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Synthesis, characterization and treatment of alane (aluminium hydride, AlH_3)

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Abstract

This paper presents preparation methods of alane (α-AlH_3), which is known as the most stable form among its seven polymorphs. They showed the importance of both careful washing with an acidic solution or inorganic compound, and of moisture and impurities removal. The characterization of structure and morphology of α-AlH_3 thus synthesized and treated showed that solid obtained is a white powder with an onset decomposition temperature of 151 °C which can be produced at *ca.* 12 g per batch with a yield of nearly 98 %.

1. Introduction

Aluminum hydride (AlH_3) which is well-known as alane, is a promising hydrogen and energy storage material that is proposed for different uses such as rocket fuel, explosive, reducing agent in alkali batteries and as hydrogen source for low temperature fuel cells.

Aluminum hydride is considered as one of the most interesting additives in space propulsion because of its capability of releasing hydrogen during decomposition and/or combustion and its high density, which makes this material an excellent candidate if it can be safely and cheaply produced.[1]-[2].

Aluminum hydride is a metastable crystalline solid at room temperature, it decomposes by an endothermic reaction to generate aluminum and H_2 gas as reported in the following equation [3]:

$$AlH_3 \rightarrow Al + 3/2\ H_2$$

The formation of a passivation layer of alumina on its surface can protect it from its decomposition and from the environment. This attractive material for hydrogen storage has a hydrogen content of 10.1 wt. % [4] and volumetric hydrogen capacity of 0.148 g/mL, which is twice as much as the value of liquid hydrogen (0.070 g/mL) [3]-[4].

Aluminum hydride presents at least seven different polymorphic crystal structures (α, α', β, γ, δ, ε crystalline phases, and solvated solid ζ phase), α-AlH_3 being the most stable ($H_f°$ = -11.4 kJ mol^{-1}) [5] which is interesting for space propulsion applications. The best described alane phases are α, β and γ [8]-[10] with regard to their structures, morphologies and synthesis conditions which are presented in Table 1.

Aluminum hydride structure published by Turley and Rinn in 1969 possesses a trigonal space group, $R\bar{3}c$, for α-AlH_3 crystals with a hexagonal shape for its unit cell and lattice parameters a = 4.449 Å and c = 11.804 Å [9]. The structure of α-AlH_3 shows that the corners of the hexagonal unit cell are formed of AlH_6 octahedra whereas H bridges connect two octahedrons to each other. The unit cell of AlH_3 is composed of atoms of aluminum (Al) and hydrogen (H) linked between each other by single bonds of different distances: 1.715 Å (Al–H), 2.418 Å (H–H) and 3.236 Å (Al–Al) and a volume of 33.5 $Å^3$ per AlH_3 unit cell [10] as reminded in Figure 1.

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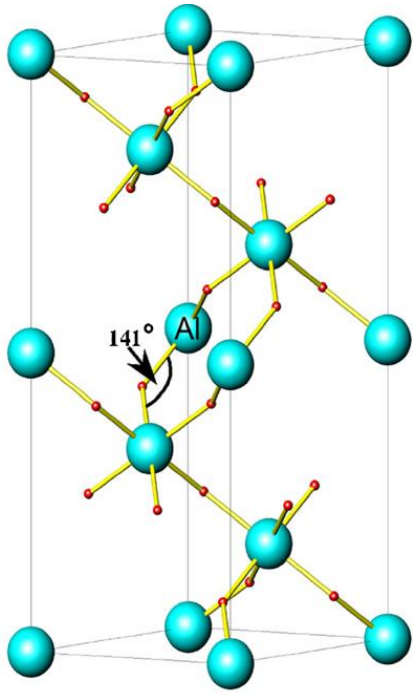

Figure 1: Interconnection of the AlH_6 octahedra in the structure of α-AlH_3 composed of Al–H–Al bridging bonds with an angle of 141 ° [10]

The preparation methods of α-AlH_3 are various and sometimes in disagreement:

(i) Organometallic reaction between $LiAlH_4$ and $AlCl_3$ in ether, followed by solvent removal under reduced pressure and crystallization by adding a second solvent (e.g. toluene) [10];

(ii) Reaction between $LiAlH_4$ and other chlorides [11];

(iii) Solid state reaction under hydrogen pressure, avoiding the use of a solvent [12].

The rentable method for the preparation of AlH_3 is based on Schlesinger reaction [13], where an ether solution of aluminum chloride ($AlCl_3$) reacts with a lithium aluminum hydride solution ($LiAlH_4$) in ether/toluene medium, in presence of an ether solution of lithium borohydride ($LiBH_4$) according to Equation 1.

Equation 1 $$AlCl_3\,(soln) + 3\,LiAlH_4\,(soln) \xrightarrow{LiBH_4\ ;\ Ether\,/\,Toluene} 4\,AlH_3{\cdot}Et_2O\,(soln) + 3\,LiCl\,(s)$$

Followed by solvent removal under reduced pressure and crystallization to obtain the alpha alane as shown in Equation 2.

Equation 2 $$AlH_3 \cdot Et_2O\,(soln) \xrightarrow{Crystallization\ in\ solvent} AlH_3\,(s)$$

During the crystallization as the ether is removed, alane etherate with a spherical crystal shape is produced firstly in the solution, and by increasing the temperature of the reaction, α' represented by a needlelike morphology is formed and further transforms into cubic crystallites of α-AlH_3 at higher temperature.[14]

The addition rate of the reactants and solvent at the beginning of the reaction, the initial dilution ratio of toluene/ether, impurities, the rate of removing the ether and the temperature of crystallization are the important factors during the synthesis of α-AlH_3. For example, if the ether is removed too quickly from the solution, spherical

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particles representing a complex of alane etherate will be formed instead of the α-AlH_3, while if it is removed too slowly, the procedure will be too long and become expensive [14].

Table 1: Properties of alane polymorphs [10]. LAH: $LiAlH_4$; AH: $AlCl_3$; LBH: $LiBH_4$

Polymorph	**Synthesis condition** (LAH: AH: LBH)	Temp. / time	**Structure**	**Morphology**	**ΔH_{trans} / kJ mol^{-1} H_2)**
α – AlH_3	1: 4: 1	65 °C / 6.5 h	$R\bar{3}c$ a = 4.449 Å c = 11.804 Å	Cubes	-
α' – AlH_3	1: 4: 0	75 °C / 2-4 h	Cmcm a = 6.470 Å b = 11.117 Å c = 6.562 Å	Fuzzy balls	- 1.1 (α' → α)
β – AlH_3	1: 4: 1	65 °C / 1 h	$Fd\bar{3}m$ a = 9.004 Å	Irregular	- 1.0 (β → α)
γ – AlH_3	1: 4: 0	60 °C / 4 h	Pnnm a = 7.336 Å b = 5.367 Å c = 5.756 Å	Needles	- 1.9 (γ → α)
$AlH_3 \cdot nEt_2O$	0: 4: 0	25 °C / 1 h	Amorphous	Translucent spheres	-

All stabilization methods of alane or agents work to inhibit its decomposition and to obtain a more thermally stable solid even at ambient temperature. Different stabilization routes are described in the literature:

(i) Washing the alane with an acidic solution [15] like hydrochloric acid, sulfuric acid, hydrogen bromide acid

(ii) Coating the alane with a surface stabilizing agent [15]

(iii) Other stabilizers like donors or acceptors of electrons [15]

This paper discusses different parameters that govern the formation of pure α-AlH_3, its stabilization and its crystalline shape.

