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Effect of $BiVO_4$ additive on the hydrogen storage properties of MgH_2

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ABSTRACT

The MgH_2 with 16.7 wt.% $BiVO_4$ composite prepared by ball milling method presented favorable thermodynamic and kinetic performances, and the effect of $BiVO_4$ on the hydrogen storage properties of MgH_2 was investigated. The onset desorption temperature of the composite is 538 K, 98 K lower than that of the as-milled MgH_2. The composite releases 1.1 wt.% hydrogen at 573 K within 1200 s, while pristine MgH_2 hardly release hydrogen under identical conditions. Moreover, the composite absorbs 1.99 wt.% hydrogen at 423 K, 2.12 times than that of pristine MgH_2. The dehydrogenation activation energy of MgH_2 is reduced from 122.29 kJ/mol to 84.33 kJ/mol with the addition of $BiVO_4$. The $BiVO_4$ additive also facilitates the H diffusion and alters the rate-controlling step of MgH_2 in the hydrogen absorption process. It may be believed that the active V-containing species formed during the dehydrogenation process would greatly improve the hydrogen storage performances of MgH_2.

1. Introduction

Hydrogen is widely considered to be a potential candidate for solving the shortage of fossil energy and serious environmental pollution for the future due to its efficient, clean and abundant resource [1,2]. However, the main obstacle in the application of hydrogen energy is the storage of hydrogen, thus the development of safe and efficient hydrogen storage technology is urgently required [3]. Over the past decades, all kinds of hydrogen storage materials with high hydrogen content, such as Mg-based materials [4,5] are intensively investigated, especially for MgH_2 due to its dramatic advantages including high gravimetric storage capacity (7.6 wt.%), good reversibility and low cost [6].

However, relatively high thermodynamic stability and sluggish hydrogen sorption kinetics of MgH_2 limit its practical application [7]. Numerous efforts have been made to improve the hydrogen storage performances of MgH_2, of which reducing particle size to nanoscale by mechanical milling is an effective method, which can increase contact area, provide more nucleation sites and shorten H diffusion distance [8,9]. Various types of catalysts or additives including transition metals [10,11], metal oxides [12–14], metal halides [15,16] and metal sulfides [17,18] also have been attempted to ameliorate the hydrogen absorption/desorption properties of MgH_2. Liang et al. [19] found that TMs (Ti, V, Mn, Fe and Ni) could improve the hydrogen storage properties of MgH_2, V and Ti showed superior catalytic effects on the reaction kinetics of Mg-H system.

Among the transition metals, vanadium and its derivative compounds have been at the forefront of applied research as catalysts on improving the hydrogen storage performances of MgH_2. Grigorova et al. [13] reported that a high absorption capacity of the MgH_2–V_2O_5 composite (6.3 wt.% H_2) was attained after hydriding at 573 K, but the hydrogen desorption proceeded very slowly at the same temperature. Conceição et al. [20] had shown that the addition of V, VC and VCl_3 compounds significantly improved hydrogen absorption and desorption kinetics in comparison to the MgH_2. Shahi et al. [21] found vanadium and its compounds (V, V_2O_5 and VCl_3) all could decrease the decomposition temperature and enhance the desorption kinetics of $Mg(NH_2)_2$/LiH mixture. Thereby, it is reasonable to speculate that the active V-containing species may have a positive effect on the hydrogen sorption behaviors of MgH_2, because of the multiple valences and high catalytic activity of V.

