Influence of different amounts of FeCl$_3$ on decomposition and hydrogen sorption kinetics of MgH$_2$

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ABSTRACT

In the present work, the hydrogen storage properties of MgH$_2$-X wt.% FeCl$_3$ (X = 5, 10, 15 and 20) are investigated experimentally. It is found that the MgH$_2$ + 10 wt.% FeCl$_3$ sample exhibits the best comprehensive hydrogen storage properties, in terms of the onset dehydrogenation temperature, the hydrogen amounts de/reabsorbed as well as the relative de/rehydrogenation rates. The onset dehydrogenation temperature of the 10 wt.% FeCl$_3$-doped MgH$_2$ sample is reduced by about 90 °C compared to the as-milled MgH$_2$, and the sorption kinetics measurements indicate that the FeCl$_3$-doped sample displays an average dehydrogenation rate 5–6 times faster than that of the undoped MgH$_2$ sample. Higher levels of doping introduce negative effects, such as lower capacity and slower absorption/ desorption rates compared to samples with lower FeCl$_3$ doping levels. The apparent activation energy for hydrogen desorption is decreased from 166 kJ•mol^{-1} for as-milled MgH$_2$ to 130 kJ•mol^{-1} by the addition of 10 wt.% FeCl$_3$. It is believed that the improvement of the MgH$_2$ sorption properties in the MgH$_2$/FeCl$_3$ composite is due to the catalytic effects of the in-situ generated Fe species and MgCl$_2$ that are formed during the heating process.

1. Introduction

Its large gravimetric density (7.6 wt.% H$_2$), abundant resources, low cost and good reversibility are advantages of MgH$_2$ compared with other metal hydrides or complex hydrides such as LaNi$_5$ [1] and LiAlH$_4$ [2–5]. These advantages make MgH$_2$ an attractive material as a potential candidate for solid-state hydrogen storage. Nevertheless, the high decomposition temperature and slow desorption/absorption kinetics are two problems that limit the use of MgH$_2$ as a hydrogen storage material. Many extensive efforts have been carried out to overcome these problems, including the use of a catalyst [6,7], mechanical treatment to produce nanocomposites [8–10] and combination with other metal/complex hydrides (destabilisation systems) [11–20]. Among them, the introduction of catalysts into MgH$_2$ has produced a significant effect on the hydrogen sorption properties of MgH$_2$. Various catalysts have been doped into MgH$_2$ by mechanical milling such as metal [21–27], metal oxide [28–36], metal halide [7,37–47], carbon materials [48–55] and alloys [56–59].

Previous studies have shown that the addition of a transition-metal compound on MgH$_2$ significantly improved the hydrogen sorption properties. This enhancement can be

associated with the catalytic role of transition metal cations to the dissociation process of hydrogen molecules. Liang et al. [23] reported that the added 5 wt.% transition metal (Ti, V, Mn, Fe, Ni) improved the de/rehydrogenation kinetics of MgH_2 compared to undoped MgH_2. Meanwhile, the addition of metal halides as catalysts significantly improved the hydrogen storage properties of MgH_2 [7,37,38]. Like the other additive group, the real catalytic mechanism of metal halides on MgH_2 is still an open question. Jin et al. [37] studied the effects of NbF_5 on the hydrogenation properties of MgH_2 and concluded that the actual catalyst was Nb hydride, not NbF_5. It was suggested that NbF_5 melts during high-energy ball milling and this promotes the formation of extremely fine, film-like Nb hydride preferentially along the grain boundaries of nano-crystalline MgH_2 by a liquid/solid reaction and suppresses the grain growth of MgH_2 quite effectively. Ma et al. [41,42] compared the catalytic effects of TiF_3 and $TiCl_3$, and found that TiF_3 showed a superior catalytic effect over $TiCl_3$ in improving the hydrogen sorption kinetics of MgH_2, which was attributed to the catalytic effects of the F anion. From combined XPS examination and designed experiments, Ma et al. suggested that a considerable amount of F participated in the generation of a metastable active Ti–F–Mg species. Recently, Mao et al. [7] studied the catalytic effect of $NiCl_2$ and $CoCl_2$ on the hydrogen sorption of MgH_2 and suggested that besides the catalytic effect of Mg_2Ni and Mg_2Co as a dehydrogenation product, the chlorine-based product, $MgCl_2$, may also play an important role in improving the hydrogen sorption kinetic properties of MgH_2.

