

# Modeling of Synthesis of Aluminum Hydride via Binary Hydrides of Alkaline Earth Metals

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**Abstract:** In this article given the mathematical modeling of energy-intensive substances obtaining, which allows expanding the resource base, providing the possibility of using various binary hydrides in the process of aluminum hydride -  $AlH_3$  synthesis.

Due to the absence of soluble hydride forms of binary hydrides of alkaline-earth ( $MH_2$ ) metals, it is necessary to carry out at least 4-6 steps of the process for the production of aluminum hydride. Polynomials for the programmed synthesis of  $AlH_3$  with autoinitiation have been developed.

A programmed synthesis of aluminum hydride with autoinitiation was developed and implemented, which allows expanding the raw material base enabling the synthesis of other metal hydrides.

**Keywords:** Hydride, aluminium, synthesis, programmed synthesis, autoinitiation.

Aluminum hydride –  $AlH_3$  has a particular importance between aluminum hydride compounds. Alum-hydrides of alkali metals -  $MAIH_4$  - are the main starting materials for the production of aluminum hydride in the laboratory and in industry [1].

Aluminum hydride is a very reactive substance, which is also an effective hydrogen carrier. It is used as a source of hydrogen, an active reductant of the functional groups of organic compounds. Significant energy intensity causes the use of  $AlH_3$  as a component of solid rocket fuel. Being a carrier of  $AlH_3$ -groups, aluminum hydride is used for the production of aluminum hydrides and metal polyhydrides.

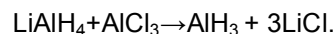
In [2-10], systematic studies of the interaction of aluminum hydrides of metals of the 1<sup>st</sup> and 2<sup>nd</sup> "A" groups with electrophilic reagents ( $AlCl_3$ ,  $HCl$ ,  $RHal$ ,  $AlH_3$ ,  $LiAlH_4$ ,  $LiBH_4$ ) were performed. The idea of the mechanism for the formation of aluminum hydride as a heterocyclic cleavage process of an aluminum hydride molecule under the influence of the acceptor action of an electrophile:



In the main reaction for the production of  $AlH_3$  via  $LiAlH_4$  and  $AlCl_3$ , it was possible to fix the  $AlH_4$ -groups in solutions of aluminum hydride by the introduction of soft electrophiles such as halide alkyls, which makes it possible to increase the effective concentration of  $AlH_3$  and is perspective for increasing the productivity.

There is no data on programmed synthesis of  $AlH_3$  through alum-hydrides of alkaline earth metals.

Traditionally  $AlH_3$  produced through  $LiAlH_4$  and  $AlCl_3$  by reaction of [2-4]:

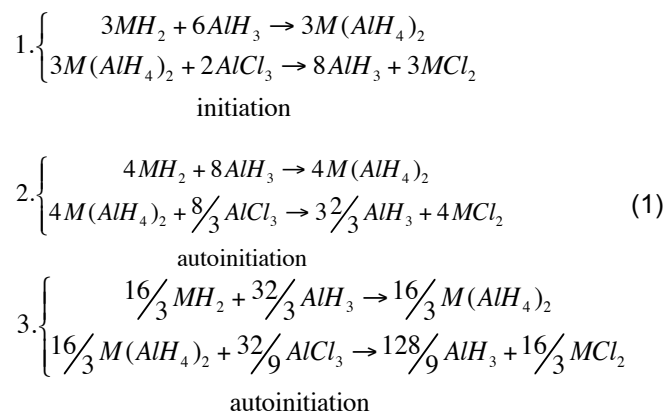


In [5] described the programmed synthesis of  $AlH_3$ .

The programmed synthesis of  $AlH_3$  in interaction with binary hydrides of alkaline earth metal (AEM) with aluminum chloride by autoinitiation is studied in this paper.

The principle of the programmed method of synthesis of hydrogen compounds of aluminum through  $MH_2$  (where M - Ca, Sr, Ba) and  $AlCl_3$  consists in initiating of the process of  $AlH_3$  with the part of metal hydride and subsequent separately stepwise dispensing of reagents as  $AlCl_3$  and  $NH_2$ .

