Preparation, characterization and thermal stability of gamma alane AlH_3

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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]: (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 the purpose of hydrogen storage, this material could be an excellent candidate if it could be cheaply produced. It has a volumetric hydrogen capacity (1.48 g mL^{-1}) greater than that of liquid hydrogen and a hydrogen capacity exceeding 10 wt.-%. AlH_3 is stable at room temperature despite having an equilibrium hydrogen pressure between 1 and 10 kbar at 298 K. The stability is generally attributed to a surface oxide layer that acts as a kinetic barrier to decomposition and protects the alane from the environment.

There are at least seven AlH_3 phases found in the literature and except for the alpha (the most stable) and gamma phases, crystal structures for the other phases remain unknown. The experiment shows that the thermal stability and ease of preparation of alane are strongly dependent upon purity of the reactants. The presence of impurities or moisture affects strongly the thermal stability. Since 2005, we have been observing a recent and strong renewed interest for alane.

After an up to date review on the different synthesis procedures, the preparation of pure gamma phase [2] using an organometallic synthesis method in two steps will be presented:

$$3\ LiAlH_4\text{(in ether)} + AlCl_3\text{ (in ether) (+ }LiBH_4\text{)} \rightarrow 4\ AlH_3{\cdot}Et_2O\text{(solvated)} + 3\ LiCl\text{(s)}$$

$$AlH_3{\cdot}Et_2O\text{(solvated) (heat treatment under vacuum)} \rightarrow AlH_3\text{(s)}$$

The first step was followed by ^1H and ^{27}Al NMR spectroscopy and the results will be discussed in line with previous data. The pure gamma phase was identified by powder X-ray diffraction. In situ XRD tests, from 30 °C to 220 °C, show that the decomposition of γ-alane follows two parallel paths, the major process leading to the direct formation of aluminum and hydrogen and the second process to the formation of alpha phase. The thermal analysis of γ-AlH_3 (Fig.1) mainly displays an endothermic process starting at 170 °C.

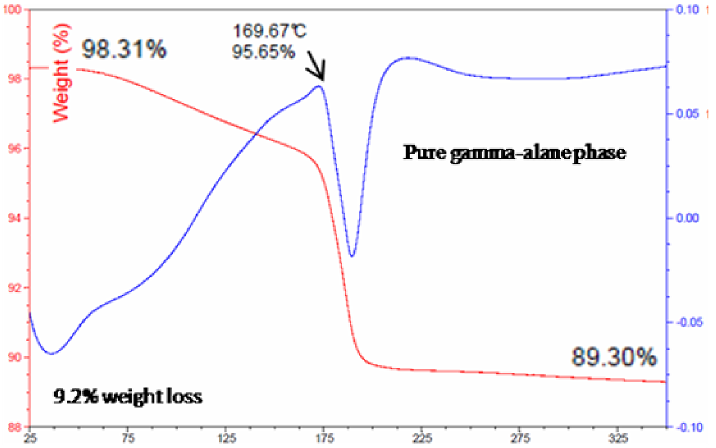

Figure 1: TGA-TDA test of gamma-alane versus temperature. Heating rate 10 K min^{-1}.

[1] Zidan, R. Aluminum Hydride (Alane) 2010, in *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*, Ed. M. Hirscher, Wiley-VCH, Verlag GmbH & Co. KGaA, Weinheim (Germany) 249-277.

[2] Yartys, V. A., Denys, R. V., Maehlen, J. P., Frommen, C., Fichtner, M., Bulychev, B. M., and Emerich, H., "Double-Bridge Bonding of Aluminum and Hydrogen in the Crystal Structure of γ-AlH3," *Inorganic Chemistry*, Vol. 46, No. 4, 2007, pp. 1051-1055.