2. Experimental

2.1 Preparation method

2.1.1 Reactants and solvents

Table 2: Characteristics of reactants and solvents used for alane synthesis

Chemical compound	**Molecular formula**	**Supplier**	**Purity**	**Note**
Lithium borohydride	$LiBH_4$	Sigma Aldrich	≥ 95 %	
Aluminum chloride, anhydrous, powder, trace metals basis	$AlCl_3$	Sigma Aldrich	99.99 %	
Lithium aluminum hydride solution	$LiAlH_4$	Sigma Aldrich	-	1 mol L^{-1} in diethyl ether
Diethyl ether, anhydrous	$C_2H_5OC_2H_5$ (Et_2O)	Sigma Aldrich	≥ 99.7 %	contains 1 ppm BHT as inhibitor
Toluene, anhydrous	$C_6H_5CH_3$	Sigma Aldrich	99.8 %	Packaged under argon in resealable ChemSeal bottles
Hydrochloric acid	HCl	VWR chemicals	37 %	

All reactants and solvents are of high purity, as impurities and water can be highly deleterious to the quantitative formation of alane in its α crystalline form. A manifold of inert gas (high purity argon) and vacuum is used for

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elimination of water vapor and molecular oxygen in the reaction vessels. Impurities and moisture can be responsible for the formation of other alane allotropes, even at low concentration. In particular, the γ-crystalline phase, but α' and ε crystalline phases can be obtained as well, concomitantly with metallic aluminium. Prior to each synthesis, diethylether freshly transferred from their bottle was distilled.

2.1.2 Apparatus and equipment

Table 3: Characteristics of the apparatus used for alane syntheses

Equipment	Supplier	Reference
Pump RV3	Edwards	A65201903
Pump RV5	Edwards	A65301903
Balance scout Pro 120/1MG	Fisher Scientific	M54585
Cryo-polystat 37 R4 450W 8L	Fisher Scientific	M8662R
Glove box	Jacomex	
Vacuum-argon lines	Home made	

The manifold of inert gas and vacuum used in our laboratory for all the preparations of the samples of alane .It consists of dual Schlenk line with several ports. The upper Schlenk line is connected to a source of purified argon (Ar) gas, while the lower one is connected to a vacuum pump.

2.1.3 Synthesis method

The alane samples were prepared by a two-step procedure using an organometallic synthesis method under argon [13]. The first step of the reaction is represented by Equation 3.

$$\text{Equation 3}\quad AlCl_3\,(soln) + (LiBH_4) + 3\,LiAlH_4\,(soln) \longrightarrow 4\,AlH_3 \cdot Et_2O\,(soln) + 3\,LiCl\,(s) + (LiBH_4)$$

In this study, α-AlH_3 is produced by the following steps:

(1) $AlCl_3$ and $LiBH_4$ are transferred into a flask below 0 °C, with the presence of ether under stirring. Then, a solution of $LiAlH_4$ (1 mol L^{-1} in ether) is added to react with $AlCl_3$ to give a white precipitate of LiCl.

(2) Then toluene is added dropwise to the mixture. The solution containing the ether complex [Al $(AlH_4)_3(C_2H_5)_2O$], the excess of $LiAlH_4$, $LiBH_4$ and the toluene were held under stirring so that all the precipitate goes down to the balloon and then the upper solution is filtered into another flask.

(3) The third step allows to transform the obtained $AlH_3 \cdot Et_2O$ complex to non-solvated AlH_3.

This synthesis route in solution using toluene was selected among others as it was expected to reach the twofold objective of yielding α-AlH_3 with the highest purity while getting crystals of both acceptable size and shape by following this synthesis route, rather than any other one. The same reproducible procedure was used to tentatively synthesize 3, 6 and 12 g alane per batch.

2.2 Stabilization method

The alpha alane prepared by the route described by the equations (3) and (4) was first washed slowly with an organic solution of tetrahydrofuran (THF), then by different volumes of an aqueous solution of hydrochloric acid (HCl, 5 %, 10 % and 15 %). It was intended to study the influence of these washing steps on the elimination of moistures and impurities (excess of $LiAlH_4$, $LiBH_4$ and LiCl), and thus to stabilize alane.

Another way to stabilize the alane is by mixing an inorganic compound like magnesium chloride ($MgCl_2$) with the solution as already proposed by Matzek [16]. This chloride was added after elimination of LiCl precipitate.

An interesting way to stabilize the alane consists in re-dissolving it in a mixture of ether/toluene, which is also called "Recrystallization". After removing almost all the initial volume of ether from the solution, solvent removal was cycled several times. For this, additional volume of ether were added to the solution to tentatively promote the transformation of the intermediate phases to the alpha-phase, helping to increase the size of the particles and obtaining α-alane in a cubic shape. Additive ether is recovered from the solution at the end of the reaction.

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3. Instrumentation and analyses

Crystalline phase of the reaction products were identified using powder X-ray diffraction (XRD) in the Bragg-Brentano configuration. They were performed using Cu K_α radiation on a Bruker-AXS D-5005 apparatus. Alane powder was put on a dedicated sample holder which was covered with a Kapton film to protect alane from ambient atmosphere. This was intended not to run the risk to record X-ray diffraction pattern of samples being chemically transformed, if applicable, when being contacted to air during the measurement.

Thermal stability and behaviour of the alane reaction products was monitored using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The DTA-TGA experiments were carried out between 25 and 350 °C using a thermal analysis apparatus SDT Q600, TA Instruments, under an argon flow (100 mL min^{-1}), with a heating ramp of 5 °C min^{-1}. Crystallite morphologies were inspected using SEM performed on a Jeol JSM 5600-LV microscope, for which the maximum magnification is 300 000×.

4. Results and discussion

4.1 Characterization by XRD and SEM

4.1.1 Scale up of production of α-AlH_3

Samples of 12 g of α-AlH_3 were prepared by the same route as for 6 g synthesis. Reactant quantities and the volume of the solvent were doubled without changing in the volume of toluene used for the synthesis of 6 g. The actual obtention of pure α-AlH_3 highlighting the reproducibility of this synthesis to get 12 g per batch was checked from X ray diffractograms which are shown in Figure 2.

