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Effect of $LaFeO_3$ on hydrogenation/dehydrogenation properties of MgH_2

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Abstract: $LaFeO_3$ was used to improve the hydrogen storage properties of MgH_2. The MgH_2+20 wt.%$LaFeO_3$ composite was prepared by ball milling method. The composite could absorb 3.417 wt.% of hydrogen within 21 min at 423 K while MgH_2 only uptaked 0.977 wt.% hydrogen under the same conditions. The composite also released 3.894 wt.% of hydrogen at 623 K, which was almost twice more than MgH_2. The TPD measurement showed that the onset dissociation temperature of the composite was 570 K, 80 K lower than the MgH_2. Based on the Kissinger plot analysis of the composite, the activation energy E_{des} was estimated to be 86.69 kJ/mol, which was 36 kJ/mol lower than MgH_2. The XRD and SEM results demonstrated that highly dispersed $LaFeO_3$ could be presented in MgH_2, benefiting the reduction of particle size and also acting as an inhibitor to keep the particles from clustering during the ball-milled process.

Keywords: magnesium hydride; hydrogen storage composite; hydrogen properties; hydrogenation kinetics; rare earths

Energy poverty is a great challenge in the world due to the excessive energy utilization and waste of the non-renewable coal and petroleum. Yet in other ways, the traditional resource which is not inexhaustible and irreversible may be a good reason for exploring new materials such as the hydrogen storage materials to solve the mentioned issues[1–4]. Magnesium hydride, especially MgH_2, has drawn attentions to substitute the traditional resources owing to its high abundance but low cost. As a solid hydrogen storage material, MgH_2 has many advantages such as excellent reversibility and cycle performance. However, its practical application is hampered due to the high dissociation temperature and thermodynamics stability[5,6].

In recent years, many groups have devoted to avoid the disadvantages of magnesium hydride through the formation of ternary hydride or even the catalytic activity phase to improve its hydrogen kinetics. Therefore, many methods were invented such as preparation of thin particle size by mechanically ball-milling, modification of the surface of the matrix and addition of some metal element catalysts, such as transition metal fluorides[7–9], transition metal oxides[10,11]. Friedrichs et al.[12] reported that the addition of Nb_2O_5 contributed to improving the hydrogen/dehydrogen behaviors of MgH_2 as a consequence of the intimate contact between MgH_2 and Nb_2O_5. Furthermore, it was found that the hydrogen desorption kinetics was much remarkably improved by adding Cr_2O_3 or Nb_2O_5 as co-catalyst to the MgH_2[13]. In addition, the rare earth perovskite-type oxides that belong to the ABO_3 compounds have been widely used as catalytic materials in the field of fuel cell electrodes[14,15]. The catalytic activity of the perovskite-type oxides can be comparable to some noble metal catalysts in certain conditions[16]. Deng et al.[17] reported that $LaCrO_3$ electrodes showed remarkable electrochemical reversibility and might be a promising candidate for future electrochemical materials. As a catalyst, the perovskite-type oxides have not been applied for hydrogen desorption of MgH_2. Our group had confirmed the Fe and La was quite reactive, showing better catalytic during ball-milled with MgH_2. Therefore, in this work, $LaFeO_3$ was selected as a new additive to ball-mill with MgH_2, and its effects on the absorption/desorption performances of MgH_2 were systemically investigated.

1 Experimental

MgH_2 was purchased from the Sigma Alfa Co., and $LaFeO_3$ was synthesized by stearic acid combustion method[18].The synthesized $LaFeO_3$ was mixed with pure MgH_2 in a mass ratio of 1:4. Then the mixture was put into a stainless steel container corresponding to some stainless steel balls and with a ball to powder ratio of 20:1. The ball-milling was undertaken by setting the planetary miller at a speed of 500 r/min for 2 h, and 5

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min rest for each 30 min cycle. Ball milling was performed under Ar atmosphere to prevent the residual air and oxygen from forming MgO and other contaminants. All the experiment on handling these samples were performed at the argon glove with H_2O and O_2 amount <1 ppm.

The effect of $LaFeO_3$ on the dissociation temperature of MgH_2 during dehydrogenation was investigated by means of temperature-programmed-desorption (TPD). Five hundred milligrams of sample were loaded in the sample chamber and then put into the furnace. The test temperature was set to increase from room temperature to 773 K with a heating rate of 10 K/min. The hydrogen sorption kinetics was performed at different temperatures with an initial pressure of 3 and 0.001 MPa of hydrogen, respectively. The phase composition and crystallite size were characterized by X-ray diffraction technology using Cu Kα radiation with a scanning speed of 4(º)/min from 10º to 80º. SEM was used to investigate the structural morphology of pure MgH_2.

