PECULIARITIES OF AlH_3 DECOMPOSITION

Dulya M.S.*, Lukashev R.V., Klyamkin S.N.(1), Bulychev B.M.(1), Tarasov B.P.
Institute of Problems of Chemical Physics of RAS,
Prospekt Akademika Semenova 1, Chernogolovka Moscow reg., 142432 Russia
(1) Lomonosov Moscow State University,
Chemistry Department, Leninskiye Gory, Moscow, 119992 Russia
Fax: +7 (496) 5221743 E-mail: mdulya@gmail.com

Introduction

Data on the decomposition kinetics of AlH_3 are contradictory and insufficient. Conclusions on the kinetic model of the decomposition are based on one of the following methods: volumetric, non-isothermal kinetic analysis, or nuclear magnetic resonance. The studies were carried out in different temperature ranges and the initial compound was not consistently characterized [1]. In the first studies on the decomposition dynamic of AlH_3 authors determined the time of notable loss of hydrogen amount (~1 mass.%, 5–12 days) at the isothermal (60°C) treatment of aluminum hydride under vacuum till the constant mass loss [2].

Thus the activation energy evaluated for non-solvated AlH_3 by authors of [3] was 72.2±2.5 kJ/mole within the range of 50–100°C. The authors attributed the decomposition to the autocatalytic reaction of the first order.

To lower the thermal stability of aluminum hydride one uses mechanical activation (m/a), and doping with metal hydrides (LiH, MgH_2, TiH_2, VH_x), transition metal oxides (Nb_2O_5, TiO_2), graphite and lithium amide [4–5] during the planetary ball milling. This allows one to decompose the aluminum hydride phase in the compositions at lower temperatures (125–135°C) and preserve high content of the hydrogen (> 5 mass. %).

We conducted a comparative study of data of the kinetic analysis, the volumetric and non-isothermal DSC-TG methods, obtained both for the initial and ball-milled aluminum hydride. Influence of the ball-milling was estimated on the decomposition kinetics of both the non-solvated aluminum hydride and its composition with graphite.

Experimental

Initial aluminum hydride was obtained by the Schlesinger method. The product was the crystal α-modification of aluminum hydride with the lattice parameters $a = 4{,}457$ Å, $c = 11{,}786$ Å, that corresponds to the literature data [6]. Both the initial aluminum hydride and its mixtures with 10 mass. % of carbon component (graphite of the "SEA" grade) were treated in a planetary ball mill Fritsch "Pulverisette 6" under argon. All procedures with the powdered materials were carried out in a glove box under inert atmosphere. Materials obtained were investigated with the use of X-ray diffraction analysis on a diffractometer ARL X'TRA TERMO, scanning electron microscopy on a microscope JEOL JEM-100 CX, and thermal analysis on an apparatus STA 409 Luxx of NETZSCH company.

After the mall milling of both the aluminum hydride and its mixture with the carbonaceous component we didn't found any new compounds in the products. In the X-ray diffraction patterns of the products a significant broadening of peaks corresponding to the α-AlH_3 phase was noticed. This broadening evidences the defectiveness being increased and that the dimensions of coherent-scattering regions (CSR) are getting smaller in these samples [7].

Assessment of the decomposition kinetics of AlH_3

The amount of hydrogen evolved was determined by the volumetric method taking into account atmospheric pressure and room temperature, as well as by the TG analysis, in non-isothermal mode and under inert gas environment.

Mathematical treatment of the experimental data of the volumetric measures was performed using the Erofeev-Avrami's equation $\alpha = 1 - \exp(-k \cdot \tau^n)$, where α – conversion degree, τ – time, k – rate constant, n – parameter depending on the reaction mechanism. Hydrogen desorption from AlH_3 is governed by the diffusion only without any formation new additional nuclei ($n = 1{,}7$). Hydrogen desorption from both the ball milled AlH_3 and the one with graphite carries out via similar mechanisms ($n = 3.2$ and 3.3, accordingly) and is limited by the interphase boundary processes.

Non-isothermal kinetic analysis

Calculation of the kinetics parameters was completed using the NETZSCH Thermokinetics software. The method ASTM 698 is based on plotting experimental points corresponding to DSC peaks maxima in the coordinates $\lg \beta - 1000\, T^{-1}$ followed by linear fitting of the plot. The slope of

the line allows one to calculate the activation energy, and the *y*-intercept — the pre-exponential factor (Fig. 1). In all model-independent methods this factor is estimated using the first order reaction rate equation.

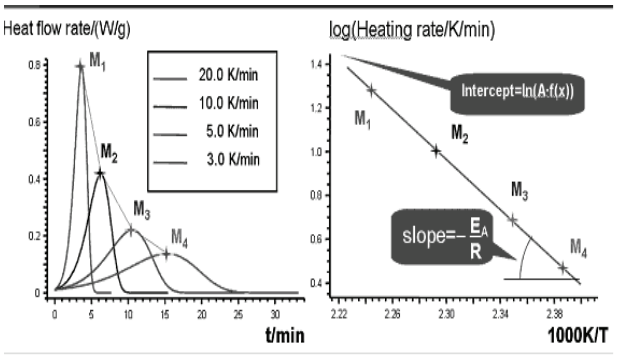

Fig. 1 Determination of the activation energies by the method of model-independent kinetics.

Analysis of the initial DSC and TG curves showed that the decomposition of aluminum hydride proceeded most likely in one stage. Accordingly, to estimate the activation energy in this case the model-independent standard method ASTM E698 is suitable.

Analogous measurements conducted for the ball-milled aluminum hydride and for its composite with graphite (10 mass. %) allowed one to refer the aluminum hydride to a substance of a low thermal stability. The activation energy and the pre-exponential factor were estimated by analyzing the weight losses and changes in the peak areas at different heating rates (1, 5, 10, and 24 ^{o}C/min).

Conclusions

Ball milling of aluminum hydride decreases its thermal stability but this procedure is accompanied by a partial decomposition of the hydride. Addition of graphite during the ball milling hinders the decomposition of AlH_3.

Two kinetics determination methods of the hydrogen desorption used in the work are complementary and in a good agreement with each other. Ball milling dramatically change the mechanism of hydrogen desorption from aluminum hydride (changing in the reaction parameter *n*), however addition of graphite does not and significantly decreases the energy barrier of the reaction.

References

1. Ismail IMK, Hawkins T. Kinetics of thermal decomposition of aluminum hydride: I-non-isothermal decomposition under vacuum and in inert atmosphere (argon). Thermochimica Acta 2005;439:32–43.

2. Petrie MA, Bottaro JC, Schmitt RJ, Penwell PE, Bomberger DC. United States Patent US 6,228,338 B1 (2001).

3. Zakharov VV., Tskhai AN. Russ. J. Inorg. Chem. 1992;37(9):997.

4. Tarasov VP., Muravlev YuB., Bakum SI., Novikov AV. Dokl. Phys. Chem. 2003;393:4.

5. Dulya MS., Bulychev BM., Tarasov BP. Effect of ball milling and additions of metal hydrides and amides on thermal stability of AlH_3. Abstracts Book of X Int. Conf. "ICHMS'07" (Crimea, Ukraine), 2007, p. 34–35.

6. Konovalov SK, Bulychev BM. The P,T-State diagram and solid phase synthesis of aluminum hydride. Inorg. Chem. 1995;34:172–175.

7. Lukashev RV, Klyamkin SN, Bulychev BM, Tarasov BP. Influence of the mechanical activation on the thermal stability of the AlH_3 in Al-C-H system. Abstracts Book of X Int. Conf. "ICHMS'07" (Crimea, Ukraine), 2007, p. 30–31.