

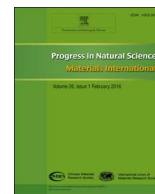
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Original Research

Preparation and catalytic effect of porous Co_3O_4 on the hydrogen storage properties of a Li-B-N-H system[☆]You Li^a, Yi Zhang^{a,b}, Mingxia Gao^a, Hongge Pan^a, Yongfeng Liu^{a,c,*}^a State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province and School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China^b Center of Material Science, National University of Defense Technology, Changsha 410073, China^c Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China

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ABSTRACT

A porous Co_3O_4 with a particle size of 1–3 μm was successfully prepared by heating Co-based metal organic frameworks MOF-74(Co) up to 500 °C in air atmospheric conditions. The as-prepared porous Co_3O_4 significantly reduced the dehydrogenation temperatures of the $\text{LiBH}_4\text{-2LiNH}_2$ system and improved the purity of the released hydrogen. The $\text{LiBH}_4\text{-2LiNH}_2\text{-0.05/3Co}_3\text{O}_4$ sample started to release hydrogen at 140 °C and released hydrogen levels of approximately 9.7 wt% at 225 °C. The end temperature for hydrogen release was lowered by 125 °C relative to that of the pristine sample. Structural analyses revealed that the as-prepared porous Co_3O_4 is in-situ reduced to metallic Co, which functions as an active catalyst, reducing the kinetic barriers and lowering the dehydrogenation temperatures of the $\text{LiBH}_4\text{-2LiNH}_2$ system. More importantly, the porous Co_3O_4 -containing sample exhibited partially improved reversibility for hydrogen storage in the $\text{LiBH}_4\text{-2LiNH}_2$ system.

1. Introduction

Hydrogen is one of the most promising alternative energy sources that could replace fossil fuels [1–3]. However, viable, safe, inexpensive and efficient hydrogen storage is still highly desirable for using hydrogen energy in automobiles [4–8]. Recently, metal borohydrides have attracted substantial attention due to their high gravimetric and volumetric hydrogen densities [9,10]. For instance, LiBH_4 has a hydrogen capacity as high as 18.3 wt% [11]. Unfortunately, high dehydrogenation temperatures, sluggish dehydrogenation kinetics and poor hydrogen storage reversibility prevent metal borohydrides from use in practical applications, especially mobile applications [11,12]. There have been numerous attempts to destabilize metal borohydrides by adding elemental metals, carbon-based species, metal hydrides, oxides and halides [13–19]. In 2005, Pinkerton et al. reported, for the first time, that all hydrogen in LiBH_4 could be released when in combination with LiNH_2 to form a new $\text{LiBH}_4\text{-2LiNH}_2$ system [20]. This system offers a theoretical hydrogen capacity of 11.9 wt% below 350 °C, and the strong affinity between protic H^+ in LiNH_2 and hydridic H^- in LiBH_4 provides the driving force for hydrogen release. However, hydrogen release from the Li-B-N-H system often suffers from contamination with significant NH_3 levels,

and the dehydrogenation temperature does not yet meet the requirements for mobile applications [20,21]. More importantly, hydrogen release from the $\text{LiBH}_4\text{-2LiNH}_2$ system is exothermic in nature, which complicates rehydrogenation of the dehydrogenation products.

One of the most effective approaches for reducing the dehydrogenation temperature and improving the hydrogen purity of the $\text{LiBH}_4\text{-2LiNH}_2$ system is to introduce transition metal additives, including Pt, Pd, Fe, Ni, Co, and Ti or their chlorides and oxides [22–28]. Pinkerton et al. reported that the midpoint temperature of hydrogen release from the $\text{LiBH}_4\text{-2LiNH}_2$ system is reduced by 43 °C with the addition of 5 wt% Pd [22]. Moreover, a 112 °C reduction in the hydrogen release temperature was attained after adding 11 wt% NiCl_2 [23]. Recently, Zhang et al. synthesized successfully metallic Ni nanoparticles supported on carbon (nano-Ni@C) and observed approximately 10.0 wt% of hydrogen release from the 10 wt% nano-Ni@C-added $\text{LiBH}_4\text{-2LiNH}_2$ system within 25 min at 220 °C [24]. Similar phenomena were also observed for Co-based additives [25–28]. Tang et al. demonstrated that more than 8 wt% of hydrogen was released from the 5 wt% CoCl_2 -containing $\text{LiBH}_4\text{-2LiNH}_2$ system at temperatures as low as 155 °C [25]. The Co and/or Co_2B serve as active catalytic species. In addition to transition metals and their halides, transition metal oxides can also effectively catalyze hydrogen release from the $\text{LiBH}_4\text{-2LiNH}_2$ system