Recently, it has been found that doping metal complex oxides as catalysts favored to enhance the hydrogen storage performances of MgH_2. Li et al. [22] reported that dehydrogenation performance of MgH_2 was significantly improved after doping with ferrite ($CoFe_2O_4$, $ZnFe_2O_4$, $MnFe_2O_4$ and $Mn_{0.5}Zn_{0.5}Fe_2O_4$) nanoparticles, and $CoFe_2O_4$ showed the best catalytic performance among the ferrites. Juahir et al. [23] investigated the effect of Co_2NiO nanoparticles on the hydrogen storage properties of MgH_2 and MgH_2 + 10 wt.% Co_2NiO sample exhibited favorable hydrogen

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absorption/desorption behaviors, the catalytic effect of Co_2NiO additive was largely attributed to the formation of active species of Mg-Co alloy and $Co_{1.29}Ni_{1.71}O_4$ during the heating process. A recent study by Cheng et al. [24] showed that the addition of nanometric $LiFePO_4$ could lower the dehydrogenation temperature and accelerate the sorption kinetics of MgH_2. Mustafa et al. [25] reported that that addition of $SrFe_{12}O_{19}$ nanopowder significantly enhanced the hydrogen sorption properties of MgH_2. Inspired by these findings, $BiVO_4$ is a sort of containing vanadium multicomponent oxide and has attracted considerable attention for its excellent photocatalytic activity [26], so it is believed that $BiVO_4$ can show great catalytic effect and advance MgH_2 hydrogen storage performances. Herein, $BiVO_4$ is chosen as an additive and the effect on the hydrogen storage properties of MgH_2 is investigated and the corresponding reaction mechanism is also explored in this work.

2. Experimental

The starting material MgH_2 (98%) was purchased from Alfa Aesar and $BiVO_4$ was synthesized by the solvothermal method [27]. $Bi(NO_3)_3{\cdot}5H_2O$ and NH_4VO_3 (the molar ratio of $Bi(NO_3)_3{\cdot}5H_2O$:NH_4VO_3 was fixed at 1:1) were dissolved in 40 mL of 65% HNO_3 and 40 mL of 2 M NaOH solutions separately, and each solution was stirred at room temperature for 30 min. After that, these two solutions were mixed together and stirred for another 1 h to get a stable mixture. Then, the mixture was sealed in a 100 mL Teflon-lined stainless autoclave and heated at 180 °C for 6 h under autogenous pressure. Finally, the precipitate was filtered, washed and dried under vacuum at 80 °C for 12 h.

The MgH_2 powder mixed with the as-prepared $BiVO_4$ in a mass ratio of 5:1. The composite of MgH_2–16.7 wt.% $BiVO_4$ was mechanically milled at an operating speed of 500 r/min under Ar atmosphere for 2 h with a 15 min rest period every half an hour using a QM-ISP2 planetary. The ball to powder weight ratio was 20:1. For comparison, pristine MgH_2 powder was treated under identical conditions. All operations of the samples were performed in the glove box filled with a high purity argon atmosphere to prevent oxidation and moisture.

The hydrogen absorption and desorption measurements were carried out in a pressure–composition–temperature (P–C–T) apparatus (made by Beijing Nonferrous Metal Research Institute, China). Temperature-programmed-desorption (TPD) analysis of the samples was implemented from room temperature to 550 °C with a heating rate of 5 °C/min. The de/rehydrogenation kinetic experiments were executed at the desired temperature with an initial hydrogen pressure of 0.01 MPa and 3.0 MPa, respectively. In order to further explore the dehydriding performances of the doped MgH_2 sample, a simultaneous thermal analyzer (DTG-TA60) was conducted to investigate the thermal behaviors of the samples from room temperature to 550 °C under an argon flow of 50 mL/min at the heating rates of 5, 10, 15 and 20 °C/min, respectively.

The phase structure of the samples was characterized by X-ray diffraction (XRD) using Cu Kα radiation with 2θ angle ranged from 10° to 80° at a scanning rate of 4°/min. X-ray photoelectron spectroscopy (XPS) was performed with the PHI-1600 ESCA spectrometer. The morphology of the samples was determined by scanning electron microscopy (SEM, HITACHI S-4800).

