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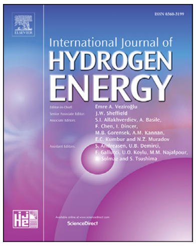

Improved reversible dehydrogenation properties of MgH_2 by the synergetic effects of graphene oxide-based porous carbon and $TiCl_3$

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ABSTRACT

In this study, we used a combination of graphene oxide-based porous carbon (GC) and titanium chloride ($TiCl_3$) to improve the reversible dehydrogenation properties of magnesium hydride (MgH_2). Examining the effects of GC and $TiCl_3$ on the hydrogen storage properties of MgH_2, the study found GC was a useful additive as confinement medium for promoting the reversible dehydrogenation of MgH_2. And $TiCl_3$ was an efficient catalytic dopant. A series of controlled experiments were carried out to optimize the sample preparation method and the addition amount of GC and $TiCl_3$. In comparison with the neat MgH_2 system, the MgH_2/GC-$TiCl_3$ composite prepared under optimized conditions exhibited enhanced dehydrogenation kinetics and lower dehydrogenation temperature. A combination of phase/microstructure/chemical state analyses has been conducted to gain insight into the promoting effects of GC and $TiCl_3$ on the reversible dehydrogenation of MgH_2. Our study found that GC was a useful scaffold material for tailoring the nanophase structure of MgH_2. And $TiCl_3$ played an efficient catalytic effect. Therefore, the remarkably improved dehydrogenation properties of MgH_2 should be attributed to the synergetic effects of nanoconfinement and catalysis.

Introduction

The widespread implementation of hydrogen fuel cell technology requires advanced hydrogen storage materials that can reversibly store large amounts of hydrogen under moderate conditions [1]. Magnesium hydride (MgH_2) and other light metal hydrides received considerable attention as potential hydrogen storage media [2]. Particularly, MgH_2 is considered to be one of the most promising hydrogen storage materials due to its relatively high hydrogen capacity (7.6 wt %), the abundance and low cost of Mg [3]. But its practical

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application is significantly restricted by the high thermodynamic stability of MgH_2, with a formation enthalpy of approximately 75 kJ mol^{-1} H_2, and sluggish hydrogenation/dehydrogenation kinetics [4]. Several strategies have been developed to address the thermodynamic and kinetic problems, e.g. incorporating composite phases [5–8], catalyst doping [9–14] and nanoconfinement using scaffolds [15–19]. In a general view, these technological advances have enabled significant improvements in the reversible dehydrogenation properties of MgH_2.

Catalytic effect play an extraordinarily important role in destabilizing the Mg–H bonding and accelerating the absorption/desorption rate in MgH_2 system. Additional catalysts are generally supposed to act as activation agents to form intermediate metastable states, improving the reaction rate [20–33]. To achieve this, various additives, such as transition metals [20–22], metal oxides [23,24], and metal halides [25–29], have been introduced to the Mg hydride system. Recent studies on the catalytically enhanced magnesium hydride demonstrated that different compounds could result in significant improvement in the dehydrogenation/rehydrogenation properties. Among these selected doped-additives, titanium compounds especially titanium chloride ($TiCl_3$) had the superior catalytic activity [30,31]. Due to the high affinity of titanium cation and chloride anion toward H in MgH_2, $TiCl_3$ destabilized the Mg–H bonds and promoting its dissociation.

Nanoconfinement of MgH_2 using carbon materials scaffolds, such as mesoporous aerogels and activated carbon fiber, results in remarkably reduced particle/grain size of MgH_2 and shortened hydrogen diffusion distance in the hydrogenation/dehydrogenation reactions [32,33]. As a consequence, the resulting nanocrystalline MgH_2 possesses significantly improved hydrogen exchange kinetics compared to bulk materials. A large number of theoretical calculations and experimental studies have confirmed that nanoconfinement could substantially overcome the activation energy barriers of MgH_2 and improve the desorption kinetics. Graphene is an excellent candidate to host hydrogen storage materials with unique layered nanostructure, light weight, excellent thermal conductivity, and high chemical stability. Xia et al. [17] prepared monodisperse MgH_2 nanoparticles assembled on graphene, with outstanding hydrogen storage performance. The studies showed the particle size of MgH_2 was decreased down to nanometer scale, and the aggregation and growth of Mg-based hydrides were also effectively prevented during the de-/rehydrogenation.

