Improvement in hydrogen storage properties of MgH₂ catalyzed with BaTiO₃ additive

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Abstract. The MgH₂+20 wt. % BaTiO₃ composites is prepared by ball milling MgH₂ with 20 wt. % BaTiO₃, and the effect of BaTiO₃ on the hydrogen storage properties of the MgH₂ is investigated. TPD (Temperature-programmed-desorption) results showed that with addition of BaTiO₃, the onset dehydrogenation temperature of the composite is 270 °C, which is 149 °C lower than that of pure MgH₂. And the hydrogen absorption / desorption rates of MgH₂ + 20 wt.% BaTiO₃ are 2.21 times and 2.12 times of pure MgH₂ at certain temperatures and hydrogen pressures, respectively. Furthermore, BaTiO₃ additives decreased the dehydring activation energy of MgH₂ from 116 kJ/mol to 108 kJ/mol. BaTiO₃ plays an effective catalyst role in the hydrogenation / dehydrogenation process of MgH₂.

1. Introduction

Hydrogen as a high density energy carrier has been attached great importance on its clean and inexhaustible properties [1]. The application of hydrogen needs a support from high capacity storage materials, such as MgH₂, which shows a high hydrogen storage capacity of 7.6 wt.% [2, 3]. However, MgH₂ suffers from high dehydrogenation temperature and poor kinetics, which limit its commercial application [4, 5].

In order to improve the hydrogen storage properties of MgH₂, many kinds of additives has been reported to be doped into MgH₂, such as transitional elements (Ti, V, Nb et al.) [6, 7], transition metal oxides [8], borides [9], fluorides [10, 11] and sulfides [12-14]. Barkhordarian et al. [15] and Hanada et al. [16] reported the remarkable improvement of hydrogen sorption kinetics by ball milling certain contents of Nb₂O₅ and MgH₂, and the studies of Ma et al. [17, 18] further certified that the Nb crystals distributed in the composites can work as the gateway to facilitate hydrogen transportation, and result in an improvement of the hydrogen storage properties of MgH₂. In recent years, Ti-based catalysts, including Ti, TiO₂, TiCl₅, TiF₅, were employed to decrease the desorption temperature of MgH₂ [19, 20]. When ball milled with MgH₂, the titanium oxides were found to result in significantly effects on reducing the onset dehydrogenation temperature of MgH₂, and increased the hydrogenation and dehydrogenation rates [21].

More recently, metal composite oxides [22, 23], were used as catalysts to improve the hydrogen storage properties of MgH₂. Bariccoa et al. [24] investigated the effects of doping a perovskite-type BaRuO₃ into MgH₂, and reported that not only the RuO₆ octahedral structure could be penetrated by H₂, but the BaRuO₃ could destabilize MgH₂, which decreased the dehydrogenation temperature of
MgH₂. Besides, our group found that with 20 wt.% addition of MgTiO₃, the hydrogen storage performances of MgH₂ were remarkably improved [25].

In this paper, in consideration of the excellent catalytic effects of perovskite-type oxides and Ti-based additives, and the beneficial effect of perovskite-type structure compound on the diffusion of H₂ as mentioned above, a Ti-based perovskite-type BaTiO₃ was adopted as catalysts to further improve the hydrogenation/dehydrogenation properties of MgH₂. The effect of BaTiO₃ on the hydrogenation/dehydrogenation properties are studied, and more importantly, the effect mechanism is elucidated.

2. Experimental methods
The initial materials MgH₂ (98 %) and BaTiO₃ (99.5 %) were commercially purchased from Sigma-Aldrich. The MgH₂ powder was mixed with 20 wt.% BaTiO₃ powder which was mechanically milled for 2 h using a QM-ISP2 planetary, repeating 30 min milling and 15 min rest, with 500 r·min⁻¹ under Ar atmosphere. The ball to powder weight ratio was about 40:1. All the sample manipulation was performed in an Ar-filled glove box to prevent getting in touch with oxygen and moisture.

The effect of BaTiO₃ addition on the dissociation temperature of the pure MgH₂ during the dehydrogenation was investigated by the temperature programmed desorption (TPD) apparatus. The hydrogen absorption/desorption kinetics of the samples was measured using a pressure-composition-temperature (P-C-T) characteristic measurement apparatus. Hydrogen absorption and desorption measurements were performed at desired temperature, with an initial hydrogen pressure of 3.0 MPa, and 0.1 MPa initial hydrogen pressure was given for the hydrogen desorption.

Samples after mechanical grinding and after hydriding/dehydriding cycling were characterized by X-ray diffraction (XRD) with Cu Kα radiation, using D/MAX-2500/PC. The 2θ angle was varied from 10° to 80°. Hydrogen desorption properties were investigated by a simultaneous thermal analyzer (DTG-60A) under flowing Ar at a rate of 100 mL·min⁻¹, which were rising from room temperature to 500 ºC with a heating rate of 5, 10, 15 and 20 ºC·min⁻¹.

