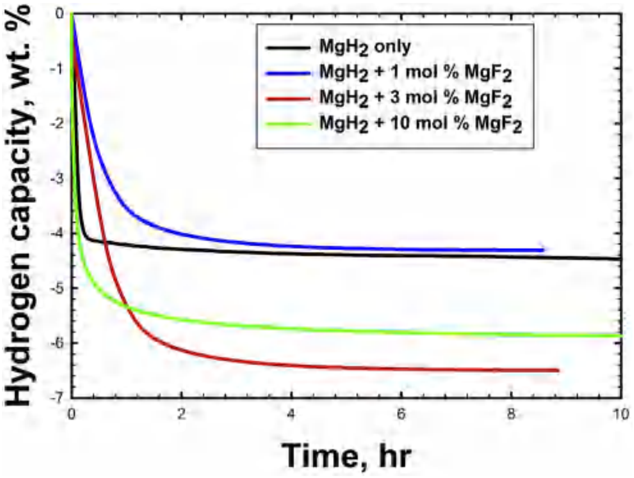

Fig. 1 – Effect of the addition of MgF_2 on hydrogen desorption capacities/kinetics. (desorption at 673 K and 0 bar).

The MgH_2-x mol% MgF_2 (x = 1, 3, and 10) composites show greater hydrogen desorption capacities than that of pure Mg at 673 K. The amount of hydrogen desorbed from MgH_2 with 3 and 10 mol% MgF_2 was 6.49 and 5.85 wt%, respectively, while uncatalyzed MgH_2 released 4.44 wt% of hydrogen (Fig. 1). In contrast, a 1 mol% MgF_2 sample desorbs 4.31 wt% of hydrogen, less than that of the pure MgH_2 sample, which is likely due to the insufficiency of MgF_2 in prohibiting the Mg grain growth. The composite processed with 3 mol% MgF_2 has a significantly higher hydrogen desorption capacity than that of the composite with 10 mol% MgF_2, which could render this composite less practical for onboard storage. Higher catalyst loading might increase the number of favorable H_2 dissociation sites; therefore, it increased the hydrogen dissociation [25]. In contrast, lower catalyst loading might not sufficiently cover

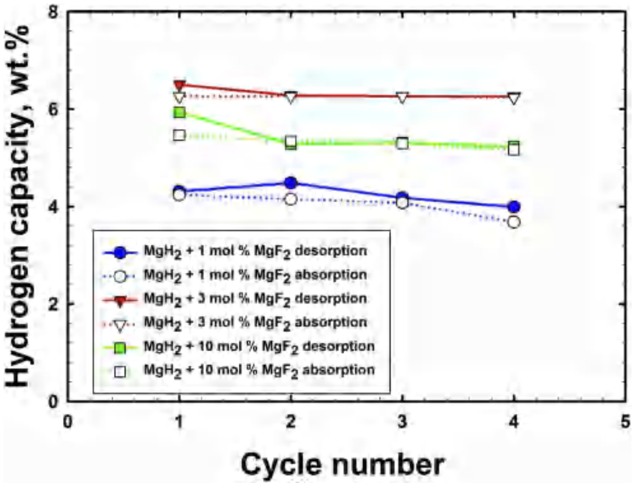

Fig. 2 – Effect of the addition of fluoride on the cycling behavior of MgH_2 (desorption at 673 K and 0 bar, and absorption at 573 K and 45 bar, composites milled for 1 h at 400 rpm with no transition metal catalyst added).

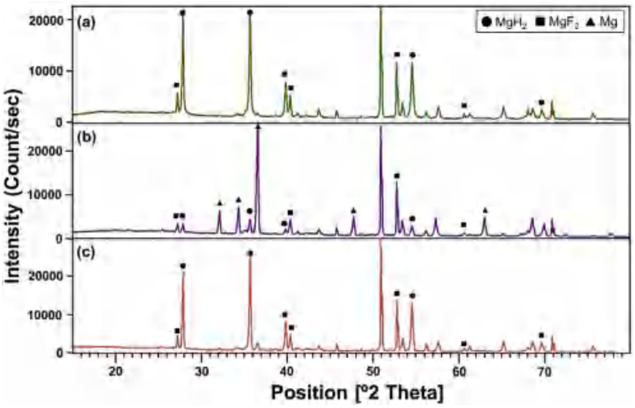

Fig. 3 – XRD patterns of MgH2 + 3 mol% MgF_2 samples; (a) fresh sample, (b) after desorption at 673 K under 0 bar, and (c) after absorption at 573 K under 45 bar.

the Mg surface, resulting in localized catalytic enhancement; therefore, 3 mol% MgF_2 is identified as the optimal catalyst loading condition.

