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Hydrogen storage in Mg–$LiBH_4$ composites catalyzed by FeF_3

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HIGHLIGHTS

- The effect of FeF_3 on the Mg–10 mol%$LiBH_4$ is investigated.
- Mg–10 mol%$LiBH_4$ + 5 mol% FeF_3 shows improved dehydrogenation kinetic properties.
- In-situ formation of the FeB species is detected.

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ABSTRACT

Mg–10 mol% $LiBH_4$ composite plus small amounts of FeF_3 is investigated in the present work. The presence of $LiBH_4$ during the milling process noticeably modifies the size and morphology of the Mg agglomerates, leading to faster hydrogenation and reaching almost the theoretical hydrogen capacity owing to enhanced hydrogen diffusion mechanism. However, the dehydrogenation of the system at low temperatures (≤300 °C) is still slow. Thus, FeF_3 addition is proposed to improve the dehydrogenation kinetic behavior. From experimental results, it is found that the presence of FeF_3 results in an additional size reduction of the Mg agglomerates between ~10 and ~100 μm and the formation of stable phases such as MgF_2, LiF and FeB. The FeB species might have a catalytic effect upon the MgH_2 decomposition. As a further result of the FeF_3 addition, the Mg–10 mol%$LiBH_4$–5 mol% FeF_3 material shows improved dehydrogenation properties: reduced dehydrogenation activation energy, faster hydrogen desorption rate and reversible hydrogen capacities of about 5 wt% at 275 °C.

1. Introduction

The design of adequate materials for hydrogen storage is the main challenge for application of the "hydrogen economy" to the transport sector. Metal hydrides, complex hydrides and nanotubes, among others, have been investigated as hydrogen carriers [1–6]. Despite all the effort put in improving such solid materials, unfortunately none of the available candidate storage materials meet the DOE technical targets, which involve reversible hydrogen capacity of 1.8 kWh kg (>6 wt% H; year 2017) at moderates pressures and temperatures with fast de/hydrogenation kinetics, high cycle stability, low enthalpy effects and low cost [7].

In particular, MgH_2 has high reversible storage capacity (7.6 wt% H) and low cost; but the main drawback is that its high enthalpy does not allow low desorption temperatures (<300 °C). Several investigations showed that the hydrogen storage capacity and kinetic behavior of MgH_2 can be improved by applying different strategies such as the synthesis of nanocrystalline hydrides through

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high energy mechanical milling, the addition of catalysts such as transition metal oxides and halides and the combination of MgH_2 plus complex hydrides with light weight elements, mainly with $LiBH_4$ due to its high hydrogen content of 18.3 wt% H [8–30].

Johnson et al. [13] and Mao et al. [14] obtained enhanced hydrogen absorption kinetic properties at low temperatures for Mg via the addition of small amounts of $LiBH_4$. Microstructural, morphological and thermal analyses showed that the MM of Mg + 10 mol% $LiBH_4$ material in argon atmosphere results in a physical mixture of Mg and $LiBH_4$ with small agglomerate size distributions from 10 μm to 170 μm and grain sizes of roughly 20 nm for Mg [16,17]. Investigations on the kinetic and thermodynamic properties of the Mg + 10 mol% $LiBH_4$ material led to the conclusion that the addition of $LiBH_4$ to Mg has neither catalytic effect on the hydrogen sorption properties of MgH_2, nor influence on thermodynamic behavior of the Mg–MgH_2 hydride system, respectively. However, improved hydrogen absorption kinetic properties mainly at low temperatures (300 °C) were noticed. This behavior was attributed to the high degree of microstructural refinement and Mg agglomerates with irregular surfaces which provide shorter diffusion paths for hydrogen and more specific surface for the Mg and H interaction [16,17]. Despite the fact that the Mg + 10 mol% $LiBH_4$ material presented improved hydrogen absorption kinetic properties at 300 °C, its hydrogen desorption rate was still slow.