3. Results and discussion
3.1. Hydrogen absorption/desorption performances

![Figure 1. TPD curves of MgH₂ and MgH₂+20 wt. % BaTiO₃.](image)

(a) Temperature-desorption contents curve; (b) The first derivative curves of (a).

Figure1 presents the dehydrogenation curves of the MgH₂+20 wt.% BaTiO₃ and the pristine MgH₂ when they are heated from 100 ºC to 550 ºC at a rate of 10 ºC·min⁻¹. The pristine MgH₂ starts to release hydrogen at about 389 ºC, with a hydrogen desorption capacity of about 5.94 wt.%. In case of MgH₂+20 wt.% BaTiO₃, the onset dehydrogenation temperature is 260 ºC, and the peak temperature is 347 ºC, 119 ºC and 136 ºC lower than that of pure MgH₂, respectively, and its total dehydrogenation amount reaches 4.88 wt.% by 433 ºC. Obviously, the addition is effective to improve the thermal
decomposition characteristics of MgH$_2$ with results of decreasing desorption temperature. As for the maximum hydrogen release content, it seems that MgH$_2$+20 wt.% BaTiO$_3$ decreased almost 1 wt.% than that of pure MgH$_2$. However, it should be noticed that the 20 wt.% BaTiO$_3$ additives were not hydrogen absorption materials. Thus, the maximum hydrogen desorption amount was shown relatively less in the diagram.

**Figure 2.** Comparison of the absorption kinetics of MgH$_2$ and MgH$_2$+20 wt. % BaTiO$_3$.

Figure 2 presents the hydrogen absorption curves of the received MgH$_2$ and the MgH$_2$+20 wt.% BaTiO$_3$ at 150 °C under 3 MPa hydrogen pressure. It should be noticed that all the samples are measured after two hydrogen absorption/desorption cycles. The representative curve shows that the received MgH$_2$ absorbs only 0.977 wt. % hydrogen within 21 min, whereas under identical conditions, MgH$_2$+20 wt. % BaTiO$_3$ absorbs 2.245 wt. % hydrogen, almost 2.3 times of pure MgH$_2$. Furthermore, the linear fitting of above isothermal desorption curves shows that for the MgH$_2$+20 wt. % BaTiO$_3$ sample, the average diffusion rate of H at 150 °C is 1.41*10$^{-3}$ wt.%/s, and the value for pure MgH$_2$ is 6.37*10$^{-4}$ wt.%/s. The results illustrate at 150 °C, the hydrogen absorption rate of MgH$_2$+20 wt. % BaTiO$_3$ is almost 2.21 times of pure MgH$_2$. It is obvious that the addition of BaTiO$_3$ significantly accelerates the hydrogen absorption rate of MgH$_2$.

**Figure 3.** Comparison of the desorption kinetics of MgH$_2$ and MgH$_2$+20 wt. % BaTiO$_3$.

The isothermal dehydrogenation curve for MgH$_2$ samples with and without 20 wt. % BaTiO$_3$ at 350 °C are shown in figure 3. Within 21 min, 2.319 wt. % hydrogen was dehydrogenated for MgH$_2$. As for the MgH$_2$+20 wt. % BaTiO$_3$ composites, 3.341 wt. % hydrogen was dehydrogenated under the same condition, which was about 1.44 times than that of pure MgH$_2$. And for the MgH$_2$+20 wt. % BaTiO$_3$, releasing 90% hydrogen takes only 500 seconds, while it takes more than 1000s for pure MgH$_2$. According to the fitting curve, at 350 °C, the dehydrogenation rate of MgH$_2$+20 wt. % BaTiO$_3$ is 4.85*10$^{-3}$ wt.%/s, almost 2.12 times of pure MgH$_2$. Therefore, with the introduction of 20 wt.%
BaTiO₃, not only the hydrogen absorption rate of MgH₂, but also the hydrogen desorption rate can be remarkably improved.

3.2. Activation energy for decomposition of the MgH₂-BaTiO₃ composite

The hydrogen desorption kinetics curves of pristine MgH₂ and MgH₂-BaTiO₃ composites at different heating rates are shown in figure 4. After doping BaTiO₃, the decomposition temperature of the samples is obviously decreased. At a heating rate of 10 °C/min, in compared with pure MgH₂, the dehydrogenation peak temperature is lowered by 43 °C for MgH₂+20 wt. % BaTiO₃.