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[26,27]. The presence of 0.05 mol of CoO reduced the onset dehydrogenation temperature by 120 °C and activation energy of the hydrogen release reaction by 30% [26]. The $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}0.05/3\text{Co}_3\text{O}_4$ composite released approximately 9.9 wt% of hydrogen with an onset temperature of 130 °C [27]. More encouragingly, hydrogen release from the CoO or Co_3O_4 -supplemented samples was partially reversible as approximately 1.1 wt% and 1.7 wt% of hydrogen was recharged into the dehydrogenated $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}0.05\text{CoO}$ and $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}0.05/3\text{Co}_3\text{O}_4$ samples, respectively, representing a substantial advantage with respect to the additive-free sample. However, the present investigation mainly focused on commercial Co-based oxides, and it was unclear how the Co-based oxide particle size and morphology affect the catalytic activity.

In this work, we successfully prepared porous Co_3O_4 using a Co-based metal-organic framework (MOF) as a precursor, and the effects of as-prepared Co_3O_4 on the $\text{LiBH}_4\text{-}2\text{LiNH}_2$ system dehydrogenation behaviours were systematically investigated. The onset temperature of hydrogen release from the $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}0.05/3\text{Co}_3\text{O}_4$ sample was lowered by 125 °C, and hydrogen release was 9.7 wt% within 18 min at 200 °C. Moreover, the role of the porous Co_3O_4 was analysed and discussed.

2. Materials and methods

2.1. Sample preparation

LiBH_4 (Acros, 95%), LiNH_2 (Alfa Aesar, 95%) and Co_3O_4 (Alfa Aesar, 99.7%) were commercially available and used as received without further purification. The porous Co_3O_4 was synthesized by heating a Co-based MOF (MOF-74(Co)), which was prepared in our laboratory using the procedure reported by Dietzel et al. [29], to 500 °C in air atmosphere. The as-prepared Co_3O_4 was introduced to the $\text{LiBH}_4\text{-}2\text{LiNH}_2$ system as a catalyst precursor. The $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}x\text{Co}_3\text{O}_4$ composites, where $x=0, 0.003/3, 0.01/3, 0.05/3,$ and $0.1/3$ mol, were prepared by ball milling the corresponding chemicals on a planetary ball mill (QM-3SP4, Nanjing) at room temperature for 24 h. The ball-to-sample weight ratio was approximately 120:1. The milling process was set to rotate at 500 rpm for 0.2 h in one direction, which was followed by a pause of 0.1 h and then rotation in the reverse direction to limit increasing the temperature during milling. All sample handling was performed in a glovebox (MBRAUN 200B, Germany) equipped with a circulation purifier that kept the concentrations of O_2 and H_2O below 1 ppm.

2.2. Property evaluations

Temperature-programmed desorption (TPD) measurements were conducted using a homemade apparatus equipped with an online mass spectrometer (MS, Hiden QIC-20) to monitor the gaseous compositions produced from the sample upon heating. Approximately 20 mg of the sample was loaded into a custom-designed tube reactor; then, the temperature was gradually elevated from room temperature to 400 °C at a rate of 2 °C/min under Ar flow. Quantitative hydrogen desorption and absorption behaviours were evaluated with a homemade Sievert-type apparatus. Typically, 100 mg of sample was loaded into a stainless steel reactor inside a glovebox and gradually heated from ambient temperature to the desired temperature at a rate of 2 °C/min for dehydrogenation (initially in vacuum) and 1 °C/min for hydrogenation (under 100 bar of initial hydrogen pressure). For isothermal dehydrogenation, the samples were rapidly heated to the desired temperature and then maintained throughout the testing. The pressure and temperature data were automatically recorded. The hydrogen desorbed/absorbed levels were calculated from the equation of state. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200F3 unit installed in an argon-filled glovebox to determine the heat effect in an Ar atmosphere. Approximately 2 mg of the as-milled

sample was loaded into an Al crucible that was covered by a lid and then heated from room temperature to 400 °C at a ramping rate of 5 °C/min.

