Journal of Power Sources 248 (2014) 388–395

Contents lists available at ScienceDirect

Journal of Power Sources

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

$NaAlH_4$ dehydrogenation properties enhanced by $MnFe_2O_4$ nanoparticles

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HIGHLIGHTS

- Nanosized $MnFe_2O_4$ effect on $NaAlH_4$ desorption properties is studied for the first time.
- $NaAlH_4$ + 7 mol% $MnFe_2O_4$ desorption temperature onset is much lower than pristine $NaAlH_4$.
- The apparent activation energy of the $MnFe_2O_4$ doped sample is dramatically decreased.
- Mn species and $Fe_{0.9536}O$ phases significantly improve $NaAlH_4$ desorption properties.

ARTICLE INFO

Article history:
Received 17 June 2013
Received in revised form
5 September 2013
Accepted 22 September 2013
Available online 2 October 2013

Keywords:
Manganese ferrite
Hydrogen storage
Sodium alanate
Dehydriding temperature
Apparent activation energy

ABSTRACT

The catalytic effects of $MnFe_2O_4$ nanoparticles on the dehydrogenation properties of $NaAlH_4$, prepared by ball milling, are investigated. The onset temperatures for $NaAlH_4$ + 7 mol% $MnFe_2O_4$ are 95 °C, 152 °C and 327 °C for the three dehydrogenation steps, significantly lower compared with as-received $NaAlH_4$. The isothermal dehydriding kinetics shows that adding $MnFe_2O_4$ to $NaAlH_4$ could significantly enhance the desorption kinetics of $NaAlH_4$, 7 mol% $MnFe_2O_4$-doped sample also displays the well-maintained kinetics and only a slight capacity loss for the three cycles. From the differential scanning calorimetry and the Kissinger desorption kinetics analysis, the apparent activation energy of the 7 mol% $MnFe_2O_4$-doped sample for the three steps is 57.74 kJ mol^{-1}, 75.06 kJ mol^{-1} and 117.22 kJ mol^{-1}, resulting in 56.05 kJ mol^{-1}, 67.53 kJ mol^{-1} and 59.12 kJ mol^{-1} reduction, respectively, compared with the as-received $NaAlH_4$. Based on the Fourier Transform Infrared Spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy, $Fe_{0.9536}O$ and amorphous Mn or Mn-containing species together play a synergistic role in remarkably improving $NaAlH_4$ dehydriding properties.

1. Introduction

Solid-state lightweight metal complex hydrides have received increased attention due to their high volumetric and gravimetric hydrogen storage density [1–6], which may meet the U.S. Department of Energy 2015 targets [7]. A viable hydrogen storage system requires hydrogen storage materials with more than 5.5 wt% capacity and fast desorption kinetics. Among various complex metal hydrides [1,8–17], sodium alanates are considered to be a promising solid-state hydrogen storage media, since Bogdanović and Schwickardi [18] reported that $NaAlH_4$ could reversibly desorb hydrogen under moderate conditions after doping with Ti-containing catalyst. The absorption capacity decreases with the increasing of cycles, which declines from 4.2 wt% to 3.1 wt% at 170 °C under 15 MPa hydrogen pressure and from 2.7 wt% to 2.1 wt% at 200 °C under 6 MPa hydrogen pressure over 35 cycles, respectively. Upon heating, $NaAlH_4$ would decompose to release hydrogen in three steps according to the following reactions:

$$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2 \quad (3.7\ \text{wt\%}) \tag{1}$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + 1.5H_2 \quad (1.9\ \text{wt\%}) \tag{2}$$

$$3NaH \rightarrow 3Na + 1.5H_2 \quad (1.8\ \text{wt\%}) \tag{3}$$

Reaction (1) happens at the temperature range of 170–230 °C, reactions (2) and (3) initiate above 250 °C and 400 °C, respectively.