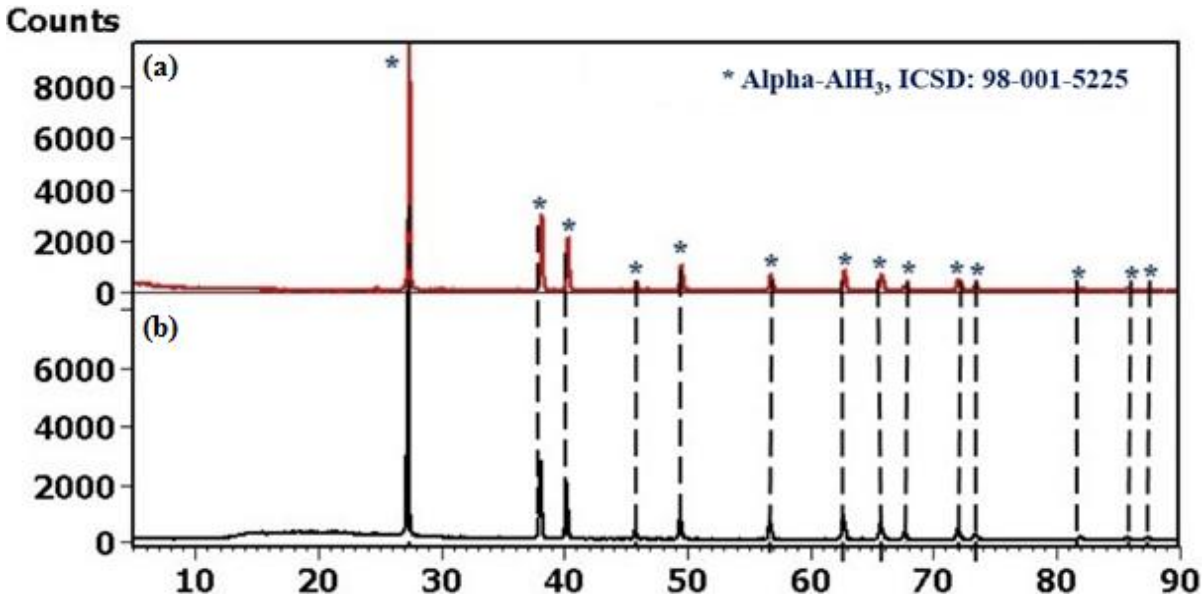

Figure 2: XRD patterns of synthesized α-AlH_3: (a) 12 g of α-AlH_3 batch, (b) 6 g of α-AlH_3 batch

4.1.2 Alpha-AlH_3 before washing treatments

The X ray diffractogram of a sample of alane synthesized, washed with distilled ether without any other washing is represented in Figure 3.

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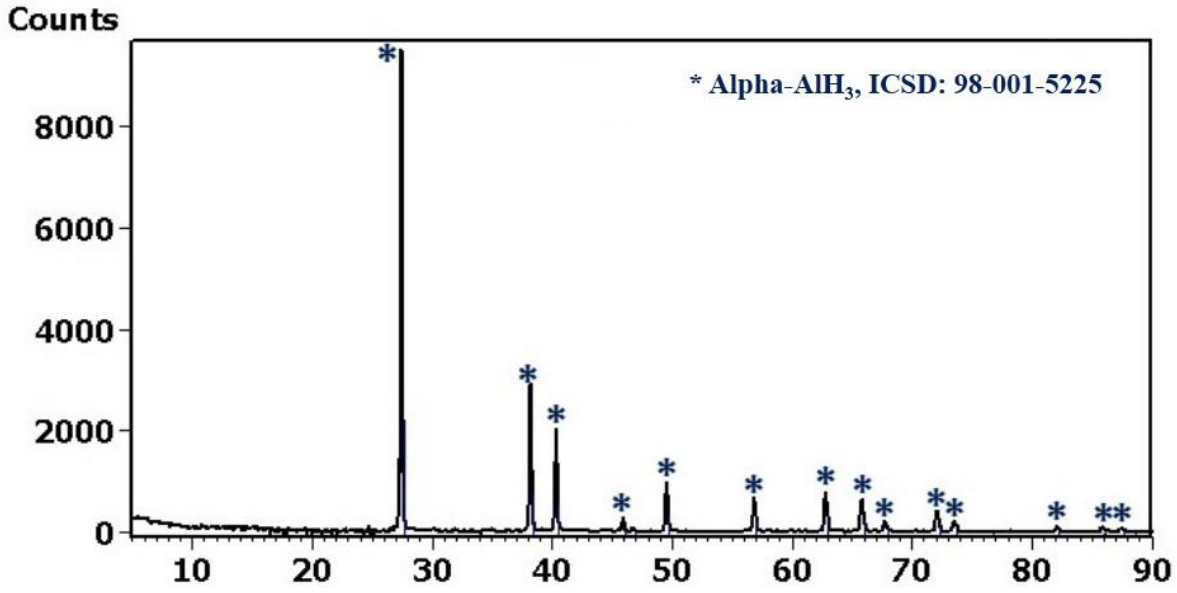

Figure 3: XRD pattern of synthesized α-AlH_3 before stabilization tests

Among potential crystalline phases expected for alane, the sole alpha phase is detected with a maximum peak intensity of 10 000 counts. Crystallites morphology for this sample has been inspected using SEM and typical views are shown in Figure 4. The presence of different crystalline shapes (cubic, desert rose, spheres and needle like) are observed. It showed the presence of phases potentially different to α-AlH_3, like solid alane etherate with a spherical shape [12] and α'-AlH_3 with a needle-like shape [14].

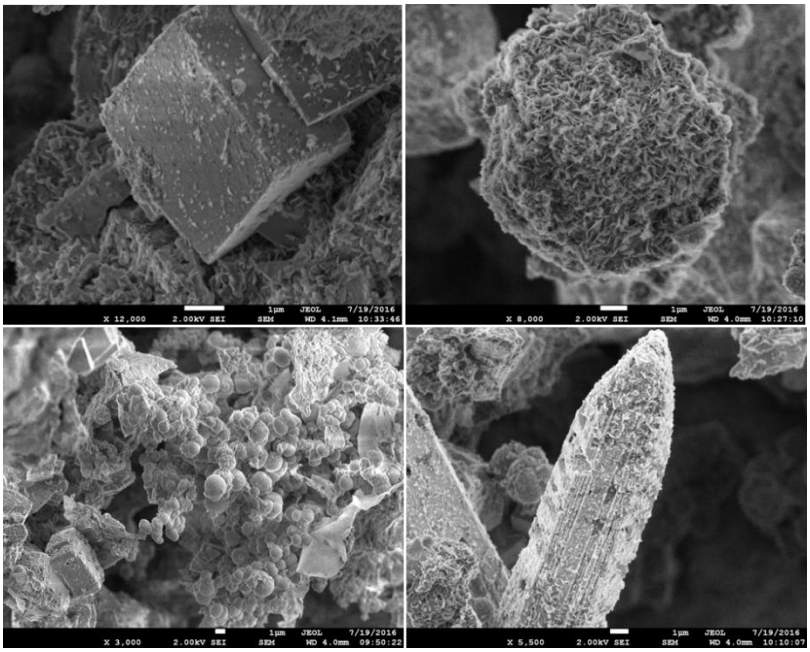

Figure 4: SEM images of a sample of AlH_3 not stabilized. White scale bars at the bottom of each photograph correspond to 1 µm

An energy dispersive spectrum (EDS) as obtained after focusing on a spherical morphology is depicted in Figure 5., showed the presence of carbon and oxygen in this spheres involving the presence of the alane etherate as reported in the literature [14].

