Effect of CeH$_{2.73}$-CeO$_2$ Composites on the Desorption Properties of Mg$_2$NiH$_4$

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A series of CeH$_{2.73}$/CeO$_2$ composites with different ratios of hydride and oxide phases are prepared from the pure cerium hydride via oxidation treatments in the air at room temperature, and they are subsequently doped into Mg$_2$NiH$_4$ by ball milling. The desorption properties of the as-prepared Mg$_2$NiH$_4$+CeH$_{2.73}$/CeO$_2$ composites are studied by thermogravimetry and differential scanning calorimetry. Microstructures are studied by scanning electron microscopy and transmission electron microscopy, and the phase transitions during dehydrogenation are analyzed through in situ X-ray diffraction. Results show that the initial dehydrogenation temperature and activation energy of Mg$_2$NiH$_4$ are maximally reduced by doping the CeH$_{2.73}$/CeO$_2$ composite with the same molar ratio of cerium hydride and oxide. In this case, the CeH$_{2.73}$/CeO$_2$ composite has the largest density of interface among them, and the hydrogen release effect at the interface between cerium hydride and oxide plays an efficient catalytic role in enhancing the hydrogen desorption properties of Mg$_2$NiH$_4$.

Keywords: Hydrogen storage materials, dehydrogenation, Mg$_2$NiH$_4$, CeH$_{2.73}$/CeO$_2$, catalysts

INTRODUCTION

With the advantages of abundant natural resources and no pollution to the environment, hydrogen has been widely considered as an ideal carbon-free energy carrier. Hydrogen energy storage technology is a prerequisite for the large-scale utilization of hydrogen energy. Light-weight solid-state hydrogen storage materials have been considered to be ideal candidates for hydrogen storage because of the high hydrogen storage density and security consideration (Mohtadi and Orimo, 2016; Wang et al., 2016). Among the existing solid-state hydrogen storage materials, Mg-based hydrogen storage materials are widely studied and considered as promising solid-state hydrogen storage materials due to the high hydrogen storage capacity, abundance on the earth and low production cost (Ouyang et al., 2013, 2017; Rusman and Dahari, 2016; Shao et al., 2018).

MgH$_2$ and Mg$_2$NiH$_4$ are two typical Mg-based hydrogen storage materials with hydrogen densities of 7.6 wt and 3.6 wt%, respectively (Reilly and Wiswall, 1968; Bogdanovi´c, 1984; Liu et al., 2016, 2019; Zhan et al., 2016; Chen et al., 2018; Ding et al., 2019). Nevertheless, the stable thermodynamics and slow kinetics of hydrogen storage properties of Mg-based materials lead to harsh conditions for dehydrogenation (Bogdanović et al., 2010; Jain et al., 2010). The hydrogen desorption temperatures of MgH$_2$ and Mg$_2$NiH$_4$ are usually as high as 250–350°C. Many efforts have been made by researchers to improve the kinetics and reduce the desorption temperatures of MgH$_2$ and Mg$_2$NiH$_4$. The commonly conducted methods include mechanical alloying, doping catalysts, nanostructuring, surface modification and so on (Terashita et al., 1999; Lin et al., 2012a, 2016; Shao et al., 2012; Eleskandarany et al., 2016; Zhang et al., 2017; Khan et al., 2018; Xu et al., 2019).
Doping catalysts by ball milling is a commonly-used and efficient method to enhance the hydrogenation/dehydrogenation kinetics of Mg-based materials (Ouyang et al., 2014a,b; Wang and Wang, 2017). To date, many additives have been explored, including oxides (Barkhordarian et al., 2003), transition metals (Hanada et al., 2005), hydrides (Ma et al., 2017), carbon-based materials (Lototskyy et al., 2013) and so on. It has been demonstrated that compounds with higher valences show higher catalytic effect on the hydrogen storage performances of Mg-based materials than that of the lower valence compounds (Bobet et al., 2002). Because of the unique 4f electron of the Ce element, Ce-based compounds are widely used in the catalysis field (Trovarelli, 1996). Long et al. (2013) reported Mg-Ce oxide powders produced by an arc plasma evaporation method. As a result, enthalpies of hydrogenation and dehydrogenation for Mg/MgH$_2$ reduce to $-71.0$ and $75.4$ kJ/mol H$_2$, respectively. Moreover, the hydrogenation activation energy is reduced to only 47.75 kJ/mol. The composite can absorb 4.07 wt%-H at 323 K in 10 h. Their study indicates that minor addition of Ce oxide can remarkably improve the absorb $4.07$ wt%-H at 323 K in 10 h. Their study indicates that minor addition of Ce oxide can remarkably improve the

