Wet Chemical Synthesis of Non-solvated Rod-Like $\alpha'$-AlH$_3$ as a Hydrogen Storage Material

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Aluminum hydride (AlH$_3$) is a promising candidate for hydrogen storage due to its high hydrogen density of 10 wt%. Several polymorphs of AlH$_3$ (e.g., $\alpha$, $\beta$, and $\gamma$) have been successfully synthesized by wet chemical reaction of LiAlH$_4$ and AlCl$_3$ in ether solution followed by desolvation. However, the synthesis process of $\alpha'$-AlH$_3$ from wet chemicals still remains unclear. In the present work, $\alpha'$-AlH$_3$ was synthesized first by the formation of the etherate AlH$_3$ through a reaction of LiAlH$_4$ and AlCl$_3$ in ether solution. Then, the etherate AlH$_3$ was heated at 60°C under an ether gas atmosphere and in the presence of excess LiAlH$_4$ to remove the ether ligand. Finally, $\alpha'$-AlH$_3$ was obtained by ether washing to remove the excess LiAlH$_4$. It is suggested that the desolvation of the etherate AlH$_3$ under an ether gas atmosphere is essential for the formation of $\alpha'$-AlH$_3$ from the etherate AlH$_3$. The as-synthesized $\alpha'$-AlH$_3$ takes the form of rod-like particles and can release 7.7 wt% hydrogen in the temperature range 120–200°C.

**Keywords:** hydrogen storage, aluminum hydride, synthesis, desolvation, desorption

**INTRODUCTION**

Aluminum hydride (AlH$_3$) is a kinetically stable metal hydride under ambient conditions. It theoretically has a high hydrogen capacity of 10 wt% and can release hydrogen at temperatures below 200°C (Sandrock et al., 2005; Graetz, 2009; Graetz et al., 2011). Therefore, it has long been considered as a promising hydrogen storage media for on-board applications. There are seven known polymorphs of AlH$_3$: $\alpha$-, $\alpha'$-, $\beta$-, $\gamma$-, $\delta$-, $\epsilon$-, and $\zeta$-AlH$_3$ (Brower et al., 1976). These AlH$_3$ polymorphs have different structures and thermal stabilities and thus have slightly different decomposition properties and mechanisms. $\alpha$-AlH$_3$ is the most stable polymorph and will undergo direct decomposition to form Al and H$_2$ with an increase in temperature (Sandrock et al., 2005; Graetz and Reilly, 2006; Orimo et al., 2006). The other polymorphs, such as $\beta$-AlH$_3$ and $\gamma$-AlH$_3$, will first transform into the more stable $\alpha$-AlH$_3$ and then decompose to form Al and H$_2$ (Graetz and Reilly, 2006). Direct decompositions of $\gamma$-AlH$_3$ and $\alpha'$-AlH$_3$ to form Al and H$_2$ without the first phase transition have also been reported in the literature (Sartori et al., 2008; Liu et al., 2013; Gao et al., 2017).

The synthesis of AlH$_3$ dates back to 1942 when Stecher and Wiberg (1942) prepared the AlH$_3$ amine complex in an impure form. The synthesis method of AlH$_3$ was then modified and improved by other researchers (Finholt et al., 1947; Chizinsky et al., 1955; Ashby, 1964). In 1976, Brower et al. (1976) summarized their findings on the synthesis of non-solvated AlH$_3$ by
the wet chemical method. They used LiAlH₄ and AlCl₃ as the starting materials and ether as the solvent. Generally, LiAlH₄ was reacted with AlCl₃ in the ether solution to form AlH₃·nEt₂O and LiCl [reaction (1)]. The precipitate LiCl was then removed by filtration, and the AlH₃·nEt₂O precipitated slowly during storage. The obtained solid, AlH₃·nEt₂O, was heated under certain conditions to remove the ether ligand [reaction (2)], which was called the desolvation process. Depending on the desolvation conditions used, AlH₃ would crystalize in different structures.

\[
3\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow{\text{ether}} 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + 3\text{LiCl} \quad (1)
\]

\[
\text{AlH}_3 \cdot n\text{Et}_2\text{O} \rightarrow \text{AlH}_3 + \text{ether} \quad (2)
\]

Non-solvated α-, β-, and γ-AlH₃ have been successfully synthesized by the wet chemical method (Brinks et al., 2006, 2007a,b; Graetz and Reilly, 2006; Orimo et al., 2006; Liu et al., 2013; Gao et al., 2017). These are the polymorphs of AlH₃ that have been intensively studied. However, the intrinsic decomposition properties of α’-AlH₃ are still unclear due to the fact that pure and non-solvated α’-AlH₃ is hard to synthesize. As far as we know, the synthesis of pure and non-solvated α’-AlH₃ by the wet chemical method has not yet been reported in the open literature. Although Brower et al. (1976) suggested that α’-AlH₃ can be synthesized by the slow desolvation of AlH₃·nEt₂O, no characterized product of α’-AlH₃ was disclosed.

