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Synthesis and Hydrogen Desorption Properties of Nanoscale α-AlH₃

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Abstract—Aluminum hydride is particularly attractive as a hydrogen storage material due to its high hydrogen volumetric capacity and relatively low hydrogen desorption temperature. However, the properties of nanoscale α -AlH₃ particles are not studied completely due to the difficulties in their synthesis. In this work, we report the synthesis of nanoscale α -AlH₃ based on a modified method, together with its activation energy measurements and hydrogen release kinetics. We have discovered that the dehydrogenation activation energy (93.23 kJ/mol) of nanoscale α -AlH₃ is remarkably lower than that of micrometer-sized α -AlH₃, which further expand practical application of AlH₃. Moreover, we demonstrate that the decomposition kinetics of nanoscale α -AlH₃ is controlled by nucleation and growth of the aluminum phase in three dimensions. This work first time provides systematic investigation of thermodynamic properties of nano-scale AlH₃, which paves the way for its practical applications.

Keywords: aluminum hydride, metal hydride, hydrogen storage, hydrogen desorption **DOI:** 10.1134/S0036024419130417

INTRODUCTION

Alternative energy sources have received great attention due to the exhaustion of fossil fuel and severe environmental pollution [1]. Among them, hydrogen energy is widely considered as a feasible secondary energy for future owing to its abundant reserves, high calorific value, nontoxicity, and various forms of utilization [2–6]. However, since it is flammable and explosive, hydrogen storage is still a bottleneck technique [3, 6-8]. Metal hydrides are generally superior to pressurized gas and other hydrogen storage methods because of their high mass and volume storage density and safe operating pressure [1]. Aluminum hydride, which has the largest hydrogen volumetric capacity (4.9 kW h/L) among metal hydrides and, moreover, low desorption temperature $(100-200^{\circ}C)$, is widely acknowledged as a fascinating hydrogen storage material [3, 4, 8–16], especially for hydrogen fuel cells. However, the high-activation barrier and the overall slow desorption kinetics measured for large cuboid AlH₃ hamper its practical application in the fuel-cell vehicles [11]. Developing a systematic understanding of dehydrogenation kinetics of AlH₃ is crucial for improving the hydrogen desorption performance.

In recent years, the synthesis and dehydrogenation thermodynamics and kinetics of AlH₃ are reported. Herley et al. [17] measured the activation energy for the acceleratory and decay period for α -AlH₃ with large particles (50–100 µm) manufactured by DOW Chemical to be approximately 157 kJ/mol. Gabis et al. [18] reported the activation energy of a larger crystallites (10–20 μ m) of α -AlH₃ to be 104 kJ/mol. Graetz et al. [19] investigated the thermal decomposition of α -, β -, and γ -AlH₃ prepared via the micro-crystallization route, consisting of small particles of 100-200 nm. It is a fact that the present investigation is limited to the sub-micrometer and micrometer sized α -AlH₃. Until 2016, Wanseop Jeong et al. [11, 20] synthesized nanoscale α -AlH₃ with diameter of approximately 50 nm by using an electrochemical method proposed by Graetz et al. [21] and Dow Chemical Co. [5]. However, it must be mentioned that this investigation did not involved the research of dehydrogenation kinetics of α -AlH₃.

In this study, nanoscale α -AlH₃ was prepared via a modified ethereal reaction method. By isothermal



Fig. 1. (Color online) Schematic diagram of the self-made isothermal hydrogen desorption reaction apparatus.

decomposition of as-prepared nanoscale α -AlH₃, its dehydrogenation kinetics systematically investigated for the first time. The activation energy and kinetic parameters of nanoscale α -AlH₃ dehydrogenation were estimated through Avrami–Erofeyev and Arrhenius equations. It has been verified that nanoscale α -AlH₃ have a smaller activation energy and a faster hydrogen evolution rate.