**EXPERIMENTAL DETAILS**

**Materials**

The Mg$_2$NiH$_4$ used in this experiment was prepared by a method of hydrogenation combustion synthesis method (HCS), which was carried out in Prof. Yunfeng Zhu's group in Nanjing Tech University (Gu et al., 2009; Zhu et al., 2017). CeH$_{2.73}$ (purity >99%) was purchased from Hunan Research Institute of Non-ferrous metals. About 0.1 g CeH$_{2.73}$ powder was located in a plastic bottle of 3 ml, in the Ar glove-box. Then it was transferred into the small side box of glove-box. The door of side box was then open to let air in for different time: 0.5, 1.5, 3, 10, and 60 min. The oxidized CeH$_{2.73}$ became CeH$_{2.73}$/CeO$_2$ composites, and 2 mol% of CeH$_{2.73}$/CeO$_2$ were then doped into Mg$_2$NiH$_4$ by ball milling at 400 rpm for 4 h.

**Characterizations**

The phase structures were analyzed by X-ray diffraction (XRD), and the phase transition during dehydrogenation was analyzed by in situ XRD analysis. The XRD analysis was carried out by an X-ray diffractometer apparatus (Ultima IV, Rigaku, Japan) with Cu-K$\alpha$ ($\lambda = 0.15405 \text{nm}$). The tube voltage and tube current were 40 kV and 40 mA, respectively. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) were used to study the hydrogen desorption behaviors at different heating rates on a METTLER TGA/DSC 3+ synchronous thermal analyzer. The microstructures of the Mg$_2$NiH$_4$-Ce$_{2.73}$/CeO$_2$ composites were observed by backscattered electron imaging using scanning electron microscope (SEM) and transition electronic microscopy (TEM).

**RESULTS AND DISCUSSION**

**Preparation of the CeH$_{2.73}$/CeO$_2$ Catalysts**

Six sets of CeH$_{2.73}$/CeO$_2$ composites prepared by oxidation treatments for different durations were analyzed by XRD. The CeH$_{2.73}$/CeO$_2$ composites are marked as S1, S2, S3, S4, S5, and S6, according to the oxidation duration of CeH$_{2.73}$ of 0, 0.5, 1.5, 3, 10, and 60 min, respectively. The diffraction patterns are shown in Figure 1. With the increase of oxidation time, CeH$_{2.73}$ gradually transforms into CeO$_2$. After oxidation of 60 min, no CeH$_{2.73}$ has left. The obtained XRD patterns were refined by a Jade 6.0 software and the phase content were calculated by the K value (RIR) method. The relative contents of the CeO$_2$ phase as increase of the oxidation time are shown in Figure 2. The oxidation data can be fitted by the Avrami–Erofeev equation deduced from the nucleation and growth process:

$$\alpha = 1 - \exp(-Br^m),$$  \hspace{1cm} (1)

where $\alpha$ is the ratio of reacted material to total material, $m$ and B are constants. The fitted m is 1.085, which is very close to 1.07, indicating the oxidation of CeH$_{2.73}$ at room temperature is a three-dimensional interface reaction process (Lin et al., 2012b). For the S4 sample, the relative content of CeH$_{2.73}$ is 54.2 wt% and the relative content of CeO$_2$ phase is 45.8 wt%, indicating almost
the same molar ratio of cerium hydride and oxide when the oxidation time is around 3 min. After the oxidation treatments, the samples were doped into Mg$_2$NiH$_4$ by ball milling.