In 2006, Brinks et al. (2006) utilized the cryomilling method to prepare α’-AlD₃ from a mixture of 3LiAlD₄ + AlCl₃. It was shown that cryomilling at a temperature as low as 77 K resulted in the formation of only AlD₃ and LiCl. The AlD₃ obtained was a mixture of 2/3α’-AlD₃ + 1/3α’-AlD₃ (Brinks et al., 2006). Another work by Sartori et al. (2009) showed that the yield of AlD₃ was increased by using 3NaAlH₄ + AlCl₃ or 3LiAlD₄ + AlBr₃ as the raw materials. In addition, the relative amount of α’-AlD₃ over α-AlD₃ was increased from 0.63–0.67 to 1.05 by the addition of FeF₃ into the 3LiAlD₄ + AlCl₃ mixture. Although α’-AlH₃ can be obtained by the cryomilling method, the unwanted product of LiCl salt is difficult to remove. Moreover, the α’-AlH₃ prepared by this method is usually accompanied by α-AlH₃ polymorphs.

In the present work, the synthesis of non-solvated and pure α’-AlH₃ by the wet chemical method is studied. The decomposition properties of α’-AlH₃ will also be preliminarily revealed.

**EXPERIMENTAL DETAILS**

**Synthesis of α’-AlH₃**

The synthesis process of α’-AlH₃ employed here is similar to that reported by Brower et al. (1976). However, some conditions needed to be modified. In detail, 1 M ether (Sinopharm Group, Analytical purity) solution of LiAlH₄ (TCI, 98% purity) was mixed with 1 M ether solution of AlCl₃ (Aldrich, 99.99% purity) at a molar ratio of 4:1. It should be noted that LiAlH₄ was used in excess. Brower et al. (1976) found that the etherate AlH₃ will decompose to Al if heated under a vacuum, but, in the presence of excess LiAlH₄, the ether can be removed without decomposition. LiAlH₄ will react with AlCl₃ upon mixing in the ether solution to form the etherate AlH₃ (AlH₃·nEt₂O) and LiCl precipitate based on reaction (3). The mixed solution was stirred for 2 min to ensure that the reaction was completed. Immediately after that, the LiCl precipitate was removed by filtration and the liquid ether was removed by slow evaporation at room temperature. The dry and white residue obtained, which was a mixture of 4AlH₃·nEt₂O + LiAlH₄, was ground to powder with a mortar and pestle for heating treatment. Powder samples were then heated at certain temperatures for various durations under certain atmospheres to remove the ether ligand [reaction (4)]. The conditions used for heat treatment significantly impact the desolvation products of the 4AlH₃·nEt₂O + LiAlH₄ mixture, as will be shown in the next section. Finally, the desolvated 4AlH₃·nEt₂O + LiAlH₄ mixture was ether-washed to remove the excess LiAlH₄, and AlH₃ was obtained.

\[
4\text{LiAlH}_4 + \text{AlCl}_3 \xrightarrow{\text{ether}} 4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + \text{LiAlH}_4 + 3\text{LiCl} \quad (3)
\]

\[4\text{AlH}_3 \cdot n\text{Et}_2\text{O} + \text{LiAlH}_4 \rightarrow \text{AlH}_3 + \text{LiAlH}_4 + \text{ether} \quad (4)
\]

**Characterizations of α’-AlH₃**

Powder X-ray diffraction (XRD, PANalytical X’Pert Pro, Cu Ka, 40 kV, 40 mA) was used to study the phase structures of the samples. The samples for XRD studies were sealed with an amorphous membrane to protect them from oxidation during the sample transformations and measurements. Scanning electronic microscopy (SEM, FEI SIRION-100, 25 kV) was used to study the morphology of the as-synthesized α’-AlH₃. The hydrogen desorption property of the as-synthesized α’-AlH₃ was studied by using a home-made Sieverts-type hydrogen sorption measurement apparatus based on the volumetric method. Experimentally, the samples were sealed in a reactor and were heated under an initial vacuum gradually from room temperature to the set temperature with a heating rate of 2°C/min.