Steps:



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**Table 1: Polynomials for Programming of AlH<sub>3</sub> Synthesis by Autoinitiation (Generalized Mathematical Model of Synthesis)**

| Reagents                                     | Step No.                                    |   |   |   |     |   |
|--|---|---|---|---|-----|---|
|  | 1   | 2   | 3   | 4   | ... | n   |
| 1 <sup>st</sup> reagent<br>MH                | a   | $\frac{\left(\frac{4}{3} + \frac{b}{100}\right)}{\left(1 + \frac{b}{100}\right)}$             | $\frac{\left(\frac{4}{3} + \frac{b}{100}\right)^2}{\left(1 + \frac{b}{100}\right)^2}$             | $\frac{\left(\frac{4}{3} + \frac{b}{100}\right)^3}{\left(1 + \frac{b}{100}\right)^3}$             | ... | $\frac{\left(\frac{4}{3} + \frac{b}{100}\right)^{n-1}}{\left(1 + \frac{b}{100}\right)^{n-1}}$             |
| 2 <sup>nd</sup> reagent<br>AlCl <sub>3</sub> | $\frac{a}{3}$                               | $\frac{a}{3} \frac{\left(\frac{4}{3} + \frac{b}{100}\right)}{\left(1 + \frac{b}{100}\right)}$ | $\frac{a}{3} \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^2}{\left(1 + \frac{b}{100}\right)^2}$ | $\frac{a}{3} \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^3}{\left(1 + \frac{b}{100}\right)^3}$ | ... | $\frac{a}{3} \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^{n-1}}{\left(1 + \frac{b}{100}\right)^{n-1}}$ |
| Initiator<br>AlH <sub>3</sub>                | $a\left(1 + \frac{b}{100}\right)$           | $a\left(\frac{4}{3} + \frac{b}{100}\right)$   | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^2}{\left(1 + \frac{b}{100}\right)^2}$           | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^3}{\left(1 + \frac{b}{100}\right)^3}$           | ... | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^{n-1}}{\left(1 + \frac{b}{100}\right)^{n-2}}$           |
| Product<br>AlH <sub>3</sub>                  | $a\left(\frac{4}{3} + \frac{b}{100}\right)$ | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^2}{\left(1 + \frac{b}{100}\right)^2}$       | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^3}{\left(1 + \frac{b}{100}\right)^2}$           | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^4}{\left(1 + \frac{b}{100}\right)^3}$           | ... | $a \frac{\left(\frac{4}{3} + \frac{b}{100}\right)^n}{\left(1 + \frac{b}{100}\right)^{n-1}}$               |

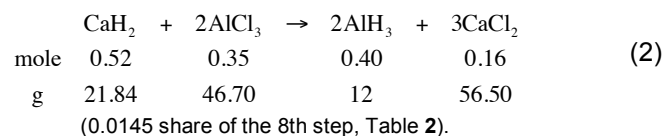
a – the initial amount of MH (mole), b – percentage of initiator excess at each step.

and so on, until the complete consumption of MH<sub>2</sub> and AlH<sub>3</sub> and producing of a predetermined number of M(AlH<sub>4</sub>)<sub>2</sub> or AlH<sub>3</sub>.

The process is conducted with providing of highly concentrated of AlH<sub>3</sub> at each stage (15-60 g/l) and its excess (MH<sub>2</sub> : AlH<sub>3</sub> = 1: 1.05 ÷ 1.3). The amount of dosed reagents is subject with the generalized model, which includes the degree of the polynomials (Table 1). Based on this model, on the «Fortran 2003» a general mathematical program was developed, calculated the used amount of the metal hydride and AlCl<sub>3</sub> in the synthesis for 16-18 stages (steps) of the process (Table 2). The following are examples of preparation of working program synthesis of aluminum-based hydrides of calcium, strontium and barium and aluminum hydride via MH<sub>2</sub> and AlCl<sub>3</sub> based on machine program (Table 2).

