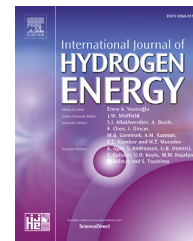




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Mechanistic insight into the promoting effect of magnesium nickel hydride on the dehydrogenation of ammonia borane

Junhong Luo^{a,b,*}, Jinchuan Wang^a, Xingwen Feng^a, Jinguang Cai^a,
Weizhi Yao^a, Jiangfeng Song^a, Changan Chen^a, Deli Luo^a

^a Institute of Materials, China Academy of Engineering Physics, Jianguyou 621908, Sichuan, PR China

^b Sichuan Juneng Nuclear Technology Engineering CO., LTD, Jianguyou 621700, Sichuan, PR China

ARTICLE INFO

Article history:

Received 19 September 2017

Received in revised form

12 November 2017

Accepted 3 December 2017

Available online 20 December 2017

Keywords:

Ammonia borane

Metal hydride

Hydrogen storage

Dehydrogenation

ABSTRACT

In this paper, we report an in-depth study of the post-milled 4AB/Mg₂NiH₄ sample, with a special focus on the promoting mechanism of Mg₂NiH₄ on the dehydrogenation of AB. A combination of X-ray diffraction (XRD), Fourier transformation infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) characterizations, together with selective isotopic labelling and other designed experiments, revealed that AB and Mg₂NiH₄ react with each other from the starting phase of the dehydrogenation process, which eventually results in the formation of Mg–Ni–B–N–H complexes. On the other hand, it was found that the reaction between AB and Mg₂NiH₄ cannot proceed directly, but requires phase transition of normal AB to its mobile phase AB* to occur first. Hence, the promoting mechanism of Mg₂NiH₄ on the dehydrogenation of AB is attributed to its promoting effect on phase transition of normal AB to AB* under mild conditions and in particular its chemical modification of AB with Mg and Ni.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The development of safe and efficient hydrogen carriers represents a key enabling factor for widespread use of hydrogen in the energy sector [1]. Ammonia borane (NH₃BH₃, AB for short), owing to its intriguingly high hydrogen density (i.e., 19.6 wt%) and moderate thermal stability, has attracted considerable interest as a promising candidate of on-board hydrogen carrier [1–4]. However, to realize its full potential in this regard, many problems still need to be solved, such as the sluggish dehydrogenation kinetics at mild temperatures (<100 °C) and the concomitant release of unwanted species (e.g., NH₃, B₂H₆, c-(NHBH)₃) [5,6]. Combined theoretical and

experimental studies revealed that these problems should originate from the fact that AB involves complicated physical/chemical transformation prior to hydrogen release and many competing side reactions during the dehydrogenation process [7–9]. Hence, identifying strategies that can alter the intrinsic dehydrogenation pathways of AB would be essential to addressing the aforementioned problems. Solvolysis [10–20] or dehydrocoupling [21,22] of AB in liquid media with efficient catalysts, nanoconfinement [23–27], addition of additives [28–30] and in particular, chemical modification of AB [1–4,31–45], are so far the major proven effective strategies.

Among the known chemical modifiers, alkali or alkaline earth metal hydrides are arguably the most effective ones

* Corresponding author. Institute of Materials, China Academy of Engineering Physics, Jianguyou 621908, Sichuan, PR China.

E-mail address: luojunhong@caep.cn (J. Luo).

<https://doi.org/10.1016/j.ijhydene.2017.12.005>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

[1–4,44,45]. Their remarkable modifying effect should stem from the substitution of one ammine H in AB by a stronger electron-donating alkali or alkaline-earth metal. This is because such replacement could not only establish an ionic M–N bonding (M refers to alkali or alkaline-earth metal), but can also concomitantly modify the chemical bonding of B–N, B–H, and N–H. As a result, the dehydrogenation of the M-substituted AB, namely metal amidoborane, follows a distinct pathway from AB [46,47], which results in improved dehydrogenation kinetics and eliminated emission of B-containing byproducts. In these cases, the high chemical potential of $H^{\delta+}$ in the NH_3 moiety of AB and $H^{\delta-}$ in the hydride to combine and form H_2 provides a major driving force for the replacement reaction. Interestingly, Weng et al. found that the complex metal hydride, Mg_2NiH_4 , can also significantly improve the dehydrogenation properties of AB but meanwhile, they suggested a distinct promoting mechanism [48]. That is, Mg_2NiH_4 promoted hydrogen release from AB just by tuning the chemical bonding structure of AB via physical interaction, without getting chemically involved in the dehydrogenation process of AB. If this is the case, the manipulation of physical interaction would be a quite sound strategy in view of its remarkable promoting effect as well as the potential ease of subsequent regeneration of the spent fuel.