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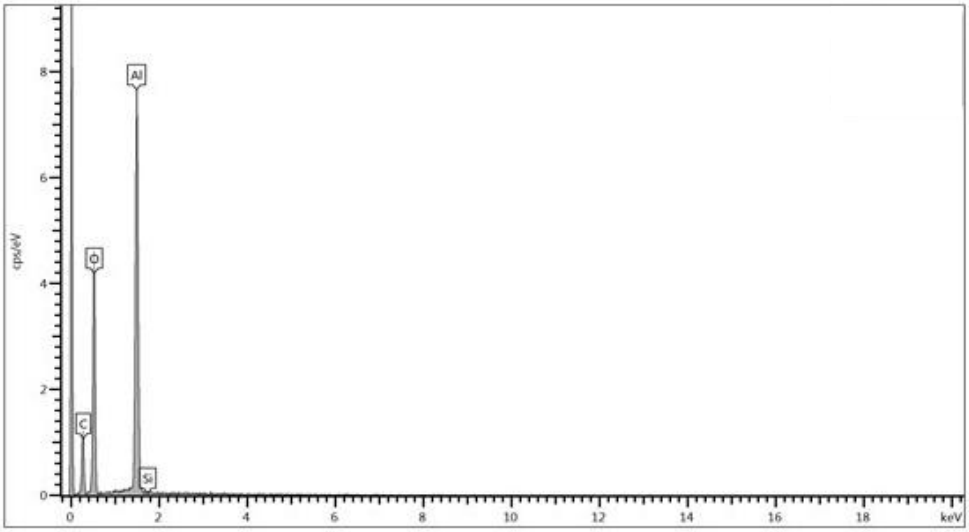

Figure 5: Elemental composition of spherical particles performed by EDS

4.1.3 Alpha-AlH_3 washing tests with tetrahydrofuran (THF)

The diffractogram of a sample of AlH_3washed with tetrahydrofuran (THF) is compared to non-washed one in Figure 6.

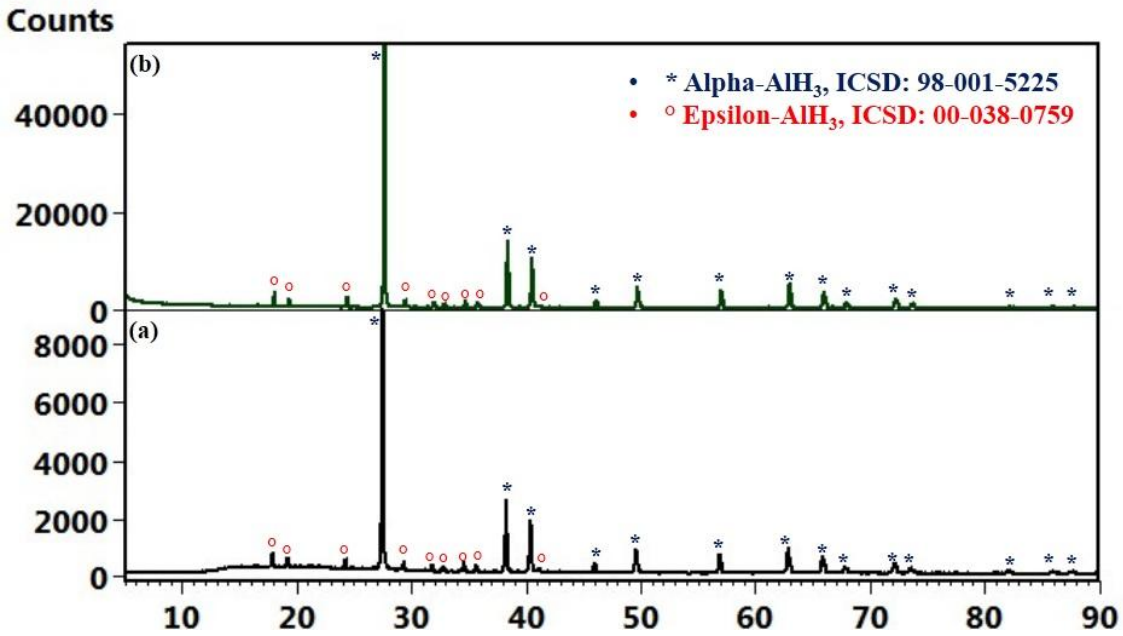

Figure 6: XRD pattern of synthesized AlH_3: (a) before washing with THF, (b) after washing with THF

The sample washed or not with THF showed always the alpha and epsilon phases. THF did not remove epsilon phase but helped to remove impurities as shown in Figure 6 (b) through the intensity increase of the peaks (8 000 counts to 53 000 counts). Impurities like $LiAlH_4$ can be removed by THF washing and this was proved by XRD characterization on a sample of AlH_3containing $LiAlH_4$ before and after washing with THF as seen in Figure 7.

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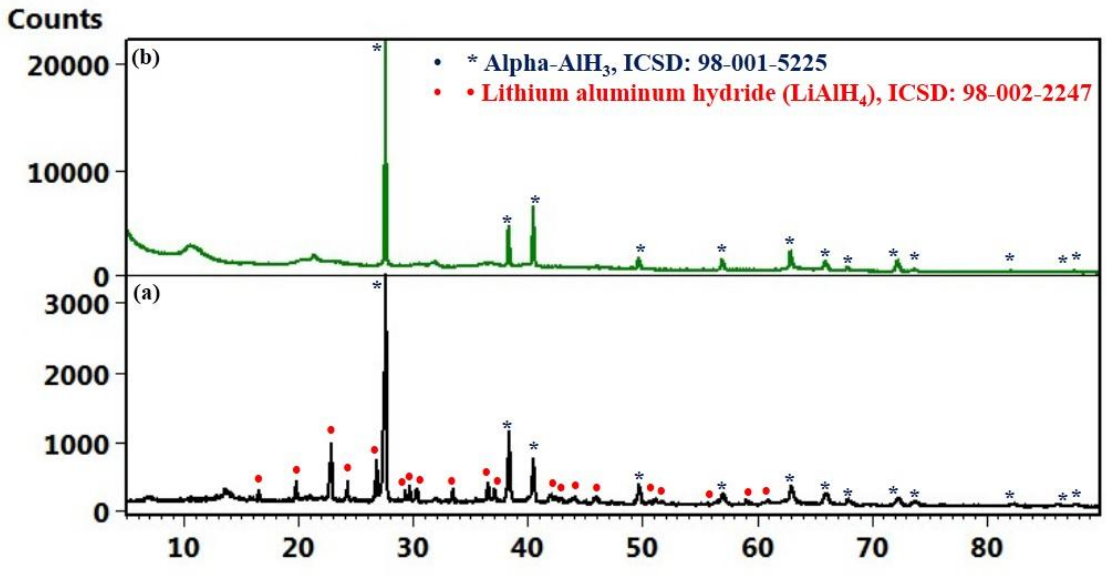

Figure 7: XRD pattern of synthesized AlH_3: (a) before washing with THF, (b) after washing with THF

Crystallites morphologies for the alane before and after washing with THF have been studied by SEM and photographs are shown in Figure 8. They show that THF helps to remove impurities.