*The working program of production of aluminum-based hydrides of alkali-earth metals and aluminum hydride via MH<sub>2</sub> (M = Ca, Sr, and Ba).*

In Table 3, the number of dosage of CaH<sub>2</sub> and AlCl<sub>3</sub> is programmed to 8 steps, 0.0145 share of the number of generic machine program (Table 2). The total amount of the reagents is as follows:



When the volume of the reaction mixture is 300 ml the given concentration of AlH<sub>3</sub> is 12/0.3 = 40 g/l. Table 3 shows the amounts of etherate AlCl<sub>3</sub> of the reaction solution at the initiation process, the reaction solution after dosing of AlCl<sub>3</sub>, and the concentration of AlH<sub>3</sub> at the initiation – and after administration of AlCl<sub>3</sub>.

*The sequence of operations during the synthesis*

*Preparation of etherate AlCl<sub>3</sub>:* Dissolve 46.7 + 1.57 = 48.27 g in 280 ml Et<sub>2</sub>O.  $C_{\text{AlCl}_3} = \frac{48.27}{280} = 0.1723$  g/ml.

*Preparation of initiator:* 1.49 (0.039 mole) LiAlH<sub>4</sub> was pour to the flask (10 per cent excess) in 20 ml Et<sub>2</sub>O and dosed to 9.1 ml (1.57 g, 0.012 mole) AlCl<sub>3</sub>, which is  $\frac{1.416 \cdot 100}{12} = 11.8$  % AlH<sub>3</sub> of synthesized.

1<sup>st</sup> step. To the initiator contribute 0.9 (0.022 mole) CaH<sub>2</sub> and the mixture is stirred intensively (initiation process). 11.3 mL (1.94 g, 0.015 mole) of etherate AlCl<sub>3</sub> is dosage. The mixture was stirred.

2<sup>nd</sup> step. 1.17 g (0.028 mole) CaH<sub>2</sub> was introduced to the reaction mass. The mixture was stirred intensively (autoinitiation process). 14.6 ml (2.52 g, 0.019 mole) AlCl<sub>3</sub> etherate while stirring.

3<sup>rd</sup> step. 1.53 g (0.037 mole) CaH<sub>2</sub> was introduced to the reaction mass. The mixture was stirred. 19.1 mL (3.3 g, 0.025 mole) AlCl<sub>3</sub> etherate dosed while stirring.

4-8 steps. CaH<sub>2</sub> and AlCl<sub>3</sub> were successively added to the reaction mass in the amounts given in Table 3.

**Table 2: The Machine Program for the Synthesis of  $\text{AlH}_3$  and Aluminum Hydrides of Metals through Simple Hydrides of these Metals (MH – the Equivalent of Metal Hydride)**