During the initial stages (before 1 h) shown in Fig. 1, the 10 mol% MgF_2 sample showed a steeper hydrogen desorption rate slope than those of the 0, 1, and 3 mol% MgF_2 samples. The desorption rate of the 3 mol% MgF_2 sample initially declines less steeply than that of the 10 mol % MgF_2; however, the amount of hydrogen released was approximately 10% greater. It can be concluded that the addition of MgF_2 slows the desorption of MgH_2, but increases the amount of hydrogen desorbed, despite the added weight.

Cycling stability of hydrogen sorption of MgF_2-x mol% MgF_2 (x = 1, 3, and 10)

A critical problem for practical application is the deterioration of the catalytic effects of the active material over repeated cycling [6]. The effect of MgF_2 loading was further evaluated using 1, 3, and 10 mol% MgF_2, and it was found that the effects of the added fluoride persist through repeated cycling. Fig. 2 shows that MgH_2-x mol% MgF_2 (x = 1, 3, and 10) is stable up to the 4th cycle. Although repeated cycling of 10 mol% MgF_2 shows a slight decrease in efficiency, large amounts of the MgF_2 (10 mol%) composite still have good cyclability of the hydrogen absorption/desorption capacity under both 573 and 673 K. The poor cycling results of 1 mol% MgF_2 are likely to be due to its insufficient catalytic enhancement. In contrast, the composite processed with 3 mol% MgF_2 showed a significant increase in hydrogen desorption capacity. The 3 mol% MgF_2 sample desorbed 6.50 wt% of hydrogen at 673 K and 0 bar, and took up 6.26 wt % at 573 K and 45 bar. In the 2nd cycle, it desorbed 6.28 wt% at 673 K and 0 bar. Although the kinetics of absorption and desorption are not noticeably improved, MgF_2 increases the utilization of MgH_2 to near theoretical values, compared to that of MgH_2 without the addition of fluoride. These findings are consistent with the catalytic effect of transition metal fluorides on the hydrogenation/dehydrogenation reactions of MgH_2.

Properties of MgH_2–MgF_2 composite

In this study, we reported the effects of the addition of MgF_2 on the hydrogen desorption capacity and kinetics of magnesium hydride. Fig. 3 shows the X-ray diffraction patterns of the fresh MgH_2 and MgF_2 mixture, and its absorption and desorption states. In the XRD pattern, it is notable that the MgF_2 peak does not decrease after the dehydrogenation-hydrogenation of MgH_2 (Fig. 3b and c). This could be caused by MgF_2 not participating in the formation of MgH_2, as it behaves as a catalyst for enhancing the hydrogen capacity and cyclability of MgH_2 to near-theoretical values. Therefore, MgF_2 could be a stable substance that is not involved in the reaction of MgH_2. These observations are similar to those from a Nb hydride catalyst, which improved the hydrogen absorption kinetics by forming a nanostructured Nb hydride along the grain boundary of nanocrystalline MgH_2 [26].

Inhibition of Mg grain growth in 3 mol% MgF_2 containing samples

In Section properties of MgH_2eMgF_2 composite, we reported that the XRD analyses of the MgH_2– MgF_2 composites showed no evidence of bulk fluorine substitution, and that MgF_2 retained its crystallinity and did not decrepitate during the absorption and desorption cycles. However, the actual role of the MgF_2 catalyst in making the 3 mol% MgF_2 composites show better sorption kinetics than pure MgH_2 is still unclear. This could be due to the balanced, homogeneous mixture of fine nanocrystalline MgH_2 and MgF_2. To understand the distribution of MgF_2 on MgH_2, MgH_2 with 3 mol% MgF_2 was

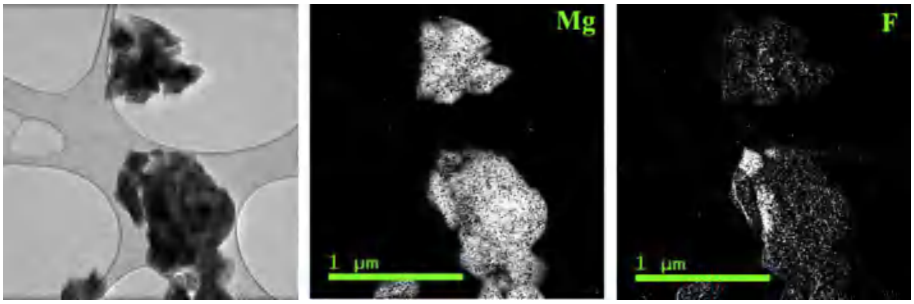

Fig. 4 – HR (or FE) TEM elemental maps of fluoride and magnesium from the F-K edge of 685 eV and Mg–K edge of 1305 eV, respectively, along with a bright-field TEM micrograph (3 mol% MgF_2 composites milled for 1 h at 400 rpm).