In order to understand the morphologies of the CeH$_{2.73}$/CeO$_2$ composite doped Mg$_2$NiH$_4$, back scattering scanning electron microscopy (BSEM) was carried out. Because the S1–S4 sample will continue to oxidize in the air, the S5 doped Mg$_2$NiH$_4$ sample was selected as the experimental material. The morphologies of the as-prepared CeH$_{2.73}$/CeO$_2$ composite (S5 sample) and the ball-milled Mg$_2$NiH$_4$ + S5 sample are shown in Figure 3. It could be clearly seen that the particle size of the as-prepared CeH$_{2.73}$/CeO$_2$ composite is about 200–400 nm. After ball milling, the particle size of the CeH$_{2.73}$/CeO$_2$ composite is greatly reduced to below 30–100 nm. Figure 3B shows that the CeH$_{2.73}$/CeO$_2$ composites, which are brighter particles, are uniformly distributed in the Mg$_2$NiH$_4$ matrix. The homogeneous CeH$_{2.73}$/CeO$_2$ composites could be beneficial for catalyzing
hydrogen storage properties for the Mg-based materials (Hong et al., 2009; Shao et al., 2011; Li et al., 2018).

**Dehydrogenation of Mg$_2$NiH$_4$ + CeH$_{2.73}$/CeO$_2$ Composites**

The decomposition behaviors of the ball-milled Mg$_2$NiH$_4$+CeH$_{2.73}$/CeO$_2$ composites are studied by TG-DSC synchronous thermal analyzer as shown in Figure 4. The DSC study of Mg$_2$NiH$_4$ + CeH$_{2.73}$/CeO$_2$ composites are at a heating rate of 20 K/min, showing the dehydrogenation initial temperature of Mg$_2$NiH$_4$ decreases after addition of CeH$_{2.73}$/CeO$_2$ composites. Among the six sets of catalysts, the S4 sample obtained by oxidation of CeH$_{2.73}$ for 3 min, exhibits the highest catalytic effect on reducing the dehydrogenation temperature of Mg$_2$NiH$_4$. The dehydrogenation temperature is decreased to 267°C, which is about 17°C lower than the that of as-milled Mg$_2$NiH$_4$ (284°C).

To further elucidate the dehydrogenation activation energy of the Mg$_2$NiH$_4$+CeH$_{2.73}$/CeO$_2$ composites, DSC experiments for the Mg$_2$NiH$_4$ + CeH$_{2.73}$/CeO$_2$ composites at heating rates of 10 K/min and 50 K/min were carried out (results not shown). The activation energy of the dehydrogenation process was calculated by using the Kissinger’s method (Kissinger, 1957),

\[
\ln \left( \frac{\beta}{T_m^2} \right) = \frac{E_{a\text{d}}}{RT_m} + C
\]

where $E_{a\text{d}}$ is the dehydrogenation activation energy, $T_m$, $\beta$, $R$, and $C$ are the peak temperature, heating rate of DSC experiments, gas constant and another constant, respectively. The relation between $T_m$ and $\beta$ is linearly fitted as plotted in Figure 5, and the activation energy was summarized in Table 1. Results show that the S4 sample by oxidation of CeH$_{2.73}$ for 3 min exhibits the best catalytic effect on reducing the dehydrogenation activation energy of Mg$_2$NiH$_4$ (from 76.3 kJ/mol to 62.6 kJ/mol). Zhang (Zhang et al., 2018) et al. suggested that alloying Mg$_2$Ni with Ti, V, Fe, or Si could reduce the hydrogenation and dehydrogenation activation energies to 60–70 kJ/mol. Our study suggests that the CeH$_{2.73}$/CeO$_2$ composites are also efficient to reduce the dehydrogenation activation energy of Mg$_2$NiH$_4$.

Combining XRD and TG-DSC study, it indicates clearly that the initial dehydrogenation temperature and activation energy of Mg$_2$NiH$_4$ are maximally reduced as the cerium hydride and cerium oxide are in the same amount. These results well-accord with our previous finding on the effect of CeH$_{2.73}$/CeO$_2$ composites on the dehydrogenation properties of MgH$_2$ (Lin et al., 2014), which means the CeH$_{2.73}$/CeO$_2$ composite with the same molar ratio of cerium hydride and oxide could be a good catalyst for the dehydrogenation properties of Mg-based hydrogen storage materials, including both MgH$_2$ and Mg$_2$NiH$_4$.