It was observed that transition metal oxides and halides reduce the temperature and speed up the rate of MgH_2 decomposition [18–30]. Oelerich et al. and Barkhordarian et al. [19–21] showed that transition metal oxides have a beneficial effect on the MgH_2 sorption kinetic behavior. It was reported that Nb_2O_5 is the most effective oxide to speed up the hydrogen sorption of MgH_2 at a low temperature of 250 °C [20,21]. Deledda et al. [23] found that the addition of 5 mol% FeF_3 reduces the desorption temperature of MgH_2 up to 230 °C and shortens the hydrogen release times to 500 s at 300 °C. Moreover, Yavari et al. [24] also reached lower desorption temperature of 250 °C and faster decomposition rates for MgH_2 by the addition of 3 mol% of FeF_3. This enhanced desorption behavior of MgH_2 was attributed to the catalytic effect of a highly reactive surface composed of MgF_2 and Fe nanoparticles formed from the MgH_2 and FeF_3 interactions [24,25]. In other works [26–30], the catalytic effect of several transition metal halides such as FeF_2, NiF_2, TiF_3, NbF_5, VF_4, ZrF_4 and CrF_2 upon the kinetic properties of MgH_2 was studied. It was found that Ti, V and Nb halides are more effective than Fe, Zr and Cr halides. Additionally, Ma et al. [30] investigated the differences between the catalytic effects of TiF_3 and $TiCl_3$ upon MgH_2. Based on the experimental results they concluded that fluorine anion has a more effective catalytic effect than chlorine one. Furthermore, they inferred that fluorine and chlorine interact with Mg in different ways. Transition metal halides also cause destabilizing effects on $LiBH_4$ [31–34]. Adding transition metal halides such as $TiCl_3$, TiF_3 and $MnCl_2$ to $LiBH_4$, it is possible to noticeably reduce the decomposition temperature up to 150 °C [32–35].

The transition metal halides addition can lower the decomposition temperature of both MgH_2 and $LiBH_4$ [22–35] and shorten the hydrogen release times from MgH_2 [23,24]. Therefore, in this work FeF_3 was added to Mg + 10 mol%$LiBH_4$ composite material in order to improve its decomposition kinetic behavior. Applying several experimental techniques and calculations in equilibrium conditions, we investigated the influence of FeF_3 upon the hydrogen sorption kinetic behavior of MgH_2. Furthermore, the interactions between the iron halide and $LiBH_4$ were also analyzed.

2. Experimental

2.1. Material preparation

Mg composite materials were prepared by ball milling in argon atmosphere by using a Fritsch–P6 planetary mill device, an 80 ml milling chamber and ball to powder ratio of 40:1. Moreover, some compounds were also mixed in mortar in order to study their interactions upon heating. As starting materials Mg (Riedel–de Haën, purity > 99.9%), $LiBH_4$ (Sigma–Aldrich, purity ≥ 90%), Fe (Sigma–Aldrich, purity > 99.99%) and FeF_3 (Sigma–Aldrich, purity > 99.99%) were used. In order to work with fresh material and to minimize the formation of species such as oxides, hydroxides, etc., all materials were prepared and stored no more than two weeks in glove boxes with oxygen and moisture controlled atmosphere before performing the measurements and characterizations. In Table 1, the composition expressed in mol%, the preparation procedure and their parameters as well as the used characterization techniques are shown. All the Mg composite materials are designated throughout the paper as shown in Table 1.

2.2. Material characterization

The investigated Mg composite materials during and after the mechanical milling (MM), after hydrogenation and dehydrogenation were characterized using the following techniques: laboratory X–ray diffraction (Lab–PXD), ex-situ and in-situ synchrotron radiation X-ray diffraction (SR–PXD), scanning electron microscopy (SEM) with dispersive X-ray spectroscopy (EDS), high resolution transmission electron microscopy (HR-TEM) with electron diffraction and EDS, differential scanning calorimetry (DSC), Fourier

Table 1

Composition in mol%, designation, preparation procedures and their parameters as well as the used characterization techniques for the investigated materials.

Material (composition in mol%)	Designation	Preparation procedure and parameters	Characterization techniques
90 Mg + $10LiBH_4$	M10L	Milled for 10 h at 400 rpm	Lab. PXD, DSC, PSD, titration measurements
60 Mg + $40LiBH_4$	M40L	Milled for 10 h at 400 rpm	Lab. PXD, FT-IR of the solid phase
85 Mg + $10LiBH_4$ + 5Fe	M10L5Fe	Milled for 10 h at 400 rpm	Lab. PXD, DSC, SEM, PSD, HR-TEM, titration measurements, equilibrium calculations
50 Mg + $40LiBH_4$ + 10Fe	M40L10Fe	Milled for 10 h at 400 rpm 50 Mg + $40LiBH_4$ and then 10Fe mixed in mortar	Lab. PXD, FT-IR of the solid phase
85 Mg + $10LiBH_4$ + $5FeF_3$	M10L5FF	Milled for 10 h at 400 rpm	Lab. and SR – PXD, DSC, SEM, HR-TEM, FT-IR of the gas phase, titration measurements, equilibrium calculations
50 Mg + $40LiBH_4$ + $10FeF_3$	M40L10FF	Milled for 10 h at 400 rpm 50 Mg + $40LiBH_4$ and then $10FeF_3$ mixed in mortar	Lab. PXD, in-situ SR – PXD, FT-IR of the solid phase, equilibrium calculations