2.3. Structural and morphological characterisation

Phase identification was conducted via powder X-ray diffraction (XRD) on a PANalytical X'Pert diffractometer with Cu K α radiation, which was operated at 40 kV and 40 mA. XRD data were collected from 10 to 90° (2θ) in increments of 0.05° at ambient temperatures. The powder samples were sealed in a custom-designed container covered with Scotch tape to protect the samples from air and moisture contamination during transfer and measurement. The vibrational characteristics of the B–H and N–H bonds were identified using a Bruker Tensor 27 Fourier transform infrared spectrometer (FTIR, Germany) with a resolution of 4 cm^{-1} . The test samples were evenly mixed with potassium bromide (KBr) at a KBr-to-sample weight ratio of approximately 150:1; then, they were cold-pressed to form pellets. After subtracting the background due to air, each spectrum was created from an average of 16 scans. The sample morphology was observed with a Hitachi S-4800 scanning electron microscope (SEM). The constituent element distribution was analysed using an energy-dispersive X-ray spectrometer (EDS) attached to a Hitachi S-4300 SEM facility. To avoid contact with air, the samples were transferred from the glovebox to the SEM facility in a sealed box with argon atmosphere. The chemical state of Co was identified using a parallel-equipped electron energy loss spectroscopy (EELS, Gatan, Pleasanton, CA) detection system. All spectra were acquired at an Co $L_{2,3}$ -edge and calibrated to the zero loss peak position.

3. Results and Discussion

3.1. Structure and morphology of the prepared samples

Fig. 1(a) shows the XRD pattern of the as-prepared Co_3O_4 . Only typical Co_3O_4 reflections were observed in the XRD profile. The weak intensities are possibly due to the small grain size and/or poor crystalline. SEM analysis (Fig. 1(b)) demonstrated that the as-prepared Co_3O_4 exhibited irregular micron-particle shapes and the particle size ranged from 1 to 3 μm . More interestingly, the as-prepared Co_3O_4 particles had many pores (Fig. 1(c)), which is distinctly different from the commercial Co_3O_4 , as shown in Fig. 1(d). As a result, the porous Co_3O_4 micron particles were successfully attained by calcining the Co-based MOF (MOF-74(Co)) at 500 °C in air atmosphere.

To evaluate the catalytic effect of as-prepared Co_3O_4 , five samples with different compositions of $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}x\text{Co}_3\text{O}_4$ ($x=0, 0.003/3, 0.01/3, 0.05/3,$ and $0.1/3$ mol) were prepared by ball milling the corresponding materials. Fig. 2 depicts the XRD patterns of the as-milled $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}x\text{Co}_3\text{O}_4$ samples. As extensively reported, the pristine $\text{LiBH}_4\text{-}2\text{LiNH}_2$ sample mainly consists of the $\alpha\text{-Li}_4\text{BN}_3\text{H}_{10}$ primary phase and a low level of $\beta\text{-Li}_2\text{BNH}_6$ after ball milling. In the presence of porous Co_3O_4 , the $\alpha\text{-Li}_4\text{BN}_3\text{H}_{10}$ phase still dominated the XRD profiles, but the $\beta\text{-Li}_2\text{BNH}_6$ reflections gradually weakened and even disappeared for $x > 0.05/3$. In addition, the diffraction peaks of Co_3O_4 emerged and intensified with increasing Co_3O_4 levels.

3.2. Catalytic effects of porous Co_3O_4 on dehydrogenation

Fig. 3 shows the TPD-MS curves of the $\text{LiBH}_4\text{-}2\text{LiNH}_2\text{-}x\text{Co}_3\text{O}_4$ ($x=0, 0.003/3, 0.01/3, 0.05/3,$ and $0.1/3$ mol) samples. The H_2 and NH_3 signals were detected while heating the pristine $\text{LiBH}_4\text{-}2\text{LiNH}_2$ system from room temperature to 400 °C. Hydrogen release from the pristine $\text{LiBH}_4\text{-}2\text{LiNH}_2$ system started at 250 °C and peaked at 326 °C with a one-step reaction (Fig. 3(a)). After adding 0.003/3 mol Co_3O_4 , hydrogen release exhibited a two-step reaction process and the dehydrogenation onset temperature was lowered to 150 °C, which is

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