**Microstructures of the Mg$_2$NiH$_4$ + CeH$_{2.73}$/CeO$_2$ Composite**

The morphology and microstructure of Mg$_2$NiH$_4$ and as-oxidized 10 min CeH$_{2.73}$/CeO$_2$ composite (S5) are shown in Figure 6a. From the HRTEM images in Figure 6b, it could be found that the composite matrix is Mg$_2$NiH$_4$, which lattice fringe corresponds to the lattice plane of (111) and (220). Particle sizes of the CeO$_2$ nanoparticles are in a large range from 50–200 to 5–10 nm, which have been clearly shown in Figures 6a,d, respectively. Moreover, it could be seen that the in-situ generated CeO$_2$ particles are embedded homogeneously in the Mg$_2$NiH$_4$ matrix after ball milling. The interfaces between Mg$_2$NiH$_4$ and CeO$_2$ composite, as shown in Figures 6c,d, are contacted closely with each other. The homogeneously distributed catalysts can lead to high catalysis effect, and thus be beneficial for the hydrogenation/dehydrogenation properties of Mg$_2$NiH$_4$. Because of the too small amount of CeH$_{2.73}$, we could not clarify their microstructures in the TEM study.

**In situ XRD of Dehydrogenation**

The phase transition of the Mg$_2$NiH$_4$ + S5 sample during dehydrogenation was further studied by in situ XRD. The obtained in situ XRD patterns are shown in Figure 7. The XRD pattern of Mg$_2$NiH$_4$ + S5 sample at room temperature contains the diffraction peaks of Mg$_2$NiH$_4$ and CeO$_2$ because the XRD intensity of CeH$_{2.73}$ is too weak. The diffraction peaks of CeO$_2$ do not obviously change during the whole dehydrogenation
process, indicating that the CeO\textsubscript{2} phase might act as a catalyst of Mg\textsubscript{2}NiH\textsubscript{4} dehydrogenation. When the temperature was raised to 250°C, the diffraction peak of Mg\textsubscript{2}NiH\textsubscript{0.3}/Mg\textsubscript{2}Ni phase appears, which means the dehydrogenation of Mg\textsubscript{2}NiH\textsubscript{4} starts. As temperature increases, the intensity of Mg\textsubscript{2}NiH\textsubscript{0.3}/Mg\textsubscript{2}Ni phase gradually enhances, and that of the Mg\textsubscript{2}NiH\textsubscript{4} peaks decreases. As temperature reaches about 330°C, the diffraction peaks of CeO\textsubscript{2} remains unchanged and no MgO is found.
The in situ XRD patterns are then refined using Jade 6.0, and the relative contents of phases are calculated by the RIR method. At 270°C, the relative content of Mg2NiH3 phase is 47.1 wt%, and the relative content of Mg2NiH4 phase is 52.9 wt%. After heating to 290°C, the relative content of the two phases changes rapidly, and the relative content of Mg2NiH3 phase increases to 81.8 wt% and Mg2NiH4. The relative content of the phase was reduced to 18.2 wt%. Subsequently, the rate of phase change during the heating process was significantly slowed down. The relative content of Mg2NiH3 phase was 89.1 wt% at 400°C, and the relative content of Mg2NiH4 phase reduces to about 10.9 wt%.

CONCLUSION

In summary, CeH2.73/CeO2 composites with different proportions of cerium hydride and oxide are synthesized from pure cerium hydride via oxidation treatments in the air at room temperature. Oxidation time of 3 min leads to formation of CeH2.73/CeO2 composite with the same molar ratio of cerium hydride and oxide, which maximally reduces the initial dehydrogenation temperature and activation energy of Mg2NiH4. The CeH2.73/CeO2 composite with the same molar ratio is a good catalyst for reducing dehydrogenation temperatures of Mg-based materials.

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DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation, to any qualified researcher.

AUTHOR CONTRIBUTIONS

KW and DC: methodology and writing - original draft. KS and TX: methodology and formal analysis. PZ: resources and supervision. WL: supervision and project administration. H-JL: conceptualization, resources, writing - review and editing, supervision, and funding acquisition.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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