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http://dx.doi.org/10.1016/j.jpowsour.2013.09.093

However, high desorption temperature, sluggish dehydrogenation kinetics and poor reversibility limit $NaAlH_4$ practical applications [6,19–21]. During the past decade researchers have been trying to overcome these drawbacks. The efforts included preparing nanocrystalline $NaAlH_4$ [6,22–24], and adding metal catalysts [25–29], C species [20,30,31], metal halides [21,32–37], metal oxides [2,5,19,38–40] and other compounds [3,41–43]. For improvement of dehydriding properties of $NaAlH_4$, generally, metal halides have better catalytic effect than metal oxides, metal oxides have better catalytic effect than metals, but some metal oxide has better catalytic effect than metal halide, such as $Nb_2O_5 > NbF_5$. Usually, the dehydriding temperature and dehydriding kinetics can be strikingly improved by adding catalyst, but the dehydriding capacity decreases remarkably with the increase of cycles [2,27,47]. Naik et al. demonstrated the superior effects of Mn^{2+} on improving the dehydrogenation properties of $NaAlH_4$ [35]. It was also reported that Fe and Fe^{3+} could ameliorate $NaAlH_4$ hydrogen storage performance [29,44]. Moreover, Zhai et al. [45] reported that $MnFe_2O_4$ could remarkably improve $LiAlH_4$ dehydrogenation. $MnFe_2O_4$ has better catalytic effect than Fe or Mn oxides alone in improving the dehydriding properties of $LiAlH_4$, $NaAlH_4$ has similar performances with $LiAlH_4$. Therefore, it is reasonable to assume that $MnFe_2O_4$ would show great potential as a catalyst to advance $NaAlH_4$ hydrogen storage performance. Motivated by the above findings, in the present work, $MnFe_2O_4$ nanoparticles were employed as catalyst precursors to study their effect on the dehydrogenation properties of $NaAlH_4$ prepared by ball milling.

2. Experimental

$NaAlH_4$ (≥93% purity) was purchased from Sigma Aldrich Co., and $MnFe_2O_4$ (≥99.99% purity, 20 nm particle size) was prepared by the nitrate–citrate auto-combustion methods. The details of the preparation procedure are given in the previous report [46]. Both materials were used directly, without any further purification. All handling (including weighing and loading) was performed in a high-purity argon-filled glove box in order to avoid oxidation and moisture. About 3 g of $NaAlH_4$ was mixed with different mole fractions (3 mol%, 5 mol%, 7 mol%, and 9 mol%) of $MnFe_2O_4$ nanoparticles, and then ball milled for 30 min in a high-energy Spex Mill. All the samples were loaded into the stainless steel vial in an argon-filled glove box. ZrO_2 balls were added with a ball-to-powder weight ratio of 15:1. The samples were ball milled for 10 min and then cooled down for 5 min after each cycle.

The dehydrogenation properties of as-received $NaAlH_4$ and doped samples were measured using a pressure–composition–temperature (PCT) apparatus (Beijing Nonferrous Metal Research Institute, China). For non-isothermal dehydrogenation, 0.5 g of the sample was loaded into the vessel, and then heated up to 500 °C at a 4 °C min^{-1} rate under 0.01 MPa atm pressure. The isothermal dehydrogenation measurements for the undoped and doped samples were performed at 120 °C and 150 °C under a hard vacuum atmosphere. Following the first complete dehydrogenation, the samples were subjected to rehydrogenation studies at 150 °C under 5 MPa hydrogen pressure for 180 min. Subsequently, the rehydrogenated samples were dehydrogenated at similar temperature.

In order to further analyze the dehydrogenation performance and calculate the desorption activation energy of the doped $NaAlH_4$ sample by means of the Kissinger method, the differential scanning calorimetry (DSC) was performed using NETZSCH STA 449C in high-purity argon (50 mL min^{-1} flow rate, 99.999% pure). About 5 mg of the sample was sealed into a 50 mL alumina crucible in the glove box, and then heated at different rates (4 °C min^{-1}, 7 °C min^{-1} and 10 °C min^{-1}), from 50 °C to 500 °C.