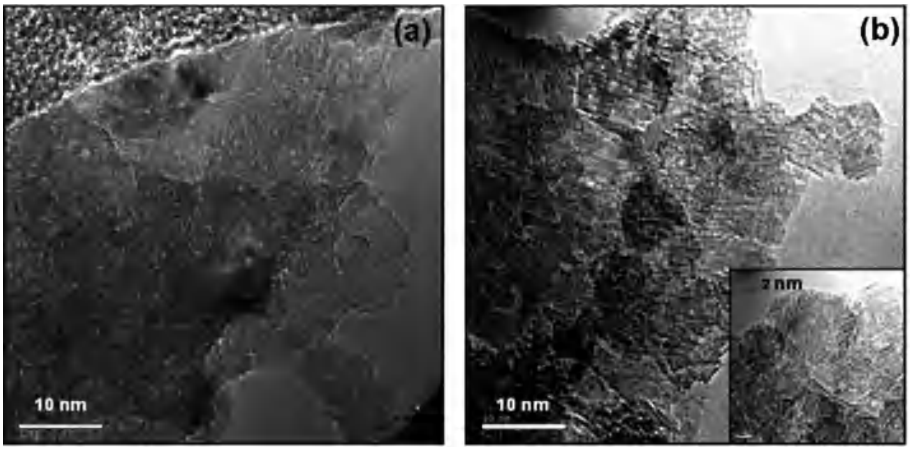

Fig. 5 – HRTEM micrographs taken of 3rd dehydrogenated samples; (a) pure MgH_2 after 3rd desorption at 673 K and 0 bar, (b) MgH2 +3 mol% MgF2 after 3rd desorption @ 673 K and 0 bar. The TEM picture shows the inhibition of Mg grain growth.

analyzed using transmission electron microscopy (TEM), bright-field imaging, and energy-filtered TEM (EFTEM) imaging (Zeiss Libra 200 FEG, 200 kV accelerating voltage), as shown in Fig. 4. The EFTEM elemental maps of fluoride and magnesium from the F–K edge of 685 eV and Mg–K edge of 1305 eV, respectively, show that the fluoride seems to have a uniform distribution over the MgH_2 particle surfaces.

High-resolution TEM (CM200 FEG, 200 kV accelerating voltage) was used to analyze the role of MgF_2 on the grain growth of MgH_2 after the 3rd hydrogenation/dehydrogenation cycle. As shown in Fig. 5, high-resolution TEM micrographs of the fluoride-containing Mg particles following cycling and desorption show sharp faceting with small grain sizes (around 10 nm), which differ from pure MgH_2, indicating that it inhibits the coarsening and sintering of MgH_2, which had also been suggested for the addition of Nb_2O_5 [16,19,26]. In contrast, without fluoride, sintering and coarsening reduce the surface area and contribute to Mg isolation. It could, therefore, be concluded that the cyclability of Mg particles following several hydrogen absorption and desorption cycles indicates that fluoride is a novel catalyst and a grain growth inhibitor on $MgH_{2.}$

Conclusion

Kinetics of hydrogen desorption reactions were investigated for commercial MgH_2 powder catalyzed with MgF_2 by ball-milling. The 3 mol% MgF_2 composite desorbs 6.50 wt% of hydrogen at 673 K, which was greater than that of pure MgH_2 (4.44 wt %), and its desorption capacity remained constant through cycling. The XRD results did not show evidence of a bulk fluorine peak after the desorption-adsorption cycle. The high-resolution TEM images demonstrated that the 3 mol% MgF_2 composite exhibited sharp faceting with small grain sizes (around 10 nm), which differs from those of pure MgH_2. It could, therefore, be concluded that the cyclability of Mg particles following several hydrogen absorption and desorption cycles indicate that MgF_2 is a novel catalyst and inhibits grain growth on MgH_2.

Acknowledgments

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