Preparation, transformation and characterization of different aluminum hydride AlH_3 phases (alanes)

W. Cong*, L. Potet*, N. Hérault*, R. Brahmi*, Y. Batonneau*, C. Kappenstein*, G. Jacob**, C. Pérut**, Y. Guélou*** and E. Labarthe***

* University of Poitiers, CNRS UMR 7285, IC2MP, 4 rue Michel Brunet, 86022 Poitiers, France

** SAFRAN-HERAKLES, Research Center Le Bouchet, 9 rue Lavoisier, 91710 Vert-le-Petit, France

***CNES, Direction des lanceurs DLA/SDT/EPM, 75612-Paris, France

Introduction

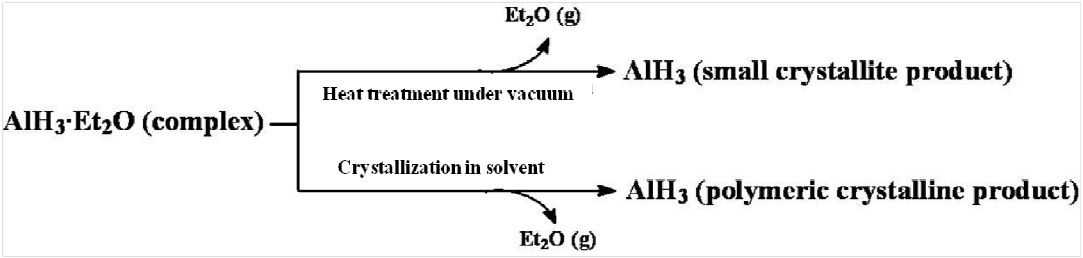
Aluminum hydride or alane AlH_3 is a very important and fascinating material that has recently attracted attention for its potential for different purposes [1, 2]: (i) as an energetic component in rocket propellants, (ii) as a reducing agent in alkali batteries and (iii) as a possible hydrogen source for low temperature fuel cells. For hydrogen storage, this material will be an excellent candidate if it could be cheaply produced. It has a density of 1.48 g cm^{-3}, a volumetric hydrogen capacity of 0.148 g mL^{-1} i.e. greater than that of liquid hydrogen (0.070 g mL^{-1}) and a hydrogen mass capacity exceeding 10 wt.-%.

There are at least seven AlH_3 solid phases found in the literature. But in fact only the most sable α-AlH_3 (H_f° = -11.4 kJ mol^{-1}) can be a candidate for the potential utilization. The development of safe, reliable, low toxic and low cost synthesis methods of pure polymeric crystalline α-AlH_3 attracted numerous studies and will be of high interest. Since 2005, we can see a recent and strong renewed interest for alane [3, 4]. Moreover, a better knowledge of the relationships between the formation of the polymeric network and the structure of the different final phases obtained will be a prerequisite to improve the synthesis.

Preparation of pure alane phases

The most common preparation of pure alane phases is presented in the scheme below. It uses an organometallic synthesis method in two steps: formation of an etherate complex followed by the removal of ether. The second step affords two possibilities to transform the etherate into the solid dry phase: (i) by heat treatment under vacuum or (ii) by precipitation in an organic solvent.

$$4\,LiAlH_4 + AlCl_3 \xrightarrow[LiBH_4]{Et_2O} 4\,AlH_3{\cdot}Et_2O\ (Complex) + 3\,LiCl\downarrow + LiAlH_4$$



Results and Characterizations

The sample phases are identified by powder X-ray diffraction (Figure 1). With the heat treatment method at different temperatures, we obtained the following AlH_3 phases:

- Pure γ-AlH_3;
- Main small crystallite α-AlH_3 plus small amount of γ-AlH_3 and traces of aluminum;

With the solvent method at different crystallization temperatures, we obtain:

- Polymeric crystalline α-AlH_3 plus γ'-AlH_3 (not identified) and traces of ε-AlH_3;
- Main polymeric crystalline α-AlH_3 plus traces of γ'-AlH_3 (not identified) and traces of ε-AlH_3;
- Pure polymeric crystalline α-AlH_3.

It must be quoted that the γ'-AlH_3 phase presents the same diffraction peaks as the γ phase, but the intensity of the peaks are completely different. The possibility to have preferential orientations of the crystallites is under study.

Conclusion

The pure γ phase alane and pure polymeric crystalline α phase AlH_3 are successfully prepared using an organometallic synthesis method. The heat treatment temperature and the crystallization temperature in solution play very important roles in the pure γ and α phase alane preparation respectively.

Other methods described in the literature will be discussed

References

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