3. Results and discussion

3.1. Phase structure and morphology

The structural analysis of the as-prepared $BiVO_4$ was carried out using X-ray diffraction (XRD) study. XRD pattern of the as-prepared $BiVO_4$ is shown in Fig. 1. It can be clearly seen that all

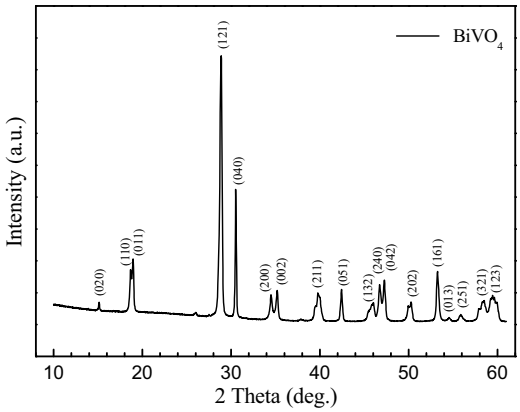

Fig. 1. XRD pattern of the as-prepared $BiVO_4$.

diffraction peaks can be well-assigned to the pure monoclinic phase of $BiVO_4$ (JCPDS card No. 14-0688), and no characteristic peaks of impurity were observed.

Fig. 2 shows the corresponding SEM images of the MgH_2 and MgH_2 + 16.7 wt.% $BiVO_4$ composite after ball milling and hydrogenation at 623 K. The MgH_2 consisted of small particles and large agglomerates after ball milling and the aggregation still existed after hydrogenation. After ball milling with 16.7 wt.% $BiVO_4$, the sample showed a smaller and more homogeneous particle size than the pure MgH_2. Interestingly, the particles of the MgH_2 + 16.7 wt.% $BiVO_4$ composite after hydrogenation became slightly smaller than those of samples after ball milling. It is well known that the morphology of samples usually affects their dehydrogenation and rehydrogenation performances. A smaller particle size will favor the hydrogen absorption/desorption kinetics, owing to its reduction of the diffusion distance of hydrogen and provide more reactive surfaces [28].

3.2. Hydrogen absorption/desorption behaviors

Fig. 3 presents TPD curves for the dehydrogenation of the as-milled MgH_2 and MgH_2 + 16.7 wt.% $BiVO_4$ composite. The pristine MgH_2 started to release hydrogen at about 636 K, and reached a total dehydrogenation capacity of 5.89 wt.% H_2 by 776 K. It can be clearly seen that the onset desorption temperature of MgH_2 decreased dramatically after doping with $BiVO_4$. The MgH_2 + 16.7 wt.% $BiVO_4$ composite began to decompose at about 538 K, which is 98 K lower than that of pristine MgH_2. However, the amount of hydrogen released dropped to 4.05 wt.% H_2. The reason may be ascribed to the fact that the $BiVO_4$ additive was not a hydrogen absorption material. Thus, the introduction of the $BiVO_4$ additive reduced the hydrogen storage capacity of the system. These results suggest that the MgH_2 + 16.7 wt.% $BiVO_4$ composite is less stable in the dehydrogenation process and has a lower onset desorption temperature.

Isothermal hydrogen desorption kinetics of the pristine MgH_2 and MgH_2 doped with 16.7 wt.% $BiVO_4$ composite were tested at 573 K under 0.01 MPa H_2. As shown in Fig. 4, the MgH_2 + 16.7 wt.% $BiVO_4$ composite could release 1.1 wt.% hydrogen within 1200 s, whereas for the pristine MgH_2, only 0.17 wt.% hydrogen was released under the same conditions. Remarkable improvement in the amount of the hydrogen desorbed and the rate of desorption could be achieved by the addition of $BiVO_4$. The comparison of the isothermal absorption behaviors for the pristine MgH_2 and the MgH_2 + 16.7 wt.% $BiVO_4$ composite at 423 K under 3 MPa H_2 is shown in Fig. 5. Within 1200 s, the hydrogen absorption capacity reached 1.99 wt.% for the MgH_2 + 16.7 wt.% $BiVO_4$ composite, which is 2.12 times than that of pristine MgH_2 (0.94 wt.%) within