| Step number | Percentage of initiator excess in% to MH | 1 <sup>st</sup> reagent MH | 2 <sup>nd</sup> reagent $\text{AlCl}_3$ | Total amount of 1 <sup>st</sup> reagent | Total amount of 2 <sup>nd</sup> reagent | Final product per n steps |
|-------------|--|----------------------------|---|---|---|---------------------------|
| 1           | 5  | 3.00                       | 1.00                                    | 3.00                                    | 1.00                                    | 4.15                      |
| 2           | 5  | 3.96                       | 1.32                                    | 6.95                                    | 2.32                                    | 5.47                      |
| 3           | 5  | 5.21                       | 1.74                                    | 12.16                                   | 4.05                                    | 7.20                      |
| 4           | 5  | 6.86                       | 2.29                                    | 19.02                                   | 6.34                                    | 9.49                      |
| 5           | 5  | 9.04                       | 3.01                                    | 28.06                                   | 9.35                                    | 12.50                     |
| 6           | 5  | 11.91                      | 3.97                                    | 39.96                                   | 13.32                                   | 16.47                     |
| 7           | 5  | 15.69                      | 5.23                                    | 55.65                                   | 18.55                                   | 21.70                     |
| 8           | 5  | 20.67                      | 6.89                                    | 76.32                                   | 25.44                                   | 28.59                     |
| 9           | 5  | 27.23                      | 9.08                                    | 103.55                                  | 34.52                                   | 37.67                     |
| 10          | 5  | 35.87                      | 11.96                                   | 139.42                                  | 46.47                                   | 49.62                     |
| 11          | 5  | 47.26                      | 15.75                                   | 186.68                                  | 62.23                                   | 65.30                     |
| 12          | 5  | 62.26                      | 20.75                                   | 248.94                                  | 82.98                                   | 86.13                     |
| 13          | 5  | 82.03                      | 27.34                                   | 330.97                                  | 110.32                                  | 113.47                    |
| 14          | 5  | 108.07                     | 36.02                                   | 439.04                                  | 146.35                                  | 149.50                    |
| 15          | 5  | 142.38                     | 47.46                                   | 581.42                                  | 193.81                                  | 196.96                    |
| 16          | 5  | 187.58                     | 62.53                                   | 769.00                                  | 256.33                                  | 259.48                    |
| 1           | 10                                       | 3.00                       | 1.00                                    | 3.00                                    | 1.00                                    | 4.30                      |
| 2           | 10                                       | 3.91                       | 1.30                                    | 6.91                                    | 2.30                                    | 5.60                      |
| 3           | 10                                       | 5.09                       | 1.70                                    | 12.00                                   | 4.00                                    | 7.30                      |
| 4           | 10                                       | 6.64                       | 2.21                                    | 18.64                                   | 6.21                                    | 9.51                      |
| 5           | 10                                       | 8.65                       | 2.88                                    | 27.29                                   | 9.10                                    | 12.40                     |
| 6           | 10                                       | 11.27                      | 3.76                                    | 38.56                                   | 12.85                                   | 16.15                     |
| 7           | 10                                       | 14.68                      | 4.89                                    | 53.24                                   | 17.75                                   | 21.05                     |
| 8           | 10                                       | 19.13                      | 6.38                                    | 72.38                                   | 24.13                                   | 27.43                     |
| 9           | 10                                       | 24.93                      | 8.31                                    | 97.31                                   | 32.44                                   | 35.74                     |
| 10          | 10                                       | 32.49                      | 10.83                                   | 129.79                                  | 43.26                                   | 46.56                     |
| 11          | 10                                       | 42.33                      | 14.11                                   | 172.13                                  | 57.38                                   | 60.68                     |
| 12          | 10                                       | 55.16                      | 18.39                                   | 227.29                                  | 75.76                                   | 79.06                     |
| 13          | 10                                       | 71.87                      | 23.96                                   | 299.16                                  | 99.72                                   | 103.02                    |
| 14          | 10                                       | 93.65                      | 31.22                                   | 392.81                                  | 130.94                                  | 134.24                    |
| 15          | 10                                       | 122.03                     | 40.68                                   | 514.85                                  | 171.62                                  | 174.92                    |

Conducted stirring intensively. The interaction criterion for the each step is the lack of chlorine in the solution. From the obtained suspension of solvate  $\text{AlH}_3 \cdot n\text{Et}_2\text{O}$  in the 8<sup>th</sup> step crystallized non-solvated  $\text{AlH}_3$  by the kinetic method. By other way at the 8<sup>th</sup> step simultaneously with  $\text{AlCl}_3 \cdot \text{Et}_2\text{O}$  is dosed in the reaction mass since the achievement of dilution of 4-8 g/l by  $\text{AlH}_3$ . From the

resulting solution  $\text{AlH}_3$  is crystallized in isothermally or kinetic mode.

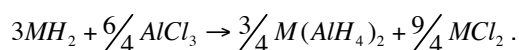
Particular attention should be paid to the separately administration and dosing accuracy of reagents  $\text{CaH}_2$  and  $\text{AlCl}_3$  (from burette) in accordance with the working program of Table 3, as well as for the maintaining of

**Table 3: The Working Program for the Synthesis of AlH<sub>3</sub> and Ca(AlH<sub>4</sub>)<sub>2</sub> through CaH<sub>2</sub> b=10% (0.0145 Portion of Machine Table)**