This paper introduces the use of $FeCl_3$ to prepare an MgH_2-metal chloride system aiming at combining the functions of both transition metal cations and chlorine anions. Different amounts of MgH_2 and $FeCl_3$ were ball milled together to prepare a set of $MgH_2/FeCl_3$ mixtures and their hydrogen storage properties and reaction mechanisms were investigated by a Sievert-type pressure-composition-temperature (PCT) apparatus, differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The catalytic effect of $FeCl_3$ on the hydrogen sorption properties of MgH_2 was investigated.

2. Experimental details

Pure MgH_2 (hydrogen storage grade), $FeCl_3$ (reagent grade, 97%) and $MgCl_2$ (anhydrous, ≥98%) were purchased from Sigma–Aldrich. Iron powder (−200 mesh, 99+% (metal basis)) were purchased from Alfa Aesar. All materials were used as received with no further purification. The MgH_2 and additives were respectively loaded into a sealed stainless steel vial together with hardened stainless steel balls in an argon atmosphere MBraun UNIlab glove box. The ratio of the weight of the balls to the weight of the powder was 40:1. The samples were then milled in a planetary ball mill (NQM-0.4) for 1 h, by first milling for 0.5 h, resting for 6 min, and then milling for another 0.5 h in a different direction at the rate of 400 rpm.

The experiments on de/rehydrogenation were performed in a Sievert-type PCT apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. For the temperature-programmed desorption (TPD) measurements, 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^{-1}, and samples were heated from room temperature to 450 °C. The de/rehydrogenation kinetics measurements were conducted at the desired temperature with initial hydrogen pressures of 0.1 MPa and 3.0 MPa, respectively.

XRD analysis was performed using a Rigaku MiniFlex X-ray diffractometer with Cu K_α radiation. θ–2θ scans were carried out over diffraction angles from 20° to 80° with a speed of 2.00° min^{-1}. Before the measurement, a small amount of sample was spread uniformly on the sample holder, which was wrapped with plastic wrap to prevent oxidation.

DSC analysis of the dehydrogenation process was carried out on a Mettler Toledo thermogravimetric analysis/differential scanning calorimetry (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 DSC apparatus. An empty alumina crucible was used for reference. The samples were heated from room temperature to 550 °C under an argon flow of 30 ml min^{-1}, and different heating rates were used.

3. Results and discussion

3.1. Dehydrogenation temperature

Fig. 1 presents the TPD performances of the as-received MgH_2, the as-milled MgH_2, and the MgH_2 doped with 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% $FeCl_3$. From the TPD curves, it is clear that raising the dopant percentage from 5 wt.% to 20 wt.% resulted in a decrease of the onset desorption temperature compared to the undoped MgH_2. The as-received MgH_2 started to release hydrogen at about 410 °C, with a total dehydrogenation capacity of 7.0 wt.% H_2 by 430 °C. After milling, the onset desorption temperature of MgH_2 was reduced to about 340 °C, indicating that the milling process also influenced the onset
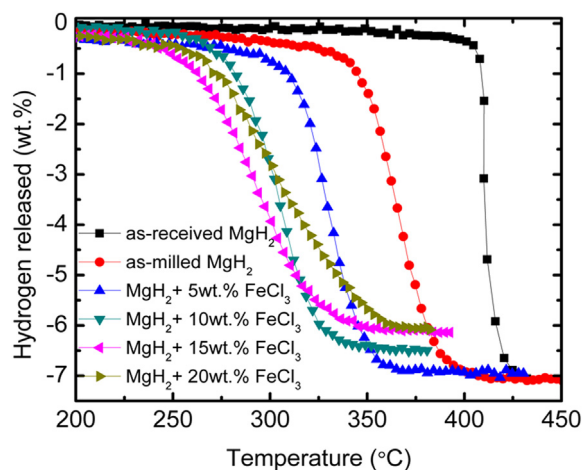

Fig. 1 – TPD patterns for the dehydrogenation of as-received MgH_2, as-milled MgH_2 and the MgH_2 doped with 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% $FeCl_3$.