Given its potential importance, we have therefore reinvestigated the AB- Mg_2NiH_4 composite, with a special attention to the promoting mechanism of Mg_2NiH_4 on the dehydrogenation of AB. In contrast to the claim made in the previous report that the physical interaction between AB and Mg_2NiH_4 was the principal reason for the property improvement of AB, our study revealed that the dominant promoting mechanism of Mg_2NiH_4 on the dehydrogenation of AB should be attributed to its chemical modification of AB with Mg and Ni, though its physical interaction with AB might have played a major role in promoting phase transition of normal AB to AB* under mild conditions.

Experimental section

Materials and sample preparation methods

AB (97% purity), Mg powder (>99%) from Sigma-Aldrich, and Ni powder (99.9% metals basis, 100 nm ~ 200 nm) from Aladdin were all used as received. The Mg_2NiH_4 and Mg_2NiD_4 were synthesized by a hydriding combustion synthesis method [49]. Specifically, the Mg and Ni powders in 2:1 M ratio were firstly mixed by ultrasonic agitation for 1 h in acetone. After most of the acetone volatilized, the Mg/Ni mixtures were further dried under dynamic vacuum conditions for overnight. The hydriding combustion synthesis was conducted under an initial hydrogen pressure (99.999% H_2 or 99.9% D_2) of about 2 MPa. The sample was firstly heated to 550 °C at a ramping rate of 5 °C min^{-1} and held at this temperature for 2 h, followed by cooling to 350 °C at 2 °C min^{-1} and then holding at this temperature for another 2 h, and finally, cooled with furnace to room temperature. The as-prepared sample was milled at 1200 rpm for 1 h and recharged following the aforementioned hydriding procedures twice to ensure sample purity.

The AB- Mg_2NiH_4 or AB- Mg_2NiD_4 mixtures in a molar ratio of 4:1 were mechanically milled under an argon (99.999% purity) atmosphere for varied time periods using a high-energetic mill (QM-3C, Nanjing NanDa) at 1200 rpm or a planetary mill (Fritsch 7) at 400 rpm. The ball-to-powder ratio was around 100:1. The postmilled samples were stored in an argon (99.999% purity)-filled glovebox, wherein the H_2O/O_2 levels were typically below 0.1 ppm.

Dehydrogenation properties tests

The thermolytic behaviors of the post-milled 4AB/ Mg_2NiH_4 or 4AB/ Mg_2NiD_4 samples were examined by synchronous thermogravimetry/differential scanning calorimetry/mass spectroscopy (TG/DSC/MS) and volumetric methods. In the thermal analyses, the samples with a typical amount of about 4 mg were heated to 300 °C at a ramping rate of 2 °C min^{-1} under a flowing argon (99.999% purity) atmosphere. The volumetric isothermal and temperature-programmed desorption (TPD) measurements were conducted under an initial pressure of <100 Pa in a carefully calibrated Sievert's type apparatus, using samples with a typical amount of 200 mg. In the isothermal measurements, temperature control was accomplished using a water bath pre-held at 40 °C. In a typical TPD test, the sample was ramped to 300 °C at 2 °C min^{-1} and then held at this temperature for around 4 h. The weight loss of the post-milled 4AB/ Mg_2NiH_4 sample during the storage periods was determined in the following manner: first, the net weight of the post-milled sample (W_1) and the total weight of the post-milled sample + test tube (W_2) were measured; after storing for different periods of time, the total weight of the aged sample + test tube (W_3) was quantified; finally, the weight loss of the post-milled samples (WL%) was determined by the following formula: $WL\% = (W_2 - W_3)/W_1 \times 100\%$.

Characterizations

Phase identification was conducted on a Bruker D8 ADVANCE diffractometer with Cu $K\alpha$ radiation, and a polymeric tape was used to minimize the H_2O/O_2 contamination of the sample. The morphology of the samples was studied by using a HITACHI S5200 (5 kV) electron microscope. The Fourier transformation infrared spectroscopy (FTIR) spectra were collected on a Bruker TENSOR 27 spectrometer (4 cm^{-1} resolution) by using the KBr-pellet method, and the obtained spectra were normalized using OPUS 6.5 software. Magnetic property measurements were conducted at room temperature on a SQUID MPMS-XL magnetometer. X-ray photoelectron spectra (XPS) were acquired with a VG ESCALAB 250 spectrometer equipped with an Al $K\alpha$ X-ray exciting source. The binding energies were referred to the C 1s peak at 284.6 eV. After the initial data were collected, a 3 keV Ar^+ sputter beam was used for depth profiling of the samples.

Results and discussion

The Mg_2NiH_4 sample prepared by hydriding combustion synthesis method is of purity, as indicated by the XRD result shown in Fig. 1a. After mechanically milling with AB at

Download English Version:

<https://daneshyari.com/en/article/7708363>

Download Persian Version:

<https://daneshyari.com/article/7708363>

[Daneshyari.com](https://daneshyari.com)