2 Results and discussion

2.1 Phase composition and structural characterization

Fig. 1 exhibits the XRD patterns of MgH_2+20 wt.% $LaFeO_3$ composite at different hydrogenation stages. In Fig. 1(1), for the as-milled sample, the most intensive diffraction peak is indexed to the β-MgH_2 phase and metastable γ-MgH_2 phase. The formation of the metastable phase γ-MgH_2 is a consequence of the mechanically ball-milling and the intensive strain[19,20]. After milling, $LaFeO_3$ can still be detected with high diffractions and broad peaks, indicating that $LaFeO_3$ exhibits amorphous phenomenon with the particle size significantly reduced in the milling process. In Fig. 1(2), after hydrogenation under 3 MPa of H pressure, no diffraction peak of metastable γ-MgH_2 is detected, while the diffraction peak of $LaFeO_3$ is accordingly identified. Therefore, it indicates that there may exist a transformation between metastable γ-MgH_2 and β-MgH_2 phase. In the case of dehydrided sample of Fig. 1(3), β-MgH_2 phase disappears with only Mg and $LaFeO_3$ present, which indicates that there is a dehydrogenation reaction from β-MgH_2 phase to Mg phase during the dehydrogenation process. During the whole process, the XRD pattern of the MgH_2+20 wt.%$LaFeO_3$ composite exhibits the peak corresponded to $LaFeO_3$, which indicates the high stability of this composite at high temperature in the presence of MgH_2.

SEM was employed to further study the structure of the composites. Fig. 2 shows the SEM images of ball-milled MgH_2+20 wt.%$LaFeO_3$ composite and pure MgH_2. The particle sizes depicted in the SEM images are decreased owing to the high energy mechanically ball-milling. It is apparent that the grain size of MgH_2 ball-milled with $LaFeO_3$ is smaller than that of pure MgH_2, demonstrating that the addition of $LaFeO_3$ is beneficial to decreasing the particle diameter of MgH_2.

Fig. 3 shows the SEM images of MgH_2+20 wt.%$LaFeO_3$ and MgH_2 after hydrogen absorption at 623 K. The particles of the composite after hydrogenation are homogeneous and highly dispersed, while the particles of the pure MgH_2 aggregates into large cluster. According to the Scherrer's law, the average particle size of the MgH_2+$LaFeO_3$ composite was calculated about 26.7 nm,

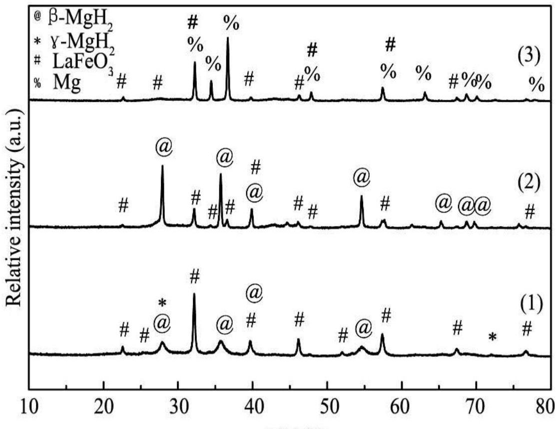

Fig. 1 X-ray patterns of MgH_2+20 wt.%$LaFeO_3$ composite
(1) Ball-milling; (2) Hydrogenation; (3) Dehydrogenation

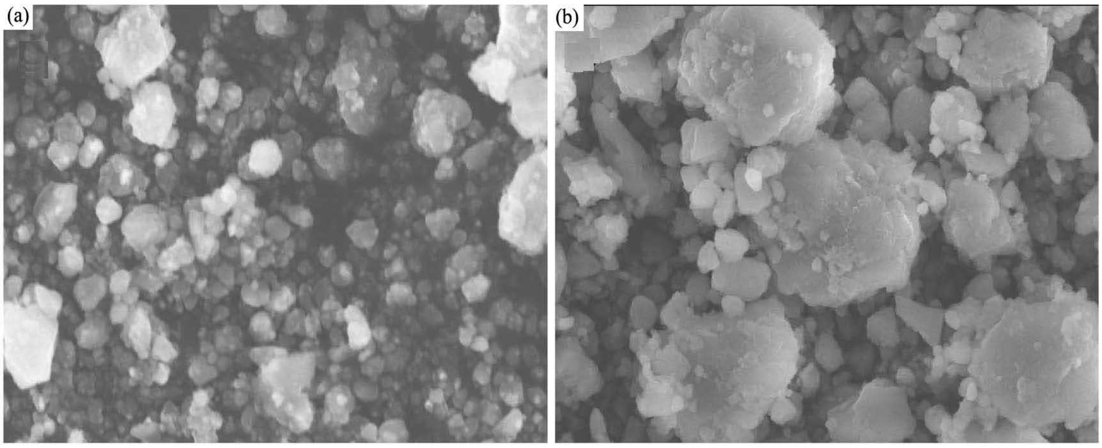

Fig. 2 SEM micrographs of MgH_2+20 wt.%$LaFeO_3$ composite (a) and MgH_2 ball-milled for 2 h (b)