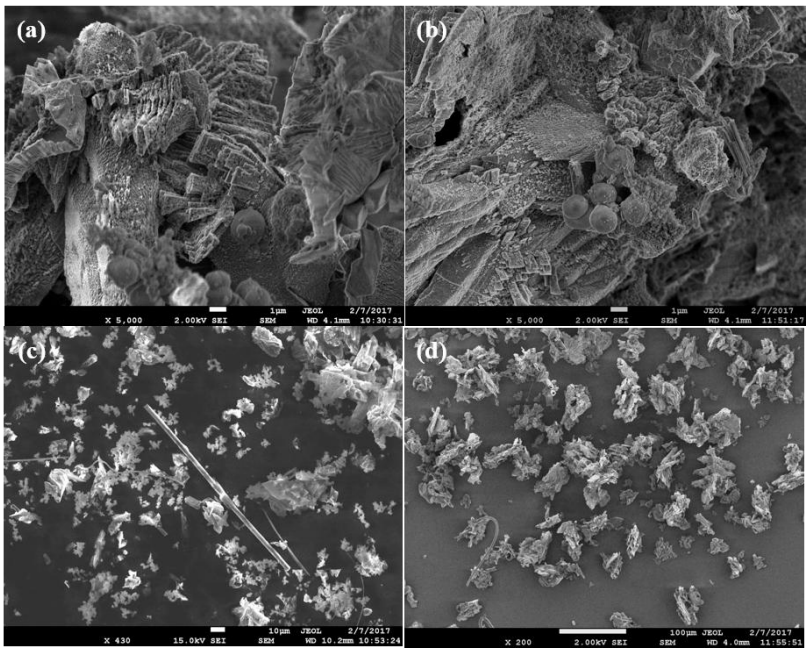

Figure 8: SEM images of a sample of AlH_3 before (a and c) and after washing with THF (b and d). Scale bars at the bottom of each photograph represent 1 µm for a and b, 10 µm for c, 100 µm for d

4.1.4 Alpha-AlH_3 washing tests with HCl solution

Samples of AlH_3 were washed with aqueous acidic solution to investigate its effects on possible stabilization of alane. The acidic solution used was hydrochloric acid (HCl). AlH_3 was washed with different percentages of aqueous HCl (5 %, 10 % and 15 %) and XRD results are represented in Figure 9.

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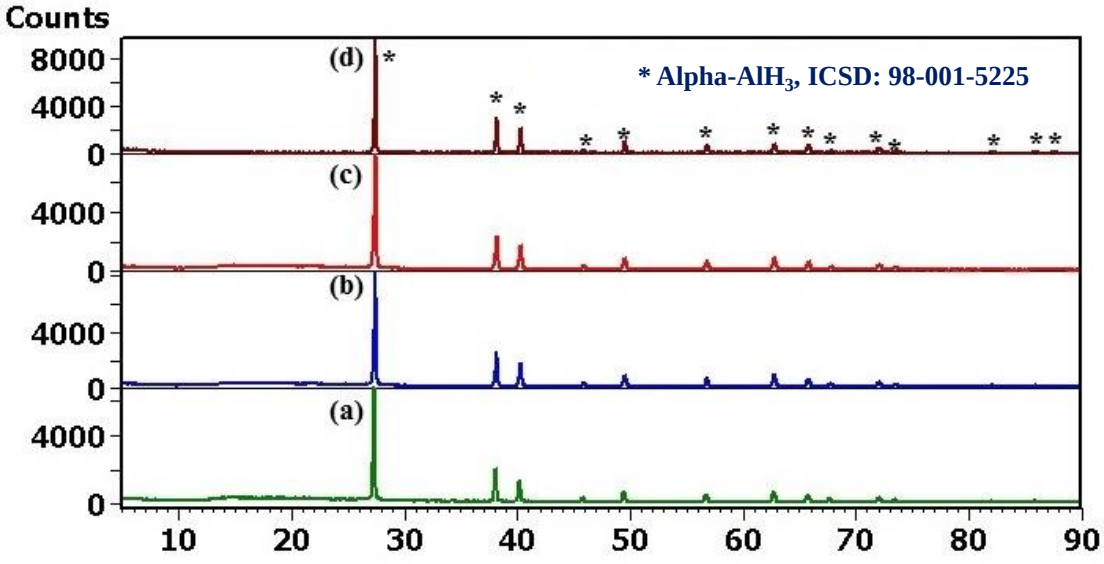

Figure 9: XRD patterns of synthesized alane: (a) not washed, (b) washed with 15 %, (c) 10 % and (d) 5 % HCl

XRD patterns show a higher increase of the peak intensity for the sample washed with 5 % aqueous HCl than for the others washed with 10 and 15 %. HCl thus can be used to eliminate the impurities and stabilize α-AlH_3. SEM characterizations of samples washed with 5 % HCl and 15 % HCl are represented in Figure 10 and in Figure 11, respectively.

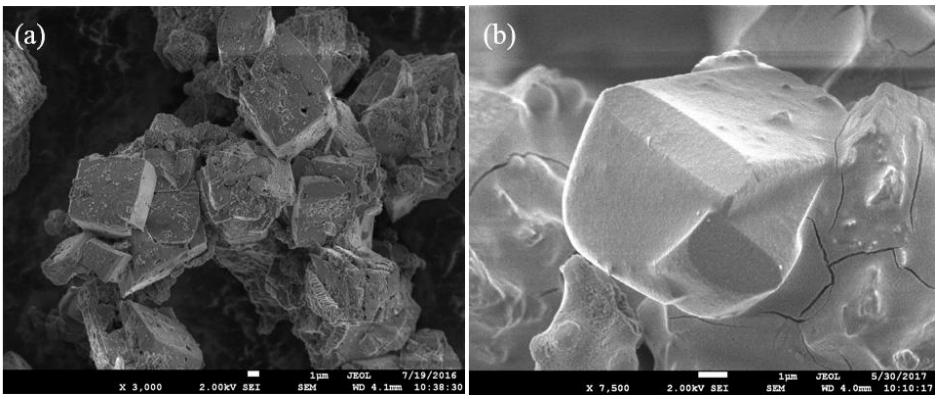

Figure 10: SEM images of a sample of AlH_3 before (a) and after (b) washing with 5 % HCl. Scale bars at the bottom of each photograph represent 1 µm

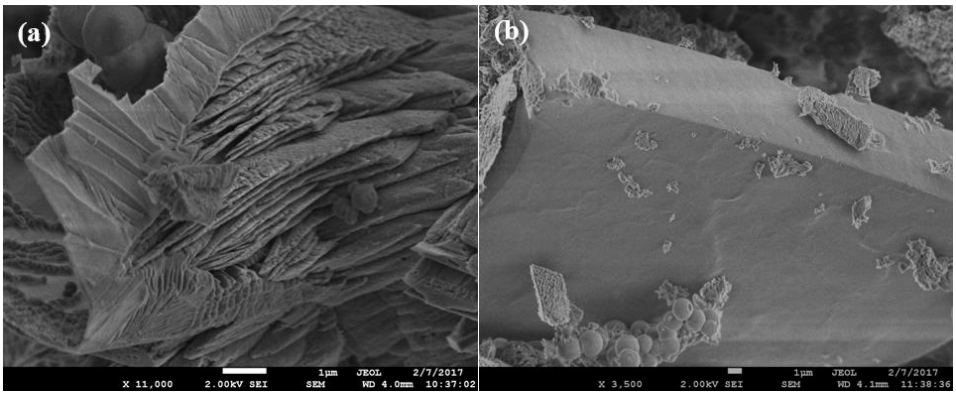

Figure 11: SEM images of a sample of AlH_3 before (a) and after (b) washing with 15 % HCl. Scale bars at the bottom of each photograph represent 1 µm