EXPERIMENTAL

Synthesis of Nanoscale α -AlH₃

 α -AlH₃ was typically synthesized using the modified ethereal reaction method developed by Brower et al. [5, 22]. The ether solution of LiAlH₄ (2 mol/L) and AlCl₃ (1 mol/L) were both prepared at -10° C. Then these solutions were mixed at -10° C to produce an etherated aluminum hydride, AlH₃ · *n*(Et₂O):

$$4\text{LiAlH}_{4} + \text{AlCl}_{3} + n\text{Et}_{2}\text{O}$$

$$\rightarrow 4\text{AlH}_{3} \cdot n\text{Et}_{2}\text{O} + 3\text{LiCl}\downarrow + \text{LiAlH}_{4}.$$
(I)

At the end of the reaction, the precipitated lithium chloride was filtered by using a sand core funnel, and then the white $AlH_3 \cdot n[(C_2H_5)_2O]$ precipitated in 1 h while stirring at room temperature. After being filtered off and placed in a vacuum oven at 45°C for 2 h, we obtained the dry etherated aluminum hydride. By heating this product at 65–75°C under vacuum for 5 h, the associated ether was removed successfully:

$$4\text{AlH}_3 \cdot n\text{Et}_2\text{O} \xrightarrow[5h]{65-75^\circ\text{C}}{5h} 4\text{AlH}_3 + n\text{Et}_2\text{O}^\uparrow.$$
(II)

Finally, the product was washed with ether to remove the excess LiAlH_4 . It must be mentioned that all sample handling was performed under inert gas.

Dehydriding of As-prepared α -AlH₃

The hydrogen desorption measurements were carried out on a self-made apparatus with a high-precision digital pressure gauge (Fig. 1). This apparatus contains the detection section and the reaction section connected through a rubber pipe. The internal volumes of these two sections are calibrated prior to measurements with the volume of 265 mL. The relationship between the pressure and the gas volume of the reservoir chamber under the given temperature, as well as the relationship between the real temperature inside the experimental device and the set temperature were also calibrated. There are two oil-baths in the detection section and the reaction section. One is employed to ensure that the temperature of the reservoir chamber is stable, considering the influence of the ambient temperature, while the other is used to keep the decomposition temperature. In the hydrogen desorption measurements, the sample chamber filled with as-prepared nanoscale α -AlH₃ is put in the oil-bath when the given desorption temperature become stable. Therefore this self-made apparatus could prevent the decomposition of the samples during it is heated to the ideal desorption temperature which occurs in many isothermal decomposition experiments. The sample chamber is relatively small, thus the fluctuation of its temperature could be ignored. During measurements, the temperature and pressure data were collected during fixed intervals of time. Hence, the amounts of hydrogen were calculated by the ideal gas equation using the obtained temperature and pressure data of the reservoir chamber. On carrying isothermal dehydrogenation experiments, 100 mg sample was loaded into the evacuated sample chamber and kept at a given temperature (130, 140, 150, 160, and 170°C) till the completion of dehydriding.

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Fig. 2. (Color online) (a) X-ray diffraction patterns, (b) SEM images, (c) TGA-DSC curves of as-prepared α -AlH₃ powder.

Characterization of As-prepared α -AlH₃

Powder X-ray diffraction (XRD) measurements were conducted on a PANalytical X-ray diffractometer (X'Pert Pro) using CuK_{α} radiation. The XRD data were analyzed by means of MDI Jade 6 software. Scanning electron microscopy (SEM, FEI SIRION 100 or Hitachi S4800) was utilized to study the morphology of the sample. With regard to the hydrogen capacity, elemental analyses were implemented utilizing a Leco CHNS-932 Micro-analyzer. The Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50) was performed in a wavenumber range from 400 to 4000 cm⁻¹ using the samples prepared by KBr pelleting method. Synchronous thermal analyses were carried out with a thermo-gravimetric analysis and differential scanning calorimetry (TGA-DSC, Mettler-Toledo TGA/SDTA851e). The samples were heated from room temperature to about 300°C with a heating rate of 10°C/min under N₂ atmosphere.

RESULTS AND DISCUSSION

Structure of As-prepared α -AlH₃

The diffraction pattern of the as-prepared α -AlH₃ (Fig. 2a) has seven peaks at 27.5°, 38.2°, 40.3°, 45.9°,

49.5°, 56.8°, 62.78°, 65.74°, and 67.7°, corresponding to (012), (104), (110), (006), (113), (202), (024), (116), and (122) planes of α -AlH₃ (JCPDF 23-0761), respectively. The diffraction peaks were sharp and intense, indicating its highly crystalline nature. No other peaks were observed, indicating the purity of the product.

