Vacuum 99 (2014) 127–134

Contents lists available at SciVerse ScienceDirect

Vacuum

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

Preparation and thermal properties of aluminum hydride polymorphs

Bo Xu [a,b], Jiping Liu [a,b,*], Xiaojun Wang [a,b]

[a] School of Material Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing 100081, China
[b] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing 100081, China

ARTICLE INFO

Article history:
Received 3 January 2013
Received in revised form
30 March 2013
Accepted 10 May 2013

Keywords:
Aluminum hydride
Preparation
Thermal properties

ABSTRACT

Aluminum hydride (AlH_3) is one of the most promising hydrogen and energy storage materials, and it has a high gravimetric and volumetric density of hydrogen. In this work, three aluminum hydride polymorphs (α-AlH_3, β-AlH_3, and γ-AlH_3) were prepared through the desolvation of AlH_3-etherate using the organometallic synthesis method, and AlH_3-etherate, which has the molecular formula of $AlH_3 \cdot 0.22Et_2O$, was also obtained. The synthesis conditions were discussed in detail, and the structure and morphology of the samples were characterized using FTIR, SEM, and XRD. The thermal properties of AlH_3 polymorphs were experimentally investigated under heating and isothermal processes. The results suggest that the α-polymorph is the most stable of the three polymorphs, and the decomposition of the less stable polymorphs, β-AlH_3 and γ-AlH_3, typically occurs via an exothermic transformation to the α-phase (≥100 °C) followed by the decomposition of α-AlH_3 phase into Al and H_2. However, a fraction of γ- and β-polymorphs decompose directly to Al and H_2 at low temperatures (<100 °C). The direct decomposition of the γ- and β-phases is faster than that of the α-phase due to the lower total formation enthalpy. AlH_3-etherate is first desolvated to γ-AlH_3, which immediately transforms into the α-phase during the heating process.

1. Introduction

Hydrogen storage has become of considerable interest for academic and industrial researchers because of the limitations associated with storing hydrogen gas under ambient condition. The growing interest in all types of nanostructured materials necessary for the implementation of next-generation technological systems is based on the current high demand for energetic resources. Solid media (e.g., complex hydrides and metal organic frameworks) are some of the promising candidates. Among these solid hydrogen storage materials, aluminum hydride (alane) has attracted considerable attention [1–4].

Aluminum hydride (AlH_3), which is the most well-known alane, is a metastable and crystalline solid at room temperature that has a volumetric hydrogen density (148 g H_2/L) more than double that of liquid hydrogen and a gravimetric hydrogen density that exceeds 10.1 wt%, which is considerably greater than that of most known metal hydrides [5]. Given the high hydrogen content of AlH_3, it is particularly suitable as a hydrogen storage medium for low-temperature fuel cells. AlH_3 is also an excellent candidate as a propellant fuel or as a high explosive because of its highly exothermic combustion, an advantageous characteristic for any energetic material, combined with its high hydrogen density. Replacing aluminum with AlH_3 considerably improves the detonation performance of high explosives and provides a 10% gain in specific impulse for approximately 20 s compared to the currently used aluminum propellants [6,7].

However, AlH_3 has several disadvantages. This material is unstable under ambient pressure and temperature, and its layered structure, which is composed of alternating planes of aluminum and hydrogen, is believed to facilitate the release of H_2 gas [8]. The decomposition of AlH_3 generates excessive amounts of H_2 gas during storage [9]:

$$AlH_3 \rightarrow Al + H_2 \quad (1)$$

The known phases of AlH_3 are α, α′, β, γ, δ, ε, and ξ, and the majority of these phases were theoretically predicted. α-AlH_3 is recognized as the most stable phase and is consequently the most investigated phase. Although a number of studies have theoretically predicted the properties of other polymorphs, experimental evidence of these properties is still scarce. Limited experimental data on the other polymorphs and their properties are available.

* Corresponding author. School of Material Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing 100081, China. Tel./fax: +86 010 68914530.
E-mail addresses: zzuxubo2001@163.com (B. Xu), liujp@bit.edu.cn (J. Liu), wangxiao_jun_1987@163.com (X. Wang).

0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.05.009

AlH_3-etherate ($AlH_3 \cdot nEt_2O$) is an important intermediate product of the desolvation reaction into AlH_3 after the chemical reaction between $LiAlH_4$ and $AlCl_3$ in ether [10]. Although experimental studies on $AlH_3 \cdot nEt_2O$ and desolvation reactions are important for optimizing the conditions for sample preparation, detailed information has not been provided to date. Therefore, a systematic experimental study of non-solvated AlH_3 polymorphs and AlH_3-etherate is necessary to understand their properties.

The previous work suggested that the α phase was most studied, followed by γ-AlH_3 in different ways [3,5,10]. However, the β phase and AlH_3-etherate, especially the latter, were not studied well, not to mention the comparative researches of them. In our work, we systematically studied the synthesis and synthesis conditions of three aluminum hydride polymorphs and AlH_3-etherate, and comparatively researched the thermal properties of them. In this study, three AlH_3 polymorphs (α-, β-, and γ-AlH_3) were prepared through the desolvation of $AlH_3 \cdot nEt_2O$ based on the organometallic synthesis method, and AlH_3-etherate ($AlH_3 \cdot nEt_2O$) was also obtained. The thermal properties of these compounds were investigated under both heating and isothermal processes.