In comparison to Figure 10 a), Figure 10 b) shows that cubic particles of AlH_3 washed with 5 % HCl can lead to more regular and smoother particles by removing smaller particulate matter found on the faces of the cubes as seen in Figure 10 a). The washing of irregular particles of a sample of AlH_3 shown in Figure 11 a) with 15 % HCl shows

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cleaner particles of larger size as seen in Figure 11 b). This washing thus appears to be useable to remove irregular forms spread on the faces of crystallites which can be seen in Figure 11 a).

Sample of α-AlH_3 showed that 5 % or 15 % of HCl can be used as washing agents to potentially stabilize α-AlH_3 by forming cleaner surfaces on the crystal as seen in Figure 10 b) and to remove impurities from the crystal lattice as shown in Figure 11 b).

4.1.5 Alpha-AlH_3 "recrystallization" test

Primary test of redissolution of alane in ether/toluene mixture has been done to assess the influence of this step on the possible stabilization of α-AlH_3. XRD characterization result of the sample is shown in Figure 12.

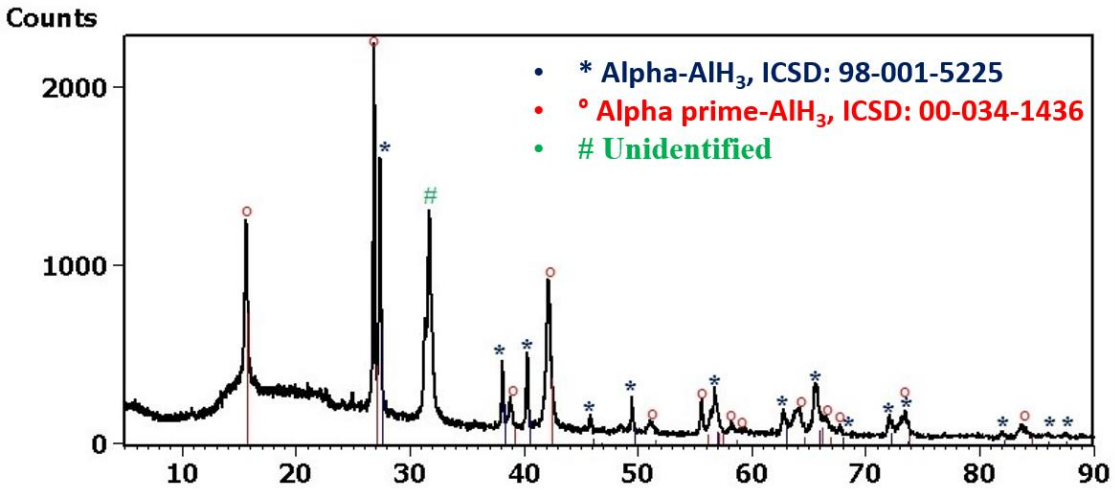

Figure 12: XRD pattern of alane after "recrystallization"

The XRD pattern obtained after the primary "recrystallization" test of alane contains reflections from two crystalline phases, namely alpha and alpha prime alane as well as a strong, unidentified peak by 32 ° 2 θ. SEM photographs of crystallite shapes thus obtained are displayed in Figure 13.

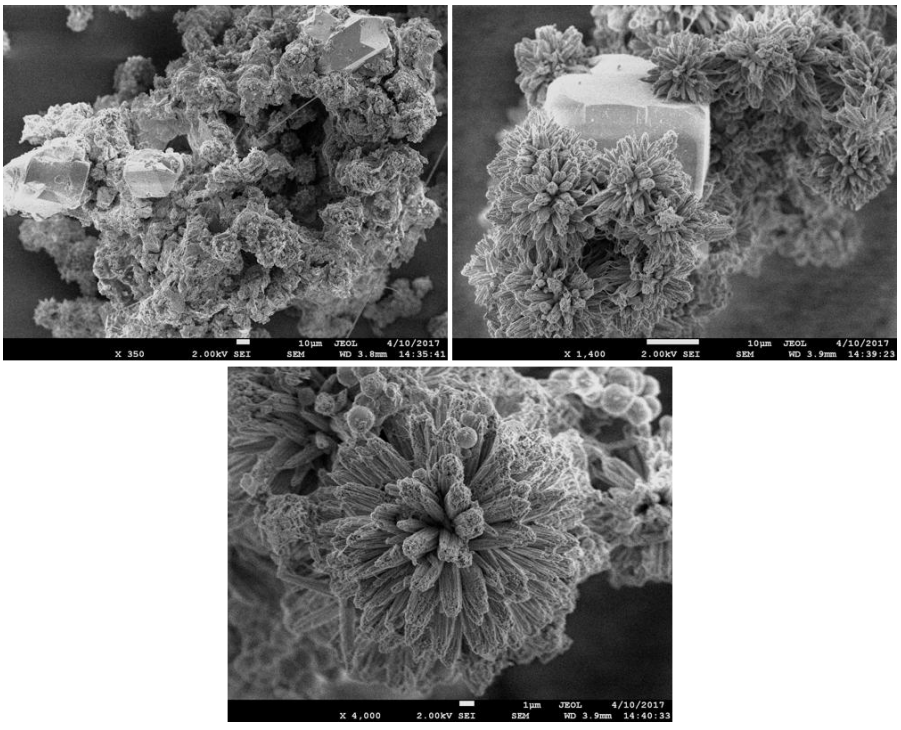

Figure 13: SEM images of a sample of AlH_3 obtained after "recrystallization". Scale bars at the bottom of each photograph represent 10 µm for photographs ontop, 1 µm for the one at the bottom

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Images obtained show the beginning of the formation of cuboids crystals surrounded by random shapes looking like flowers. This makes this method (recrystallization) promising for future works toward the improvement of crystalline shape of alfa-alane which could be obtained up to now.

4.2 Thermal properties of alane synthesized

4.2.1 Thermal properties of α-AlH_3 before washing treatment

DTA-TGA plots of a sample of α-AlH_3 synthesized and prior to any treatment addressed herein are represented in Figure 14.

