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Enhancement of hydrogen desorption in magnesium hydride catalyzed by graphene nanosheets supported Ni-CeO_x hybrid nanocatalyst

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ABSTRACT

A new hybrid nanocatalyst Ni-CeO_x/GNS (graphene nanosheets supported nanoscale Ni and CeO_x, x = 1.69) of high surface area and porosity is synthesized by impregnation-reduction method. It is demonstrated that the Ni-CeO_x/GNS nanocatalyst exhibits improved catalytic effect on the dehydrogenation performances of MgH₂ compares to individual Ni/GNS, CeO_x/GNS, or GNS. Differential scanning calorimetry (DSC) measurement proved that both the onset and peak desorption temperature of MgH₂-5 wt% Ni-CeO_x/GNS (abbreviated as MgNCG) nanocomposites can be decreased by 90.2 and 60.1 °C, respectively. Isothermal desorption kinetic test confirmed that the dehydrogenation kinetics of MgNCG nanocomposites is dozens of times higher than the pure milled MgH₂, e.g. MgNCG nanocomposites can release 6.50 wt% H₂ within 10 min at 300 °C with an initial hydrogen pressure of 5 KPa, superior to 0.16 wt% H₂ desorbed by MgH₂ under the same condition. Additionally, the activation energy (E_a) of MgNCG decreases significantly contrast with pure milled MgH₂, it is proposed that the tri-component of Ni-CeO_x/GNS nanocatalyst has a synergistic effect on the highly efficient dehydrogenation of MgH₂.

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Introduction

Primarily because of the high abundance, low cost, high gravimetric (7.6 wt%) and volumetric (110 kg/m³) hydrogen

capacities of Magnesium hydrides (MgH₂), magnesium-based hydrides are considered to be a particularly promising candidate for hydrogen storage materials [1,2]. The high operational temperature, sluggish kinetics induced by strongly endothermic dehydrogenation reaction (about 75 kJ/mol)

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[3] and slow diffusivity of H atoms through MgH_2/Mg [4], however, obviously hinder the practical application of magnesium-based hydrides in fuel cells [5,6].

To date, extensive attempts have been carried out for the development of efficient magnesium-based hydrogen storage system under mild conditions, such as catalyst doping [7–9], nanosizing [10–13], alloying [14–16], and etc. As a part of these research, a wide range of transition metals [17–19] and transition metal compounds [7,20–22] have been employed as doped-catalyst to improve the hydrogen sorption properties of MgH_2 . Among these selected doped-catalysts, nickel and nickel compounds were attached much attentions due to its much lower cost and high catalytic activity. It was widely accepted that the effective catalytic activity of Ni&Ni-based materials is mainly due to the high affinity of nickel cation toward H in MgH_2 , thus destabilizing the Mg–H bonds and promoting its dissociation [23–25]. Wronski et al. have been investigated the catalytic properties of nano-Ni as an additive to MgH_2 hydrogen storage material [23], they found that nano-Ni performed efficient catalytic properties and reduced the activity energy of MgH_2 by 50%. Li X. G et al. prepared Mg-10 wt% Ni by hydrogen plasma-metal reaction and investigated the hydrogen storage properties by DSC and H_2 desorption rate measurements [26]. It was found that the obtained sample showed much improved hydrogen desorption kinetics than pure MgH_2 , it can release 6.1 wt% H_2 in 10 min at 523 K. Guo Z. P. et al. doped the MgH_2 with 10 wt% NiCl_2 , they found that both the hydrogen desorption temperature and sorption kinetics were improved by adding NiCl_2 as catalyst, and the activity energy of 102.6 kJ/mol for MgH_2 -10 wt% NiCl_2 was 55.9 kJ/mol smaller than pure MgH_2 sample [25]. In our previous work, we reported the hydrogen sorption properties of NiB ball milled with MgH_2 , it was found that the MgH_2 -10 wt% NiB mixture started to release H_2 at 180 °C and 6.0wt% H_2 was desorbed in 10 min at 300 °C [27]. Recently, apart from Ni&Ni-based catalysts, rare metal compounds such as CeO_2 [21], $\text{CeO}_2@\text{C}$ [28], CeF_3 [29], etc. have been employed as catalysts additives to improve the hydrogen storage properties of light metal hydrides. All these three rare metal compounds have benefit effects on the hydrogen desorption of hydrides, it was proposed that the catalytic effects may ascribe to vacant CeO_2 structure or the as-formed CeH_2 & Mg–Ce alloys.