2. Experimental section

2.1. Materials

Diethyl ether (Merck, certified ACS, 99% purity) was double-distilled over sodium/benzophenone and $LiAlH_4$ and stored under a purified nitrogen atmosphere. Commercial $AlCl_3$ (Merck, anhydrous, ≥98%) was purified by sublimation in a glass ampule over aluminum metal to a purity of 99.7%. $LiAlH_4$ (Merck, ≥97%) was purified before use by dissolution in diethyl ether and filtration of a light gray residue. After the solvent was evaporated under vacuum, a white powder with a purity of 99.2% was obtained. The characterization data were obtained by quantitative element analysis, chromatography of the gaseous phase, IR spectroscopy, and XRD. Glassware was evacuated to a pressure of 10^{-3} mbar and flushed with dry oxygen-free nitrogen before use. Solids were handled in an argon-filled glove box equipped with a recirculation and regeneration system. The concentrations of water and oxygen were kept below 1 ppm during operation.

2.2. Preparation

The AlH_3 polymorphs were synthesized using the organometallic methods described in the literature [11–13]. The synthesis was extremely sensitive to the desolvating conditions (i.e., temperature and time), and small alterations resulted in the precipitation of different AlH_3 polymorphs. Note that the freshly prepared, non-passivated AlH_3 is pyrophoric and reacts violently with water and must be treated with caution. The synthesis procedures used in this study are described below.

2.2.1. Preparation of AlH_3-etherate

Initially, 0.5 M diethyl ether solutions of $LiAlH_4$ (2.4 g $LiAlH_4$, 125 mL Et_2O) and $AlCl_3$ (2.1 g, 32 mL Et_2O) were prepared; both of these solutions were precooled to −10 °C in a salt water bath. The $AlCl_3$ solution was transferred to an addition funnel using a cannula and quickly added to the $LiAlH_4$ solution with vigorous stirring. This process produced an ether solution of $LiAlH_4$ and $AlCl_3$ in a molar ratio of 4 to 1 (reaction (1)), and the reaction proceeded immediately forming an alane–ether complex and a fine, white precipitate (LiCl). The temperature of the reaction was controlled by adjusting the rate of addition of the $AlCl_3$ solution and was not allowed to increase above 0 °C. Stirring was maintained for a period of 5 min; the precipitate was allowed to settle, and using N_2 pressure, the solution was forced through a fine grade glass ball filter into a round-bottom flask fitted with a nitrogen inlet. After filtration, the solvent was slowly removed at room temperature under vacuum (10^{-3} mbar), and the remaining white residue was ground with a mortar and pestle and heated to approximately 60 °C in an oil bath for 40 min. The final product (AlH_3-etherate) was washed with ether to remove the excess $LiAlH_4$, and it was finally dried under vacuum.

2.2.2. Preparation of γ-AlH_3

Based on the above synthesis procedure, the ground white residue was heated under vacuum at 60 °C in an oil bath for 4 h. The solid was transferred to a fine-grade glass filter frit, washed several times with small aliquots of Et_2O to remove the excess $LiAlH_4$ and any remaining AlH_3-etherate, and dried under vacuum to yield 1.5 g (75%) of γ-AlH_3.

2.2.3. Preparation of β-AlH_3

A 0.80 M ether solution of $AlCl_3$ (1.667 g of $AlCl_3$ and 25 mL of ether) and a 0.8 M ether solution of $LiAlH_4$ (1.898 g of $LiAlH_4$ and 100 mL of ether) were prepared and precooled to −10 °C. The $AlCl_3$ solution was quickly added dropwise into the $LiAlH_4$ solution, which produced an ether solution of $LiAlH_4$ and $AlCl_3$ in a molar ratio of 4 to 1. The solution was stirred for approximately 2 min to ensure that the reaction went to completion (reaction (1)) and was subsequently filtered to remove the LiCl precipitate. A 0.4 M ether solution of $LiBH_4$ (0.272 g $LiBH_4$, 32 mL ether) was added to the filtrate. The ether was removed from the clear filtrate by vaporization at room temperature. The resulting product was a fluffy white powder that consisted of the generated AlH_3-etherate, unreacted $LiAlH_4$, and the added $LiBH_4$. The powder was ground using a mortar and pestle and heated under vacuum at approximately 65 °C in an oil bath for approximately 45 min. The final product, crystalline β-AlH_3, was washed with ether to remove the excess $LiBH_4$ and $LiAlH_4$.

2.2.4. Preparation of α-AlH_3

The α-polymorph was synthesized using two pathways. (I) The phase was obtained by initially preparing the γ phase as described above, but an additional heating step was performed for approximately 11 h at approximately 62 °C. During this reaction, the γ polymorph decomposes to the more stable α phase. (II) The phase was also synthesized by initially preparing the β phase as described above, but extending the heating time to approximately 6 h at approximately 65 °C. During this reaction, the β polymorph decomposes to the more stable α phase.

2.3. Instrumentation and analyses

The solid-state infrared spectra of the product were recorded in the range of 3500–400 cm^{-1} under a nitrogen atmosphere and ambient conditions using a Perkin–Elmer Spectrum GX FTIR spectrometer.

The particles were dispersed on carbon tape and a microgrid mesh for the scanning electron microscopy (SEM, Hitachi S-3400) analyses. The particles were then examined by thermogravimetric analyses and differential scanning calorimetry (TG-DSC, METTLER TOLEDO, heating rate of 5 °C/min under high-purity N_2 (>99.99%) with a flow rate of 150 cm^3/min). Specifically, isothermal measurements were performed up to a maximum temperature of 130 °C. Above this temperature, the decomposition reaction proceeded rapidly.

Powder X-ray diffraction patterns were obtained with a Philips X'PERT diffractometer (Cu Kα radiation, 2 kW, with an X'Celerator RTMS detector and an automatic divergence slit).