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Effect of CO on hydrogen storage performance of $2\text{LiNH}_2 + \text{MgH}_2$ system



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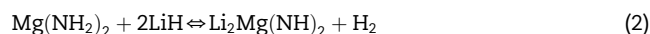
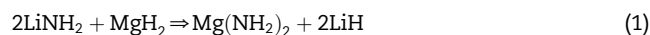
ABSTRACT

$(2\text{LiNH}_2 + \text{MgH}_2)$ system is one of the most promising hydrogen storage materials due to its suitable operation temperature and high reversible hydrogen storage capacity. In studies and applications, impurities such as CO, CO_2 , O_2 , N_2 and CH_4 are potential factors which may influence its performance. In the present work, hydrogen containing 1 mol% CO is employed as the hydrogenation gas source, and directly participates in the reaction to investigate the effect of CO on the hydrogen sorption properties of $(2\text{LiNH}_2 + \text{MgH}_2)$ system. The results indicate that the hydrogen capacity of the $(\text{Mg}(\text{NH}_2)_2 + 2\text{LiH})$ system declines from 5 wt.% to 3.45 wt.% after 6 cycles of hydrogenation and dehydrogenation, and can not restore to its initial level when use purified hydrogen again. The hydrogen desorption kinetics decreases obviously and the dehydrogenation activation energy increases from 133.35 kJ/mol to 153.35 kJ/mol. The main reason for these is that two new products Li_2CN_2 and MgO appear after $(2\text{LiNH}_2 + \text{MgH}_2)$ react with CO. They are formed on the surface of materials particles, which may not only cause a permanent loss of NH_2^- , but also prevent the substance transmission during the reaction process. After re-mechanically milling, both kinetics and dehydrogenation activation energy can be recovered to the initial level. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Li–Mg–N–H system has been regarded as a potential hydrogen storage system and received more and more attention due to its suitable operation temperature and high reversible hydrogen storage capacity of 5.5 wt.% [1–8]. It can be synthesized either by reacting $\text{Mg}(\text{NH}_2)_2$ with LiH [1] or by reacting LiNH_2 with MgH_2 [2]. A mixture of $(2\text{LiNH}_2 + \text{MgH}_2)$ is a specific example of a Li–Mg–N–H system which converts to $(\text{Mg}(\text{NH}_2)_2 + 2\text{LiH})$ at 220 °C under a hydrogen pressure of

10 MPa before any sorption reaction occurs (Eq. (1)) [3]. In this paper, the experimental material will be referred to as the $(2\text{LiNH}_2 + \text{MgH}_2)$. The subsequent reversible hydrogen desorption/absorption reaction is that shown in Eq. (2).



For practical application, the produced hydrogen source contains some reactive and inert impurities, such as CO, CO_2 ,

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O₂, H₂O, N₂ and CH₄. Many efforts have been done to study the influences of gaseous impurities on hydrogen storage alloys [9–18]. According to the reference [10], the hydrogenation performance of LaNi₅ is degraded obviously when the content of CO in hydrogen source increases. However, the research is limited for amides [19–21]. Luo [21] has showed that water-saturated air makes a small positive effect on the sorption kinetics and final hydrogen capacity of amides. So the aim of present work is to analyze the effects of CO on the hydrogen storage performance of the (2LiNH₂ + MgH₂) system. It is meaningful to study whether the hydrogen storage system is affected by CO impurity and how it works in practical application.

Experimental

The starting materials LiNH₂ (95% purity, Sigma–Aldrich) was used without further purification. The MgH₂ powder was prepared by mechanically milling Mg powder under an initial hydrogen pressure of 3 MPa for 40 h, followed by hydrogenation at 400 °C for 4 h under 8 MPa hydrogen pressure. A mixture of LiNH₂ and MgH₂ was mechanically milled with molar ratio of 2:1 for 10 h under a hydrogen pressure of 3 MPa. All the milling treatment was done by using a Spex-8000

apparatus, and the ball-to-powder ratio was around 10:1. The material handing was performed in a glovebox filled with purified argon to keep the H₂O and O₂ levels below 1 ppm.