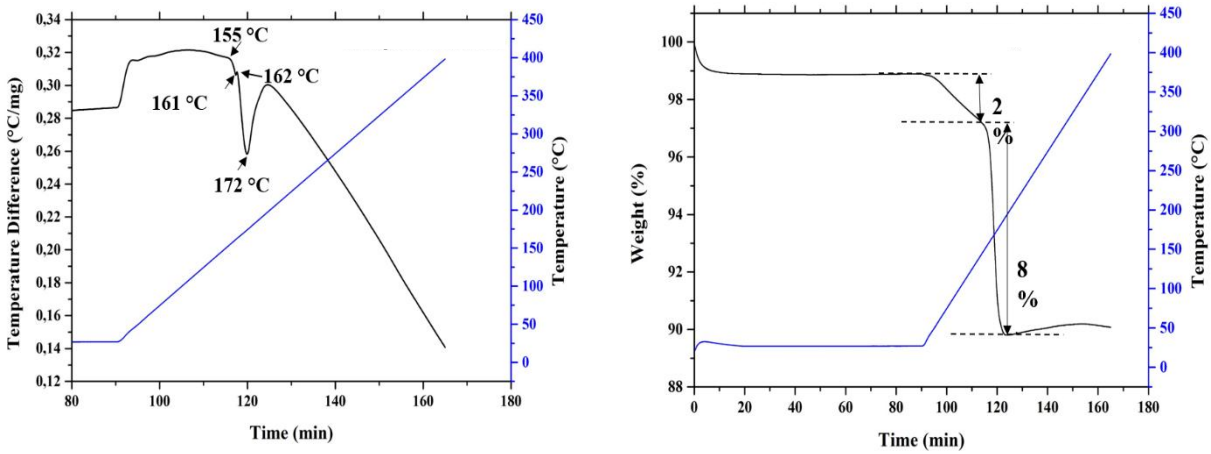

Figure 14: DTA-TGA plots of a sample of α-AlH_3 before treatment

The DTA of a sample of α-AlH_3 not stabilized represented in Figure 14 shows one shouldered endothermic peak. The shoulder contribution to the peak, a very small peak at 161 °C may originate from impurities which could not be detected by XRD. The larger contribution to this endothermic peak displays a minimum at 172 °C and is linked to the dehydrogenation of α-AlH_3 according to the following reaction: $AlH_3 \rightarrow Al + 3/2\ H_2$. This sample shows two consecutive weight losses as seen in Figure 14. The first related weight loss starts at 40 °C and ends at 155 °C and indicates the presence of impurities in its crystal lattice.

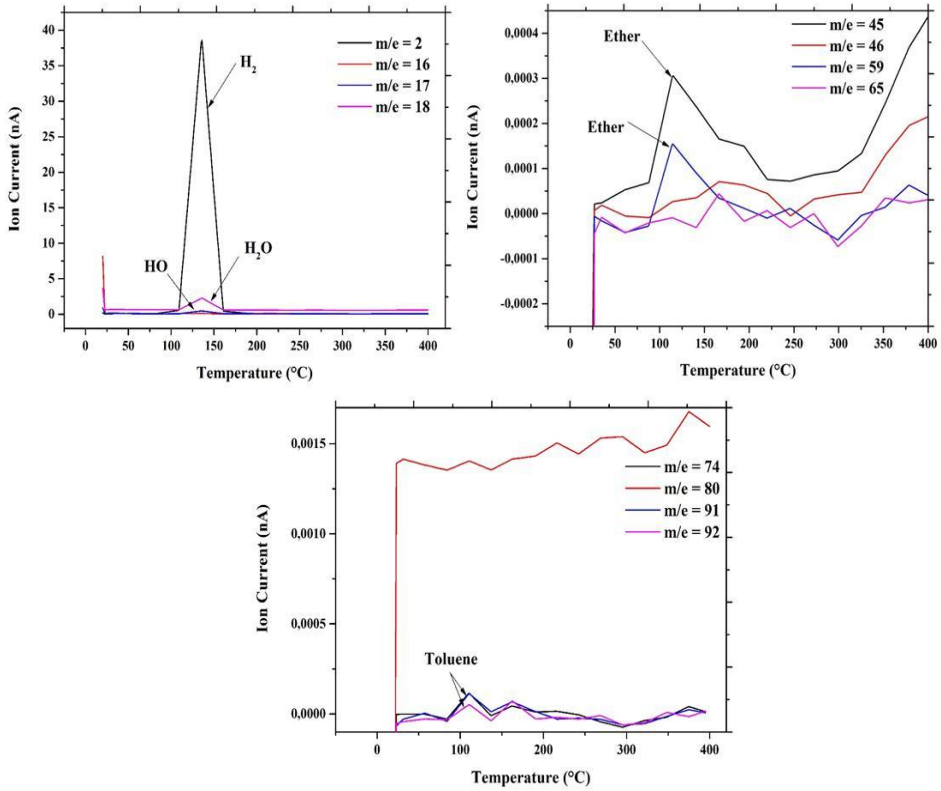

Figure 15: Mass spectroscopy (MS) of a sample of α-AlH_3

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Mass spectroscopy (MS) monitoring results of this thermal analysis is shown in Figure 15. In this temperature range, ether, toluene and water were not detected. This weight loss corresponds to other impurities which are still under investigation. The second weight loss represents the decomposition of α-AlH_3 was 8 %. The overall weight loss for this sample was 10 %, in agreement with the hydrogen weight percentage content of alane.

4.2.1 Thermal properties of α-AlH_3 after HCl and THF treatment

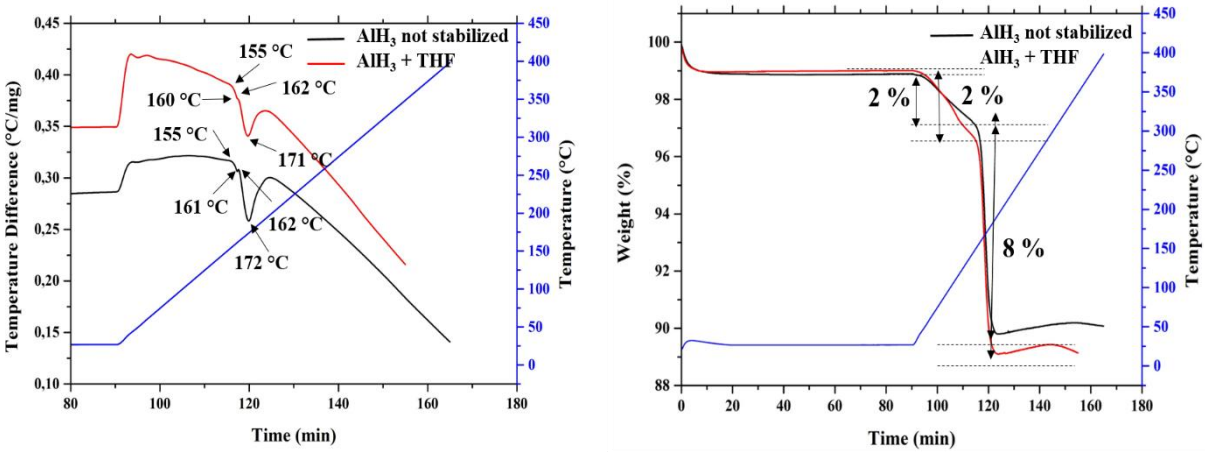

Figure 16: DTA-TGA plots of a sample of α-AlH_3 before and after been stabilized by THF

DTA-TGA of a sample of α-AlH_3 stabilized by THF, as seen in Figure 16, showed no difference with the untreated sample with almost the same decomposition onset temperature (155 °C) and an overall weight loss of 10 %.