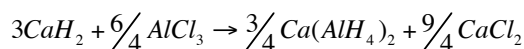
| Step No.                | CaH <sub>2</sub> , mole/g  | V ml solution during the interaction of CaH <sub>2</sub> and AlH <sub>3</sub> | C <sub>AlH<sub>3</sub></sub> during the initiation, (g/l) | AlCl <sub>3</sub> , mole/g | V of AlCl <sub>3</sub> etherate, ml | C <sub>AlH<sub>3</sub></sub> after adding AlCl <sub>3</sub> , (g/l) | ∑ CaH <sub>2</sub> , mole/g | ∑ AlCl <sub>3</sub> , mole/g | V of solution after adding the AlCl <sub>3</sub> , ml | Product per n step, mole/g | Δ g  |
|-------------------------|----------------------------|---|---|----------------------------|-------------------------------------|---|-----------------------------|------------------------------|---|----------------------------|------|
| Production of initiator | (10% lab)<br>0.039<br>1.49 | -   | -   | 0.0118<br>1.57             | 9.1+20 ml Et <sub>2</sub> O         | 49,00   | -                           | 0.0118<br>1.57               | 29.10   | 0.0475<br>1.42             |      |
| 1                       | 0.0216<br>0.90             | 29.10   | 490   | 0.0145<br>1.94             | 11.30                               | 44.90   | 0.0216<br>0.90              | 0.0145<br>1.93               | 40.10   | 0.0600<br>1.80             | 0.38 |
| 2                       | 0.0280<br>1.17             | 40.10   | 44.90   | 0.0189<br>2.52             | 14.60                               | 43.90   | 0.0497<br>2.08              | 0.0333<br>4.44               | 54.70   | 0.0800<br>2.40             | 0.60 |
| 3                       | 0.0366<br>1.53             | 54.70   | 43.90   | 0.0247<br>5.30             | 19.10                               | 44.70   | 0.0864<br>3.61              | 0.0580<br>7.74               | 73.80   | 0.1100<br>3.17             | 0.90 |
| 4                       | 0.0478<br>2.00             | 73.80   | 44.70   | 0.0322<br>4.30             | 24.96                               | 42.50   | 0.1342<br>5.46              | 0.0900<br>12.01              | 98.80   | 0.1400<br>4.20             | 0.90 |
| 5                       | 0.0622<br>2.61             | 98.80   | 42.50   | 0.0419<br>5.6              | 32.50                               | 41.10   | 0.1964<br>8.27              | 0.1319<br>17.60              | 131.30  | 0.1800<br>5.40             | 1.20 |
| 6                       | 0.0811<br>5.40             | 131.30  | 41.10   | 0.0548<br>7.30             | 42.40                               | 39.70   | 0.2800<br>11.76             | 0.1863<br>24.87              | 173.70  | 0.2300<br>6.90             | 1.50 |
| 7                       | 0.1056<br>4.45             | 175.30  | 39.70   | 0.0712<br>9.50             | 55.10                               | 39.30   | 0.3833<br>15.96             | 0.0257<br>34.38              | 228.80  | 0.3000<br>9.00             | 2.10 |
| 8                       | 0.1379<br>5.79             | 228.80  | 39.30   | 0.0930<br>9.50             | 72.00                               | 39.90   | 0.5211<br>21.84             | 0.3498<br>46.70              | 300.80  | 0.4000<br>12.00            | 3.00 |
| Σ                       | V                          | V   | -   | V                          | 301.1                               | -   | V                           | V                            | V   | V                          | V    |

the high concentration and excess synthesis of AlH<sub>3</sub> at each step. The process is conducted in suspension with high concentration of 40 g/l AlH<sub>3</sub> and about 220 g/l by the sum of products.

From the foregoing, it is clear that during the stepwise process each step may be terminated after the introduction of a binary metal hydride (autoinitiation), i.e. on the level of production of aluminum hydride. Then, to compare with the AlH<sub>3</sub> production (2<sup>nd</sup> equation), we do not let in the process of total 25% AlCl<sub>3</sub>:



For the 8 steps (Table 3), this will be:



0.52 0.026 0.13 0.39

21.84                      34.7                      53.04                      173.1

Thus, the synthesis process of aluminum hydride via binary hydrides of alkali-earth metals and AlCl<sub>3</sub> with autoinitiation is considered.

## CONCLUSIONS

A programmed synthesis of aluminum hydride with autoinitiation was developed and implemented, which allows expanding the raw material base enabling the synthesis of other metal hydrides.

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