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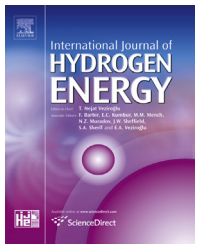

Remarkably enhanced dehydrogenation properties and mechanisms of MgH_2 by sequential-doping of nickel and graphene

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ABSTRACT

Magnesium hydride MgH_2 is an attractive hydrogen storage material because of its high volumetric and gravimetric densities, inexpensiveness and abundance. However, its high dehydrogenation temperature resulted from the unfavorable thermodynamic and kinetic barriers limits its practical applications. Herein, we first propose an efficient strategy for remarkably enhancing the dehydrogenation properties of MgH_2 by sequential-doping of nickel (Ni) and graphene (G) via mechanical milling. This method can not only accelerate the refinement of MgH_2 grains and particles, but also significantly decrease its dehydrogenation temperature relative to G single-doping and Ni/G simultaneous-doping systems. First-principles calculations indicate that the excellent dehydrogenation properties of Ni/G sequential-doped MgH_2 system are closely associated with the dual effects involving Ni solid-solution in MgH_2 lattice and interfacial catalysis between G-supported Ni catalysts and MgH_2 matrix. Upon these effects, the dehydrogenation enthalpy and dehydrogenation activation energy of MgH_2 are remarkably decreased. The finding provides a new insight into the development of high performance Mg/MgH_2 based hydrogen storage composites by optimizing the doping sequence of additives.

Introduction

Increasing fossil fuels depletion and environmental pollution have stimulated the search for alternative and sustainable clean energy. Among the renewable energy resources, hydrogen is one of the most promising clean energy carriers due to its high energy density, environmental friendliness and renewability. The safe and efficient hydrogen storage is the major challenge for the success of hydrogen economy [1,2]. As a potential hydrogen storage material, magnesium hydride

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MgH_2 has attracted considerable interest because of its high volumetric (110 g/L) and gravimetric (7.6 wt %) hydrogen storage capacities, low cost and earth abundance of Mg. However, the high dehydrogenation temperature resulted from the unfavorable thermodynamic and kinetic barriers limits the practical applications of MgH_2 [3,4]. To overcome these drawbacks, numerous modifying strategies have been proposed involving nanostructuring [5,6], chemical alloying [7,8], catalyst doping [9,10], etc. It was found that a wide range of additives or catalysts such as metals or their compounds were effective in enhancing the dehydrogenation properties of MgH_2.

The carbon materials such as graphite, carbon nanotubes, activated carbon, graphene, etc. have also attracted extensive attention as efficient catalysts to improve dehydrogenation properties of MgH_2 [11–13]. Especially, the graphene (G) with single atomic layer structure can effectively inhibit agglomeration of MgH_2 particles and benefit H atom diffusion [14]. The notable catalytic effects are associated with the high surface area, special microstructure and abundant defective edge sites of G. In our previous studies [15], the dehydrogenation properties of MgH_2 were also found to be improved by G doping. First-principles calculations revealed that the decreasing dehydrogenation temperature of MgH_2-G composites can be ascribed to the reduced dehydrogenation enthalpy and dehydrogenation activation energy of MgH_2 upon the catalytic role of G.

Recently, the carbon-supported transition metals or compounds are shown to have superior catalytic performance than those just containing carbon and transition metals or compounds individually [14,16–18]. The general consensus is that the carbon-supported catalysts control the particles size of supported materials. Meanwhile, they also provide the intimate contact between MgH_2 and catalysts to exhibit excellent interfacial catalytic effect on dehydrogenation kinetic of MgH_2. But it is worth mentioning that the transition metals such as Ni can also tune the dehydrogenation thermodynamics of MgH_2 to some extent by solid-solution in MgH_2 lattice [19]. The local lattice distortion of MgH_2 induced by transition metal doping was deduced to be the intrinsic reason for the improved dehydrogenation thermodynamics. Therefore, if the solid-solution effect of transition metals in MgH_2 and the interfacial catalytic effect between carbon-supported catalysts and MgH_2 are both realized, the dehydrogenation properties of MgH_2 will be significantly improved.

Herein, we first report a remarkable enhancement of dehydrogenation properties of MgH_2 by sequential-doping of Ni and G via mechanical milling. By adjusting the doping sequence of additives, the dual effects involving the solid-solution of Ni in MgH_2 lattice and interfacial catalysis between G-supported Ni catalysts and MgH_2 matrix were synergistically realized. The fundamental mechanisms accounting for the enhancing dehydrogenation properties of Ni/G sequential-doped MgH_2 system were further investigated based on first-principles calculations. The finding provides a new insight into the development of high performance Mg/MgH_2 based hydrogen storage composites by optimizing the doping sequence of additives.

Experimental and computational methods

Preparation of materials

In this work, the Ni/G sequential-doped MgH_2 composite was prepared from commercially available MgH_2 (99.8wt%), Ni (99.9wt%) and G (99.0wt%) by mechanical milling method. Firstly, the mixture of MgH_2 added with 10wt%Ni was milled for 1 h under argon. Then the 10wt%G was added into the as-milled MgH_2 + 10wt%Ni sample and the mixture was further milled for 1 h. The XM-4 ball mill, hardened steel crucible and some steel balls were used for milling. The ball to powder weight ratio was 30:1. The obtained sample was labeled as (MgH_2 + 10wt%Ni) (1 h) + 10wt%G (1 h), which represented the Ni/G sequential-doped MgH_2 system. For comparison, the other two composites including the G single-doped and G/Ni simultaneous-doped MgH_2 samples with the same total milling time of 2 h were also prepared and labeled as (MgH_2 + 10wt%G) (2 h), (MgH_2 + 10wt%G + 10wt%Ni) (2 h), respectively.

Examinations of microstructures and dehydrogenation properties

The phase components of as-prepared samples were examined by using X-ray diffraction apparatus (Siemens D-5000) equipped with Cu Kα radiation source. The microstructures of samples were observed by scanning electron microscopy (SEM MIRA3 LMU MI2501373CN). The thermal behaviors of samples were studied by Differential Scanning Calorimetry (DSC 2910, TA Instruments) at a heating rate of 6 °C min^{-1} and an argon flow rate of 18 ml min^{-1}.

First-principles calculations

First-principles calculations were performed with the DMol^3 package and the PW91 exchange-correlation functional was adopted for generalized gradient approximation (GGA) correction [20]. All-electron Kohn-Sham wave functions were expanded in a double numerical plus d-functions (DND) basis [21]. Sampling of irreducible wedge of Brillouin zone was performed with a regular Monkhorst-Pack grid of special *k*-points [22]. All constructed calculation models were relaxed to get the final structures with minimum total energy. The convergences criteria of relaxation were 2.0×10^{-5}Ha, 0.004Ha/Å and 0.005 Å for energy, gradient and atomic displacement, respectively.

Results and discussion

Morphological and structural characterization

Fig. 1 presents the SEM images with different magnifications of three milled samples. For G single-doped MgH_2 as shown in Fig. 1(a), it can be seen that the particle sizes of MgH_2 typically range from 500 nm up to a few microns. The G sheets are dispersedly embedded in MgH_2 particles and effectively inhibit the agglomeration of small particles which always

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