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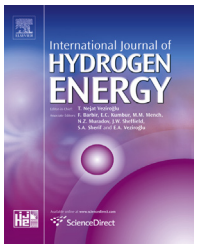

Effect of multi-wall carbon nanotubes supported palladium addition on hydrogen storage properties of magnesium hydride

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ABSTRACT

To improve the hydrogen storage performance of magnesium hydride, multi-wall carbon nanotubes supported palladium (Pd/MWCNTs) was introduced to the magnesium-based materials. Pd/MWCNTs catalysts with different amounts of Pd (20 wt.%, 40 wt.%, 60 wt.%, 80 wt.%) were synthesized by a solution chemical reduction method. Afterwards, Mg_{95}–Pd_m/$MWCNTs_{5-m}$ (m = 0, 1, 2, 3, 4, 5) were prepared for the first time by hydriding combustion synthesis (HCS) and mechanical milling (MM). It is determined by X-ray diffraction (XRD) analysis that Pd/MWCNTs can significantly increase the hydrogenation degree of magnesium during the HCS process. The microstructures of the composites obtained by transmission electron microscope (TEM) and field emission scanning electronic microscopy (FESEM) analyses show that Pd nanoparticles are well supported on the surface of carbon nanotubes and the Pd/MWCNTs are dispersed uniformly on the surface of MgH_2 particles. Moreover, it is revealed that there is a synergistic effect of MWCNTs and Pd on the hydrogen storage properties of the composites. The Mg_{95}–Pd_3/$MWCNTs_2$ shows the optimal hydriding/dehydriding properties, requiring only 100 s to reach its saturated hydrogen absorption capacity of 6.67 wt.% at 473 K, and desorbing 6.66 wt.% hydrogen within 1200 s at 573 K. Additionally, the dehydrogenation activation energy of MgH_2 in this system is decreased to 78.6 kJ/mol H_2, much lower than that of as-received MgH_2.

Introduction

Magnesium is regarded as one of the most promising hydrogen storage materials due to its low cost, abundance, lightweight and high hydrogen storage capacity of 7.6 wt.% [1–3]. However, there remains a challenge to produce a material capable of simultaneously optimizing two contradictory aspects – absorbing hydrogen quickly to form a stable thermodynamics state, while being unstable to release hydrogen at a low temperature. Both of the sluggish hydrogen desorption kinetics at moderate temperatures and the high thermodynamic stability hinder its application [4].

Several approaches have been adopted to improve the performance of MgH_2 for hydrogen storage, including (1) alloying or doping with transition metal elements (nickel, palladium, cobalt, etc. [5–9]), dioxide or fluoride [10–13]; (2) the use of titanium hydride or complex hydride as additives

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[14–16]; (3) forming MgH_2 or Mg nanostructure [17–20] and (4) forming nanocomposites with carbon scaffolds or polymers [21–24]. In recent years, mechanical milling (MM) has been widely used to prepare nanostructured Mg-based materials with large amounts of micro defects and large surface area for hydrogen diffusion [25]. Moreover, during the MM process, different kinds of additives could be added into Mg-based hydrogen storage materials to improve the hydriding and dehydriding kinetics [26–29]. Besides MM, HCS has been regarded as an innovative method to produce Mg-based hydrogen storage alloys due to its advantages such as short processing time, low energy requirement and high activity of the products [30,31]. In previous works, we suggested that the combined processing of HCS with MM (i.e., HCS + MM) has a potential to synthesize Mg-based hydrogen storage materials for vehicular applications [32–34].

In the last few years, there had been numerous studies on the use of different carbon materials, such as activated carbons of different origins, single- and multi-walled carbon nanotubes, carbon aerogels, carbon fiber [35–38], which all have potential catalytic function for Mg-based hydrogen storage materials. Besides, it is suggested that combining transition metals with carbon nanotubes as mixed dopants has a positive catalytic effect on the hydrogen storage properties of MgH_2 [36,39–41]. Yao et al. found MgH_2 with 5.0 wt.% (V + Ti) first milled for 60 h and 5 wt.% CNTs further milled for 10 h shows excellent hydrogen storage properties, and the composite absorbs 5.1 wt.% hydrogen within 5 min at the temperature as low as 423 K [40]. Ranjbar et al. reported that the hydrogen absorption kinetics and hydrogen storage capacity are both improved when Mg–10 wt.% Ni alloy, containing up to 1 wt.% Nb, was ball-milled with 5 wt.% multi-walled carbon nanotubes, absorbing ~6.0 wt.% hydrogen at 473 K under 2 MPa hydrogen pressure [41].