The strategy of combining catalysis and nano-confinement is promising, and the studies indicated the synergetic effects enhanced the hydrogen sorption performance of MgH_2 [34–39]. Liu et al. [34] reported that the porous 5 wt% Ni@rGO-containing MgH_2 sample rapidly desorbed 6.0 wt% H_2 within 10 min at 300 °C. Bhatnagar et al. [35] improved the hydrogen sorption behavior of MgH_2 catalyzed by graphene sheet templated Fe_3O_4 nanoparticles. However, graphene usually re-aggregate easily due to the strong π-π bong energy and the physical cross-linking. Therefore, developing a new type graphene with the large surface area and open pores is highly desirable. Porous graphene material is expected to be a good candidate with the high surface area and light weight.

In this work, we selected GC as the structure-tailoring agent and $TiCl_3$ as a catalytic additive to prepare a MgH_2/GC-$TiCl_3$ composite material. Specifically, we prepared the composite material using a three-step method, which involves incorporation of the $MgBu_2$ precursor into GC via infiltration, hydrogenation and milling together with $TiCl_3$. In comparison with the conventional one-step milling method, our study found that the MgH_2/GC-$TiCl_3$ composite had improved reversible hydrogen storage properties using the three-step approach. It is believed that the nanoconfinement effect decreased MgH_2 grain size and $TiCl_3$ catalyzed the dehydrogenation.

Experimental section

MgH_2 (98% purity) was purchased from Alfa-Aesar. $TiCl_3$ (99.999%) and dibutyl magnesium ($MgBu_2$, 1.0 M solution in heptane) were purchased from Sigma-Aldrich Corp. Sucrose (AR grade) and graphite were purchased from Sinopharm Chemical Reagent Corp. (China). Graphene oxide powder was synthesized from natural flake graphite powder using a modified Hummer's method [40] and sonicated for 3 h before the application.

The preparation of the graphene oxide-based porous carbon (GC) can be found elsewhere [41]. Briefly, according to different weight ratios of sucrose to graphene oxide, different volume of sucrose aqueous solution (250 mg/mL) and graphene oxide aqueous solution (5 mg/mL) were homogeneously mixed together and transferred to a 100 mL Teflon-lined autoclave, and heated to 180 °C, then kept for 12 h. After the autoclave was cooled down to room temperature, the solid product was washed with distilled water and dried in vacuum at 120 °C for 24 h to get the intermediate product. This intermediate product prepared above was then placed in a horizontal tube furnace and heated from room temperature to 800 °C for 1 h at 5 °C min^{-1} under Ar. The final product was obtained after dried in vacuum. Before using, GC was dried under vacuum at 400 °C for 12 h to remove moisture and gases from the porous structure and then transferred to an argon-purged glovebox.

The MgH_2/GC-$TiCl_3$ sample was prepared according to literature reports [42,43]. Firstly, the $MgBu_2$ aqueous was added to GC. After the mixture was dried, $MgBu_2$/GC was isothermally hydrogenated to form MgH_2/GC. Lastly, MgH_2/GC was ball milling with $TiCl_3$. And then MgH_2/GC-$TiCl_3$ sample was obtained. To remove the gas impurity such as C_2H_4, C_4H_8 and study the loading amount of MgH_2, the MgH_2/GC composite was then cycled twice with hydrogen release and uptake at a fixed temperature of 380 °C under vacuum and 10 MPa hydrogen pressure. From the released hydrogen content of MgH_2/GC, it could be concluded that approximately 78 wt% of the MgH_2 was formed and the rest is composed of other impurities [44,45]. On the basis of the desorbed H_2 content and the increased weight, the loading amount of MgH_2 is about 52 wt%. For comparison, the MgH_2-GC-$TiCl_3$ mixture in a weight ratio of 1:1:0.08 was directly ball milled for 5 h. MgH_2/GC and MgH_2–$TiCl_3$ samples were also prepared under identical conditions and used as references. Mechanically milling was under Ar atmosphere using a stainless steel vial (with