The morphology of the as-received and doped samples after ball milling was examined by scanning electron microscopy (SEM, ZEISS EVO18, Germany). The phase structure of the samples after ball milling and after dehydrogenation was determined by using the MXP21VAHF X-ray diffractometer (XRD with Cu Kα radiation, 40 kV, 200 mA) at room temperature. The 2θ angle was varied from 25° to 90° in 0.02° increments, 1 s per step. The samples were covered with the paraffin film to prevent oxidation during the XRD test.

Fourier transformation infrared spectroscopy was performed by using an infrared spectrophotometer (NEXUS670). The spectral resolution was 4 cm^{-1}. Scans were performed between 500 cm^{-1} and 2000 cm^{-1} in argon. X-ray photoelectron spectroscopy (XPS) experiments were performed in an ultra high vacuum (UHV) chamber with the base pressure of around 3×10^{-13} Pa, equipped with a Perkin–Elmer PHI-5300 XPS spectrometer.

3. Results and discussion

3.1. Dehydrogenation temperature

Fig. 1 shows the non-isothermal desorption curves of as-received $NaAlH_4$, as-milled $NaAlH_4$ and ball-milled $NaAlH_4$ doped with 3 mol%, 5 mol%, 7 mol% and 9 mol% $MnFe_2O_4$ nanopowders. The desorption curves clearly reveal that adding $MnFe_2O_4$ nanoparticles dramatically improves $NaAlH_4$ dehydriding properties, resulting in a striking reduction of the onset desorption temperature, not only for the first and second steps, but also for the third step. The onset desorption temperature for all doped samples is below 130 °C, indicating a significant decrease compared with the as-received $NaAlH_4$. For the as-received $NaAlH_4$, it starts to decompose at 179 °C, and weight loss is about 5.18 wt% after heating to 290 °C. The third step commences at 411 °C, and a hydrogen release capacity of 6.4 wt% is obtained below 450 °C. Compared with as-received $NaAlH_4$, the onset desorption temperature of as-milled $NaAlH_4$ decreased slightly by 14 °C, 11 °C and 13 °C for the three steps, respectively, due to the $NaAlH_4$ activation introduced by the ball milling [2,36].

When doping $MnFe_2O_4$ nanoparticles to the $NaAlH_4$ matrix, the onset desorption temperature of $NaAlH_4$ is further reduced. For the 3 mol% doped sample, the dehydrogenation process starts at 125 °C for the first stage, and initiates at 180 °C and 367 °C for the second

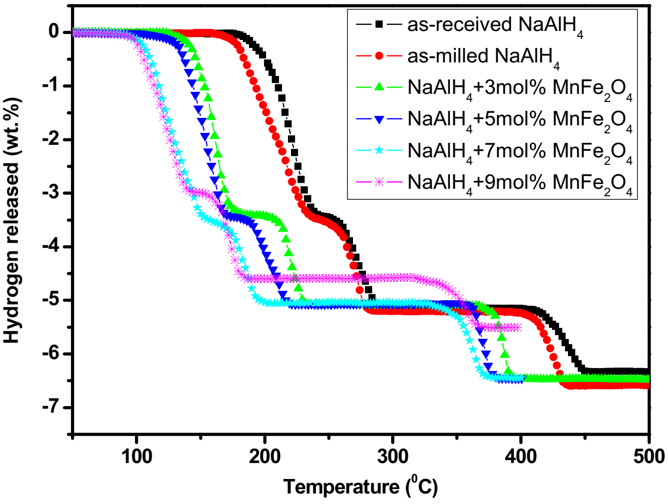

Fig. 1. Thermal desorption curves of the as-received $NaAlH_4$, as-milled $NaAlH_4$, and ball-milled $NaAlH_4$ doped with 3 mol%, 5 mol%, 7 mol% and 9 mol% nanosized $MnFe_2O_4$.