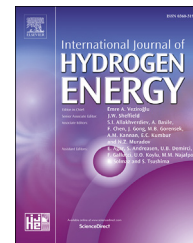




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Enhancement of hydrogen sorption properties of MgH₂ with a MgF₂ catalyst

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ABSTRACT

Effect of a MgF₂ catalyst, prepared by ball-milling, on the hydrogen desorption ability of commercial MgH₂ was investigated. When MgH₂ was catalyzed with a MgF₂ composite, it exhibited good cyclability and sharp faceting, with a small grain size (around 10 nm), which differs from those of pure MgH₂. The addition of the MgF₂ catalyst suggests that the F anion could significantly contribute to the cyclability of Mg particles and aid in the inhibition of MgH₂ grain growth.

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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, MgH₂, has the highest energy density (9 MJ/kg Mg) of all of the reversible hydrides used for hydrogen storage. MgH₂ has a high H₂ 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 MgH₂-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 MgH₂/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 $\text{MgH}_2\text{-MgF}_2$ composites. The x-ray diffraction patterns of $\text{MgH}_2\text{-MgF}_2$ composites (as-synthesized, and after 3rd and 6th desorption of $\text{MgH}_2\text{-MgF}_2$) 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).

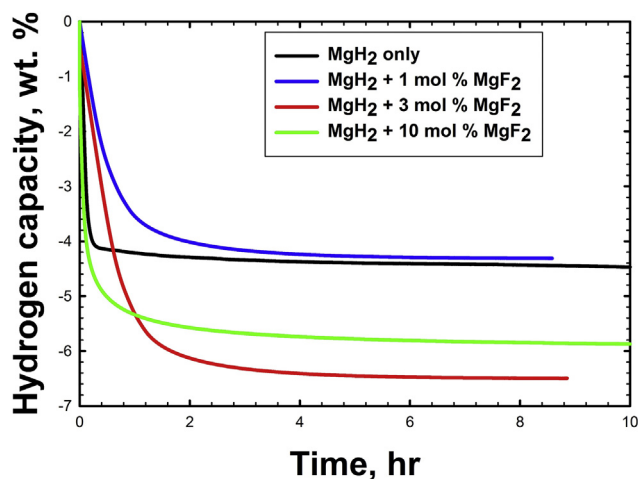


Fig. 1 – Effect of the addition of MgF_2 on hydrogen desorption capacities/kinetics. (desorption at 673 K and 0 bar).

The $\text{MgH}_2\text{-x mol}\% \text{MgF}_2$ ($x = 1, 3$, 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

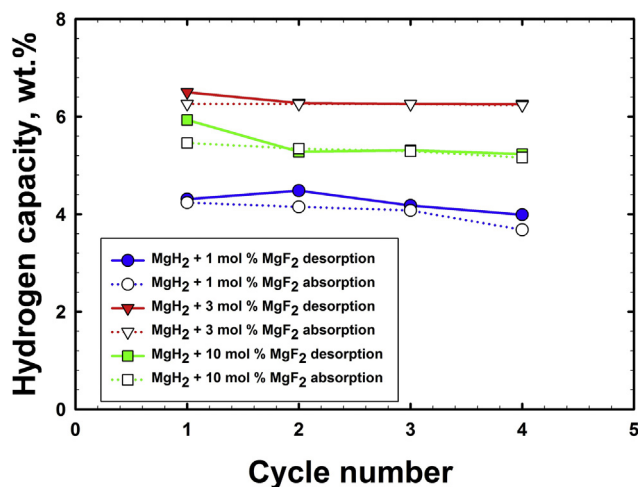


Fig. 2 – Effect of the addition of fluoride on the cycling behavior of MgH_2 (desorption at 673 K and 0 bar, and absorption at 573 K and 45 bar, composites milled for 1 h at 400 rpm with no transition metal catalyst added).

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