As can be seen from Fig. 2b, the SEM micrograph of as-prepared α -AlH₃ exhibits small crystallites which is different from a typical topographic characteristics of cubic α -AlH₃. This phenomenon may arise from the conglomeration of nanometer α -AlH₃ particles for its high surface energy. The average grain size of the as-prepared α -AlH₃ is estimated to be approximately 60 nm according to Scherrer's equation [23]:

$$D = \frac{K\lambda}{B\cos\theta},\tag{1}$$

where *D* is the average grain size, λ is the wavelength of the incident X-ray, *B* is the full width at half-maximum of a diffraction peak, θ is the Bragg angle, and *K* is a constant depending on the shape of the grains (generally assumed to be 0.89).

In order to further verify the crystal form of AlH₃ and gain an insight into the hydrogen capacity of it,



Fig. 3. (Color online) (a) XRD patterns of as-prepared α -AlH₃ heated for different time intervals; (b) infrared spectra of as-prepared α -AlH₃ before and after dehydrogenation at 160°C.

TGA-DSC measurement was carried out. As shown in Fig. 2c, the DSC curve of the as-prepared α -AlH₃ exhibits a one-step endothermic desorption process starting at 150°C and peaking at 163°C, which is in accordance with literature data. The endothermic reaction is attributed to the dehydriding of the as-prepared α -AlH₃. From the TGA curve Fig. 2c, it can be found that the weight loss rate of as-prepared α -AlH₃ is approximately 7.8 wt %. The result of elemental (H) analysis shows the average hydrogen capacity of prepared α -AlH₃ is 7.59 wt %, which is in accordance with the result of TGA-DSC analysis (Fig. 2d). This low hydrogen content value might arise from the slight decomposition during preparation, which has no influence on the hydrogen desorption experiment.

Dehydriding Properties of As-prepared α -AlH₃

The hydrogen release from α -AlH₃ follows the simple reaction $(AlH_3 \rightarrow Al + 3/2H_2)$ [24]. In order to trace the isothermal dehydrogenation of nanometer α -AlH₃, XRD measurements were carried out. The XRD patterns of as-prepared α -AlH₃ heated for different time intervals at 160°C is illustrated in Fig. 3a. The five selected time points correspond to the hydrogen desorption fraction of 0, 25, 50, 75, and 100%, respectively in accordance with the isothermal dehydrogenation curves. As shown in Fig. 3a, the desorption time of α -AlH₃ significantly affects the phase composition. After heating for 2.5 min at 160°C, five small peaks appeared, indicating the formation of Al, arising from the decomposition of α -AlH₃. With further increase in the heating time, the peaks corresponding to Al phase significantly enhanced while the α -AlH₃ phase remarkably weaken. After heating for 40 min, α -AlH₃ completely decomposed to a pure Al phase. The IR spectrum of the as-prepared α -AlH₃ before and after dehydrogenation at 160°C is presented in Fig. 3b. It shows absorption bands in 1850, 1722, 876, and 673 cm⁻¹ regions indicating the presence of Al–H bond before desorption. After desorption the curve approaching a straight line, which testify that after being heated for 40 min, the α -AlH₃ has been completely transform into Al. This is consistent with the observation from XRD.

The activation energy and pre-exponential factor for α -AlH₃ isothermal dehydrogenation can be determined using Avrami–Erofeyev and Arrhenius equations [11, 24]. The direct hydrogenation of Al to form AlH₃ can be considered irreversible as it requires extremely high hydrogen pressure (over 10⁵ bars) at room temperature [12, 13, 15]:

$$Al + 3/2H_2 \xrightarrow{10^{\circ} \text{ bar, } 25^{\circ}\text{C}} AlH_3.$$
(III)

Irreversible isothermal solid-state reactions can generally be expressed by Avrami–Erofeyev equation [3, 25, 26]:

$$[-\ln(1-\alpha)]^{1/n} = kt,$$
 (2)

where α is the fraction of material reacted in one interval (*t*). The constant *n* depends on the geometry of particle growth. In accordance with the slope of a plot of $\ln[-\ln(1 - \alpha)]$ versus $\ln t$, the rate-limiting mechanism and the appropriate kinetic equation can be determined [22]. In the nucleation and growth model, *n* is a function of the nucleation barrier and growth geometry. The value of $n \approx 1, 2, 3$ indicates the linear growth, two-dimensional growth (disk or cylinder growth), and three-dimensional growth (spheres or hemispheres growth) [25, 27]. The Arrhenius equation demonstrates the relationship between the reaction rate k(T), activation energy, and the temperature:

$$k(T) = A \exp\left(-\frac{E_{\rm a}}{RT}\right),\tag{3}$$



Fig. 4. (Color online) Decomposition of as-prepared nanoscale α -AlH₃ between 130 and 170°C plotted as (a) fractional decomposition, α , vs. *t*; (b) ln[-ln(1 - α)] vs. ln *t*; and (c) ln[-ln(1 - α)]^{1/3} vs. *t*; (d) Arrhenius plot.

where A is the pre-exponential Arrhenius parameter, $E_{\rm a}$ is the activation energy, and R is the universal gas constant.