In order to understand the fast hydrogen desorption kinetics, the activation energy of the dehydrogenation process for the pure MgH₂ and the MgH₂-BaTiO₃ was estimated with Kissinger's method [26].

\[
\frac{d}{dT} \left[ \ln \left( \frac{\alpha}{T_m^2} \right) \right] = \frac{E_a}{R} \frac{1}{T_m}
\]

Figure 4. DTA curves of different sample at various heating rates (a) MgH₂; (b) MgH₂+20 wt. % BaTiO₃; (c) Kissinger's plots.

Where \( \alpha \) is the heating rate, \( T_m \) is the absolute temperature at the maximum desorption rate, and \( R \) is the ideal gas constant. The activation energies of different composites were evaluated by the DTA using Kissinger formula. Figure 4 (c) shows Kissinger plots for the desorption reaction of MgH₂+20 wt.% BaTiO₃. The activation energy value is 116 kJ/mol and 108 kJ/mol for pristine MgH₂ and MgH₂+20 wt.% BaTiO₃ composite, respectively. The calculated results show that BaTiO₃ additives decrease activation energy during dehydriding, and therefore improve the dehydriding rate of the composite.
3.3. **Structural characterization and effect mechanism of the MgH$_2$-BaTiO$_3$ composite**

![XRD patterns of MgH$_2$-BaTiO$_3$ composite](image)

**Figure 5.** XRD patterns of MgH$_2$-BaTiO$_3$ composite.

The XRD patterns of the MgH$_2$ with 20 wt. % BaTiO$_3$ are shown in figure 5. For the dehydrogenated sample, MgH$_2$ phase is replaced by Mg phases, and a weak peak corresponding to MgO is found in both the dehydrogenated and the hydrogenated patterns, which is due to the oxidation of Mg when transferring the dehydrogenated sample during the test process. Furthermore, the results shows that BaTiO$_3$ remains stable after ball-milling, hydriding and dehydriding processes, indicating that there are no reaction between BaTiO$_3$ and MgH$_2$, but BaTiO$_3$ play a catalyst role during the hydriding/dehydriding process of MgH$_2$, which result in the decrease in desorption temperature and improvement in kinetics of MgH$_2$. According to the research results of Lin et al., the Ti-based catalysts owing to special electron distribution help in particle transfer in chemical reactions and have been applied in many chemical processing [27]. Therefore, BaTiO$_3$ play a catalytic role in the hydrogenation/dehydrogenation reactions of MgH$_2$, which helps to improve the hydrogen storage properties of MgH$_2$.

![SEM morphology of the: (a) MgH$_2$ as-milled; (b) MgH$_2$ + 20 wt.% BaTiO$_3$ composite as-milled; (c) MgH$_2$ after hydrogenation; (d) MgH$_2$ + 20 wt.% BaTiO$_3$ composite after hydrogenation](image)

**Figure 6.** SEM morphology of the: (a) MgH$_2$ as-milled; (b) MgH$_2$ + 20 wt.% BaTiO$_3$ composite as-milled; (c) MgH$_2$ after hydrogenation; (d) MgH$_2$ + 20 wt.% BaTiO$_3$ composite after hydrogenation.

In order to further study the microstructure and effect mechanism of the composite, Scanning Electron Microstructure is exploited to characterize the samples after ball-milling and hydrogenation.
process. As shown in figure 6, for the as-milled samples, the particle sizes of the MgH$_2$+20 wt.% BaTiO$_3$ shows a smaller and more homogeneous particle size compared to pure MgH$_2$. In addition, the average particle size of MgH$_2$+20 wt.% BaTiO$_3$ is also found to be smaller than that of pure MgH$_2$ after hydrogenation processes. That illustrates the addition of BaTiO$_3$ to MgH$_2$ can reduce the degree of aggregation of the particles during the ball-milling and the hydrogenation process. As reported by Peng et al. [28], smaller size particle and fewer amounts of clusters inside the hydrogen storage materials can facilitate hydrogenation/ dehydrogenation kinetics due to more H diffusion channels in the matrix. Therefore, by doping BaTiO$_3$ into the MgH$_2$ we’re able to make uniform and homogeneous microstructures that have more remarkable hydrogen storage properties compared to pure MgH$_2$.

4. Conclusions

The thermodynamic and kinetic properties of MgH$_2$+ 20wt.% BaTiO$_3$ are investigated. In comparison with the pure MgH$_2$, the onset desorption temperature of the MgH$_2$+20 wt. % BaTiO$_3$ composite decreased about 119 °C, and the hydrogen absorption capacity increased by 2.3 times at 150 °C, the desorption capacity increased by 1.44 times at 350 °C within 21 min. According to DTA results measured at different heating rate, activation energy of composites decreased from 116 kJ/mol to 108 kJ/mol for MgH$_2$+20 wt. % BaTiO$_3$. BaTiO$_3$ play a catalytic role in the hydriding / dehydridding of MgH$_2$, which is responsible for the hydrogen storage properties improvement of MgH$_2$.

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