In another hand, numerous studies reported that non-metal additives, especially carbon materials (including graphite, CNTs, fullerene, AC, graphene nanosheets) have a positive catalytic effects on hydrogen sorption of MgH_2 [30–36]. In our previous work, we also reported the catalytic effects of crumpled graphene nanosheets (GNS) or GNS coupling with metal/metal compounds, both of which have high surface area and defective edge sites, on improving the practical hydrogen sorption kinetics and capacity of MgH_2 [37–39]. It was found that these GNS-based catalysts with such structure can not only prevent the aggregation of MgH_2 during ball milling, but also provide more “catalytic active sites” for hydrogen dissociation and diffusion, thus improving the facilitate the hydrogenation/dehydrogenation properties of MgH_2 .

Herein, in this work, we reported the synthesis of a new hybrid nanocatalyst of graphene nanosheets supported nanoscale Ni and CeO_x by impregnation-reduction method. It

was reasonable to suggest that GNS coupled with Ni nanoparticles and CeO_x (O-vacancy structure) can not only decrease both the catalyst addition amount and the milling time due to easier contact of hydride surface by nanoscale GNS supported catalyst, but also can provide more synergistic catalytic active sites to enhance the hydrogen desorption of MgH_2 under more mild conditions.

Experimental

Synthesis of GNS and GNS supported nanocatalysts

Graphene oxide (GO) was prepared by improved Hummers method [40], the as-synthesized GO was then thermal exfoliated to obtain GNS under H_2/Ar (1:9 V/V) flow in a quartz tube at 550 °C for 2 h. To prepare Ni- CeO_x/GNS , 0.65 g as-obtained GNS was added into 100 mL aqueous solution of 1.45 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.155 g $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, followed by ultrasonically dispersing for 2 h. After that the well-dispersed solution was cryogenic treated and then freeze dried for 48 h. Subsequently, the freeze dried mixture was calcined in 10 v% H_2/Ar flow at 550 °C for 2 h to obtain Ni- CeO_x/GNS (theoretical value of 30 wt% Ni, 5 wt% CeO_x and 65 wt% GNS) nanocatalyst. Meanwhile, in order to comparison, the doping amount of 30 wt% Ni/GNS and 5 wt% CeO_x/GNS were synthesized separately by the same procedure.

Synthesis of Mg-based hydrogen storage materials

Typically, before any catalysts added, commercial available MgH_2 (Alfa Aesar, 98%) was pre-milled for 5 h under 0.5 MPa H_2 pressure. After that 95 wt% the pre-milled MgH_2 powder was mixed with 5 wt% as-prepared Ni- CeO_x/GNS , Ni/GNS, CeO_x/GNS , and GNS respectively. Subsequently, the mixtures were mechanically milled for another 2 h under 0.5 MPa H_2 pressure to obtain Mg-based nanocomposites. Conveniently, the milled Mg-based nanocomposites were denoted as MgNCG (MgH_2 -5 wt% Ni- CeO_x/GNS), MgNG (MgH_2 -5 wt% Ni/GNS), MgCG (MgH_2 -5 wt% CeO_x/GNS), and MgG (MgH_2 -5 wt% GNS). As a contrast, the pre-milled MgH_2 powder was also ball milled for another 2 h under the same conditions. All the hydrogen storage materials processing were handled in a high purity Ar (99.999%) filled glovebox, in which the level of H_2O and O_2 was below 1 ppm.

Characterization

For structural characterization, XRD measurements were carried out on a Rigaku (MiniFlexII, Cu K α radiation) diffractometer, N_2 absorption and desorption isotherms were performed by a Quantachrome gas sorption apparatus (Autosorb iQ), Hitachi SU8010 scanning electron microscope (SEM) and JEOL 2010 high resolution transmission electron microscope (TEM) were employed to analyze the morphology of the samples, the surface chemical and structural compositions of the samples were checked by X-ray photoelectron spectrometer (XPS, PHI 5000 Versaprobe). For hydrogen sorption measurements, a differential scanning calorimetry (DSC, TA Q20P) was used to analyze the decomposition performance of Mg-

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