The activation energy and pre-exponential parameters are determined by the slope and intercept of the Arrhenius plot, respectively. The isothermal ($\pm 1^{\circ}$ C) fractional decomposition data for α -AlH₃ are shown in Fig. 4a. All these curves show sigmoidal features with induction, acceleration, and decay periods. Figure 4b shows the plot of ln[$-ln(1 - \alpha)$] as the function of the ln*t*, and is used to measure the constant, *n* in acceleration periods, and determine the most suitable kinetic equation. The values of *n* obtained from Fig. 4b are listed in Table 1. As shown in Table 1, the average value of *n* was approximately 3, suggesting that nanoscale α -AlH₃ follows third-order Avrami–Erofeyev equation which is different from the micron and sub-micron particle which average value of *n* were closer to 2 [11, 16]. This value indicates that the growth of the Al phase of nanoscale α -AlH₃ more likely to occurs three-dimensions rather than two-dimensions [11].

The fraction of decomposed α -AlH₃ plotted as $[-\ln(1-\alpha)]^{1/3}$ is shown in Fig. 4c. The rate constants determined from the slope are displayed in Table 1. Arrhenius plots for α -AlH₃ over a temperature range of 130 to 170°C are displayed in Fig. 4d. Kinetic values for the as-prepared α -AlH₃ are equal: particle diameter d = 60 nm, $E_a = 93.23 \pm 0.81$ kJ/mol, $A = 7.49 \times 10^8 \pm 2.22$.

This two kinetic parameters are both lower than the values measured by Herley et al. [16] ($A = 3.5 \times 10^{16}$ and $E_a = 150.3 \pm 10.0$ kJ/mol) and Graetz et al. [11]

Table 1. The values of *n* obtained from Fig. 4b and isothermal decomposition rate constants (s⁻¹) for as-prepared α -AlH₃

<i>T</i> , °C	130	140	150	160	170	
п	3.06	3.18	2.75	2.733	3.29	3.00 (average)
k, s^{-1}	5.89×10^{-4}	1.32×10^{-3}	2.23×10^{-3}	4.19×10^{-3}	7.63×10^{-3}	

 $(A = 1.2 \times 10^{10} \text{ and } E_a = 102.2 \pm 3.2 \text{ kJ/mol})$ considerably. It is worthwhile mentioning that the particle diameter of as-prepared α -AlH₃ is around 60 nm, while that of α -AlH₃ prepared by Herley et al. and Graetz et al. are 100 µm and 204 nm, respectively. Thus, it can be concluded that the significantly decreasing of the pre-exponential factor and activation energy for α -AlH₃ is attributed to the smaller particle size. As the grain size of α -AlH₃ decreases, the specific surface area become larger so that its molar surface energy increases. That improves the average molar energy of the α -AlH₃, thereby reducing the gap (activation energy) between the average energy of 1 mol activated molecules and 1 mol reactants.

CONCLUSION

Single-phase nanoscale α -AlH₃ was synthesized by modified ethereal reaction method. According to Avrami-Erofeyev equation, the decomposition kinetics of nanoscale α -AlH₃ are controlled by nucleation and growth of the aluminum phase in three rather than two dimensions, different from micro and sub-micro α -AlH₃. The activation energy and pre-exponential factor of dehydriding of as-prepared nanoscale α -AlH₃ was estimated to be 93.23 kJ/mol and 7.49 × 10^8 , respectively. The activation energy is significantly lower than that for the micron and sub-micron size α -AlH₃. The activation energy of nanoscale α -AlH₃ decomposition is significantly reduced as a result of smaller grain diameter. Thus, the synthesis of α -AlH₃ with smaller particle size may be an effective way to solve the difficulties in application of AlH₃.

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