A DTA-TGA analyses of a sample of α-AlH_3 treated with hydrochloric acid (HCl) is represented in Figure 17.

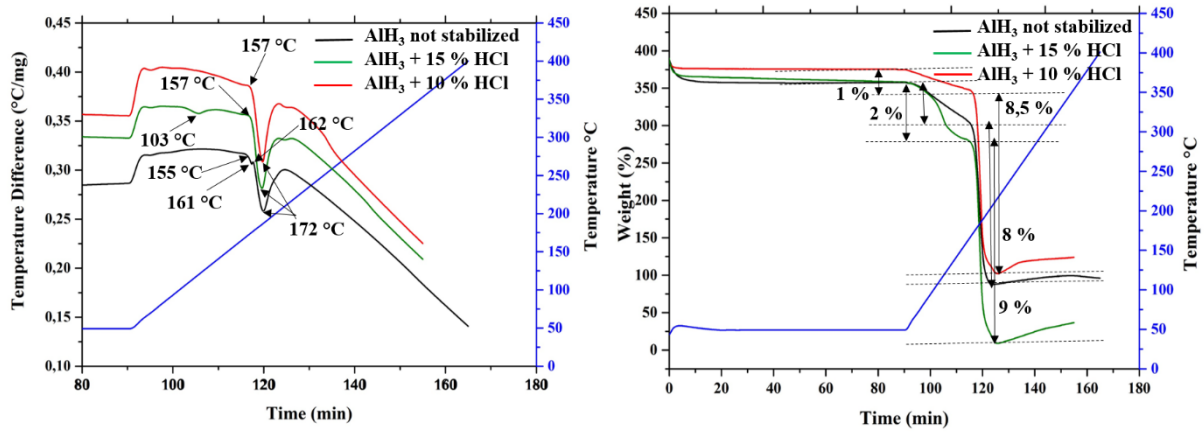

Figure 17: DTA-TGA plots of a sample of α-AlH_3 before and after washing with 10 % and 15 % HCl

An endothermic peak is observed on the DTA trace at lower temperature (103 °C) of α-AlH_3 washed with 15 % HCl and almost at the same temperature for the second endothermic peak due to the decomposition of alane. For α-AlH_3 washed with both 10 % and 15 % HCl, the second peak at 161 °C disappears showing the role of HCl to remove impurities. The TGA showed an overall weight loss of 11 % for the sample stabilized with 15 % HCl which explains the presence of the endothermic peak at 103 °C, while it showed a decrease in the weight loss for the sample stabilized with 10 % HCl and an overall weight loss of 9.5 %.

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5. Conclusion

The synthesis method of alane based on a classical organometallic reaction in ether with a second crystallisation solvent, toluene, was implemented. It had to be adapted so that pure α-aluminium hydride could be obtained after optimization steps. A scale up in the sample's mass from 3 g to 6 g and 12 g, using the same synthesis route has been realized showing the effectiveness of this preparation method to obtain α-AlH_3.

Characterizations by XRD and SEM of α-AlH_3 samples washed with tetrahydrofuran or aqueous hydrochloric acid showed the interest to use these solutions to remove impurities from the lattice of alane.

The thermal analyses of a sample of α-AlH_3 showed a potential stabilising effect of alane using aqueous hydrochloric acid, as it appears to help removing impurities remaining at the end of the synthesis within the crystal lattice. TGA analyses also showed that stabilizing with 10 % HCl helps to reduce the weight loss at 40 °C which was observed for non washed sample.

SEM study on a sample synthesized by "recrystallization" showed that this could pave a promising way to obtain α-AlH_3 in its cubic crystallite shape, but still a closer control of different parameters is required, such as the number of crystallization cycles, temperature, the control of ether vaporisation and the additive volume of solvent to obtain α-AlH_3 in its cubic shape.

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References

[1] R. Zidan. 2010. Aluminium hydride (Alane). Handbook of hydrogen storage: new materials for future energy storage. Germany 249-277.

[2] R. Zidan. B. L. Garcia-Diaz, C. S. Fewox, A. C. Stowe, J. R. Gray, A. G. Harter. 2009. Aluminium hydride: a reversible material for hydrogen storage, Chemical Communications. 25: 3717-3719.

[3] B. Xu, J. Liu, X. Wang. 2014. Preparation and thermal properties of aluminum hydride polymorphs. Vaccum. 99: 127-134.

[4] J. Graetz, J. J. Reilly. 2006. Thermodynamics of the α, β and γ polymorphs of AlH3. Journal of Alloys and Compounds 424: 262–265.

[5] J. W. Turley and H. W. Rinn. 1969. Crystal structure of aluminum hydride. Inorganic chemistry. 81(1): 18-22.

[6] V. A. Yartis, R. V. Denis, J. P. Maehlen, C. Frommen, M. Fichtner, B. M. Bulychev, B. M. H. Emerich. 2007. Double-Bridge Bonding of Aluminum and Hydrogen in the Crystal Structure of γ-AlH3, Inorganic Chemistry. 46(4): 1051-1055.

[7] H. W. Brinks, W. Lengley. C. M. Jensen, J. Graetz, J. J. Reilly, B. C. Hauback. 2007. The crystal structure of β-AlD_3. Journal of Alloys and Compounds. 433(1-2):180-183.

[8] Alex Paraskos. Jami Hanks. Gary Lund. 2007. Synthesis and characterization of alpha alane ATK Launch systems. IMEM conference. Miami. October 16.

[9] J. W. Turley, H. W. Rinn. 1969. The crystal structure of aluminum hydride. Inorganic chemistry. 18-22.

[10] J. Graetz. J. J. Reilly. V. A. Yartys. P. Maehlen. B. M. Bulychev. V. E. Antonov, B. P. Tarasov. I. E. Gabis. 2011. Aluminum hydride as a hydrogen and energy storage material: Past, present and future. J. Alloys and Compounds. 509S-S517-S528.

[11] H. Zang, Y. S. Loo, H. Geerlings, J. Lin, W. S. Chin. 2010. Hydrogen production from solid reactions between $MAlH_4$ and NH_4Cl. International Journal of Hydrogen Energy. 35(1): 176-180.

DOI: 10.13009/EUCASS2017-478

[12] L. V. Dinh, D. A. Knight, M. Paskevicius, C. E. Buckley, R. Zidan. 2012. Novel methods for synthesizing halide-free alane without the formation of adducts. Applied physics A: materials science & processing. 107(1): 173-181.

[13] S. I. Bakum, S. F. Kuznetsova, N. T. Kuznetsov. 2010. Method for the preparation of aluminum hydride. Russian Journal of Inorganic Chemistry. 55(12): 1830–1832.

[14] G. K. Lund, J. M. Hanks, H. E. Johnston. Method for the production of α-alane. 2007. United states patent No 7,238,336.

[15] M. A. Petrie *et al.* Preparation of aluminum hydride polymorphs, particularly stabilized α-AlH_3. 2001. United states patent No 6,228,338 B1.

[16] N.E. Matzek. Stabilization of aluminum hydride. 1974. United states patent No 3,852,043.