The transition metal Pd nanoparticles have better hydrogen absorption and desorption kinetics at room temperature and lower thermodynamic stability. It is even more valuable that Pd plays an important role in the combination and dissociation of molecular hydrogen [42,43]. Therefore, we anticipate that the addition of Pd/MWCNTs to the MgH_2 system should be beneficial to enhance the kinetics of hydrogen absorption/desorption. In this paper, we hope to combine the advantage of high activity of the HCS + MM product and the catalytic effect of Pd/MWCNTs in Mg-based hydrogen storage materials. The effect of Pd/MWCNTs addition on the structures and hydrogen absorption/desorption properties of Mg-based hydrogen storage materials has been investigated.

Experiment details

Original powders of Mg (99.72 wt.% in purity and <100 μm in size), Pd (99.9 wt.% in purity and 1 μm in size), $PdCl_2$ (AR, 99 wt.% in purity), ethylene glycol (CP, 98 wt.% in purity) and MWCNTs (>97 wt.% in purity and 40–60 nm in external diameter) were purchased from the commercial providers.

MWCNTs treatment

The surface of MWCNTs was treated to ensure functionalization. MWCNTs were added to 50 ml concentrated nitric acid under stirring in an oil bath, with an increase of the temperature to 413 K. It was further refluxed and stirred for 6 h to remove impurities, and washed with distilled water till the pH value of the rinsed solution reached around 7, and finally dried under vacuum.

Preparation of Pd/MWCNTs catalyst

Pd/MWCNTs catalyst was synthesized by a solution chemical reduction method. 0.1 g of MWCNTs was dispersed into ethylene glycol by ultrasonic vibration for 1 h. Further, the required certain proportion of aqueous solution of $PdCl_2$ (make sure that mass ratio of Pd: MWCNTs is 1:4, 2:3, 3:2 and 4:1, respectively) was added to the solution under the condition of magnetic stirring for 4 h. The pH of the entire solution was adjusted to more than 10 by adding NaOH (2.5 M), and the solution was refluxed and magnetically stirred in an oil bath at 383 K for 6 h to ensure complete reduction of Pd. In this reaction as the formula (1), ethylene glycol acted as a reducing, stabilizing, and dispersing agent. Finally, the suspension was filtered, while the solid was washed by distilled water repeatedly until being neutral and dried in a blowing dry oven at 358 K. The sample was labeled as Pd/MWCNTs. The different amounts of Pd loading were maintained to be Pd_m/$MWCNTs_{5-m}$ ($m = 1, 2, 3, 4$).

$$xPd^{2+} + xH_2(HO)CC(OH)H_2 \overset{NaOH/\Delta}{\rightarrow} Pd_x - \text{colloids} + x(HO)CC(OH)H_2 + 2xH^+ \quad (1)$$

Preparation of Mg–Pd/MWCNTs composite

The as-synthesized Pd/MWCNTs and Mg mixed in a certain mass ratio (5:95) were homogenized by ultrasonic vibration in acetone for 30 min. After being completely dried in air, the powders were directly used for HCS. During the HCS process, the samples were first heated up to 853 K at a heating rate of 10 K/min under 2 MPa hydrogen atmosphere and kept at that temperature for 1 h. They were then cooled down to 613 K and held for 4 h. Finally, the samples were cooled down to room temperature. More details of HCS were described in our previous studies [31]. Afterwards, the HCS product was mechanically milled for 10 h in a stainless steel vial with stainless steel balls under Ar atmosphere with the ball to powder ratio of 30:1. MM was conducted with a 400 r/min milling rate by a planetary milling apparatus. For comparison, the Mg_{95}–Pd_5 and Mg_{95}-$MWCNTs_5$ were also prepared by the same process. The as-prepared HCS products were denoted as Mg_{95}–Pd_m/$MWCNTs_{5-m}$ ($m = 0, 1, 2, 3, 4, 5$).

Sample characterization

The microstructures of the catalysts, HCS and HCS + MM products were examined by means of XRD with Cu-K_α radiation (40 kV and 35 mA), FESEM (S4800) and HRTEM (JEM-2010 UHR). The software Rietica was used for the quantitative phase analysis of the catalysts based on the Rietveld method [44]. The average grain sizes of MgH_2 and Pd were estimated from the XRD patterns according to the Rietveld refinement. Samples of TEM characterization were prepared by ultrasonic