**RESULTS AND DISCUSSION**

On the synthesis of AlH₃ by the wet chemical reaction in the ether solution, the conditions (desolvation aid, temperature, time, atmosphere) used in the desolvation stage [reaction (4)] significantly affect the desolvation product of AlH₃·nEt₂O (Brower et al., 1976). α-AlH₃ can be obtained by heating the AlH₃·nEt₂O at 60–80°C under a vacuum in the presence of excess LiAlH₄ and LiBH₄, while γ-AlH₃ is formed when the AlH₃·nEt₂O is heated at 60–70°C under a vacuum in the presence of only excess LiAlH₄ (Brower et al., 1976). It should be noted that the AlH₃·nEt₂O should be desolvated in the presence of excess LiAlH₄ (and LiBH₄), with which AlH₃·nEt₂O can easily transform to AlH₃ without decomposition (Brower et al., 1976).

In the present work, the AlH₃·nEt₂O was heated under a gaseous ether atmosphere, which is the key factor for producing α’-AlH₃. The ether atmosphere was generated by injecting a gaseous ether (40-60°C) into the reaction vessel. After heating to 60–80°C, the AlH₃·nEt₂O mixture was desolvated in a gaseous ether atmosphere. Figure 1 shows the XRD patterns of the desolvation products of AlH₃·nEt₂O heated at 60°C for various durations under an atmosphere of gaseous ether. It can be seen that traces of α’-AlH₃ formed after desolvation for 2 h. With an increase in
the desolvation duration, more and more \( \alpha' \)-\( \text{AlH}_3 \) formed. The \( \text{AlH}_3 \cdot n\text{Et}_2\text{O} \) can totally transformed to \( \alpha' \)-\( \text{AlH}_3 \) after desolvation for 6 h.

When the desolvation of the \( \text{AlH}_3 \cdot n\text{Et}_2\text{O} \) was conducted at 75°C, the transformation to \( \alpha' \)-\( \text{AlH}_3 \) proceeded more rapidly. Figure 2 shows the XRD patterns of the desolvation products of \( \text{AlH}_3 \cdot n\text{Et}_2\text{O} \) after heating at 75°C for various durations under an atmosphere of gaseous ether. It was observed that some traces of \( \alpha' \)-\( \text{AlH}_3 \) formed after desolvation for only 1 h. After 4 h of desolvation, the \( \text{AlH}_3 \cdot n\text{Et}_2\text{O} \) had completely transformed to \( \text{AlH}_3 \), which was a mixture of \( \alpha' \)-\( \text{AlH}_3 \) and \( \alpha \)-\( \text{AlH}_3 \). This means that some of the \( \alpha' \)-\( \text{AlH}_3 \) may have transformed into more stable \( \alpha \)-\( \text{AlH}_3 \) during heat treatment at 75°C. Therefore, a lower desolvation temperature (e.g., 60°C) is preferred in order to produce pure \( \alpha' \)-\( \text{AlH}_3 \).

The morphology of the as-synthesized \( \alpha' \)-\( \text{AlH}_3 \) was studied by SEM techniques, as shown in Figure 3. It can be seen that the as-synthesized \( \alpha' \)-\( \text{AlH}_3 \) takes the form of rod-like particles with lengths of about 1 \( \mu \text{m} \) and widths of about 100 nm. This unique particle morphology may benefit the hydrogen desorption process of \( \alpha' \)-\( \text{AlH}_3 \) because it possesses more surface area than other morphologies such as spheres of similar dimensions.

The hydrogen desorption curve of the as-synthesized \( \alpha' \)-\( \text{AlH}_3 \) with a heating rate of 2°C/min is shown in Figure 4. As can be seen that it starts to release hydrogen at 120°C and reaches a hydrogen desorption capacity of 7.7 wt% when the temperature is increased to 200°C. After hydrogen desorption, \( \text{Al} \) is formed. It should be noted that the practical capacity is somewhat lower than the theoretical value, which may be due to the impurity of the sample. This decomposition temperature range is similar to that of \( \alpha \)-\( \text{AlH}_3 \) and \( \gamma \)-\( \text{AlH}_3 \) (Graetz and Reilly, 2006; Liu et al., 2013).
CONCLUSION

Non-solvated $\alpha'$-AlH$_3$ was successfully synthesized by the wet chemical reaction of LiAlH$_4$ and AlCl$_3$ in ether solution followed by desolvation. The conditions used in the desolvation stage are the essential factors in producing $\alpha'$-AlH$_3$. Desolvation under a gaseous ether atmosphere is the key to the transformation of AlH$_3$nEt$_2$O into non-solvated $\alpha'$-AlH$_3$. The as-synthesized $\alpha'$-AlH$_3$ particles are rod-like and can release 7.7 wt% hydrogen in the temperature range 120–200°C. The purity of the $\alpha'$-AlH$_3$ needs to be improved in future work.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article supplementary material.

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AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest: LX and SL were employed by the company Global Energy Interconnection Research Institute Co., Ltd.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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