The temperature programmed desorption of the (2LiNH₂ + MgH₂) sample was carried on a home-made reaction system. The (2LiNH₂ + MgH₂) mixture yielded two samples. Sample 1 was the reference group which experienced hydrogenations with purified H₂ while sample 2 was the experimental group which was hydrogenated with H₂ containing 1 mol% CO. The samples were subjected to repeated hydrogen desorption (against vacuum) and absorption (8 MPa) in which the samples were always heated from room temperature to 220 °C by 1 °C/min. For the experimental group, the sample was following subjected to experience recovery experiment by repeating hydrogenation/dehydrogenation with purified H₂.

Hydrogen desorption kinetics was also carried on the system discussed above. The sample was hydrogenated with purified H₂ in the first cycle and following be hydrogenated with H₂ containing 1 mol% CO in the other 5 cycles. All desorptions (against vacuum) and absorptions (8 MPa) were carried at the temperature of 220 °C.

Differential scanning calorimetry (DSC) was conducted using Mettler-Toledo DSC 1 to study the dehydrogenation activation energy of samples. Samples of about 18 mg for each were heated from 30 °C to 350 °C at various heating rate, including 1, 3, 5, 8 and 10 °C/min, under the flow of high pure Ar gas (99.999%) at 30 mL/min. XRD analysis was carried out by using X'pert Pro MPD diffractometer with CuK α radiation at 40 kV and 40 mA over the range of 10–90°. The IR absorption spectrum of N–H and C–N was collected in diffuse reflectance infrared Fourier transform mode.

Results and discussion

Temperature programmed desorption

Fig. 1 shows the temperature programmed hydrogen desorption of the reference group (Fig. 1(a)) and the experimental

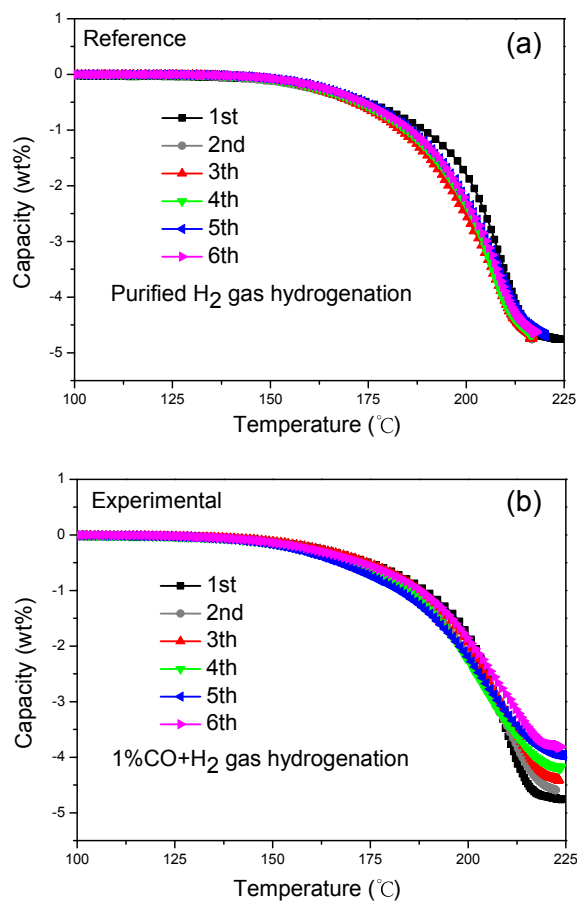


Fig. 1 – Temperature programmed hydrogen desorption curves for (a) the reference group and (b) the experimental group measured from room temperature to 220 °C by 1 °C/min.

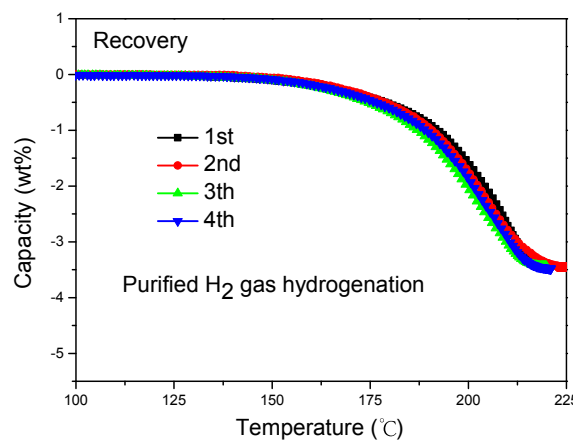


Fig. 2 – Temperature programmed hydrogen desorption curves for the experimental group in recovery experiment measured from room temperature to 220 °C by 1 °C/min.

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