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 - $MAlH_4$ - 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 1st and 2nd "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:

$$MAlH_4 \rightarrow MH + AlH_3.$$

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.

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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]:

$$LiAlH_4 + AlCl_3 \rightarrow AlH_3 + 3LiCl.$$

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:

$$1.\begin{cases} 3MH_2 + 6AlH_3 \rightarrow 3M(AlH_4)_2 \\ 3M(AlH_4)_2 + 2AlCl_3 \rightarrow 8AlH_3 + 3MCl_2 \end{cases}$$
$$\text{initiation}$$
$$2.\begin{cases} 4MH_2 + 8AlH_3 \rightarrow 4M(AlH_4)_2 \\ 4M(AlH_4)_2 + \tfrac{8}{3}AlCl_3 \rightarrow 3\tfrac{2}{3}AlH_3 + 4MCl_2 \end{cases} \qquad (1)$$
$$\text{autoinitiation}$$
$$3.\begin{cases} \tfrac{16}{3}MH_2 + \tfrac{32}{3}AlH_3 \rightarrow \tfrac{16}{3}M(AlH_4)_2 \\ \tfrac{16}{3}M(AlH_4)_2 + \tfrac{32}{9}AlCl_3 \rightarrow \tfrac{128}{9}AlH_3 + \tfrac{16}{3}MCl_2 \end{cases}$$
$$\text{autoinitiation}$$

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Table 1: Polynomials for Programming of AlH_3 Synthesis by Autoinitiation (Generalized Mathematical Model of Synthesis)

Reagents	Step No.					
	1	2	3	4	…	n
1st reagent MH	a	$\frac{\left(\frac{4}{3}+\frac{b}{100}\right)}{\left(1+\frac{b}{100}\right)}$	$\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^2}{\left(1+\frac{b}{100}\right)^2}$	$\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^3}{\left(1+\frac{b}{100}\right)^3}$	. . .	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^{n-1}}{\left(1+\frac{b}{100}\right)^{n-1}}$
2nd reagent $AlCl_3$	$\frac{a}{3}$	$\frac{a}{3}\frac{\left(\frac{4}{3}+\frac{b}{100}\right)}{\left(1+\frac{b}{100}\right)}$	$\frac{a}{3}\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^2}{\left(1+\frac{b}{100}\right)^2}$	$\frac{a}{3}\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^3}{\left(1+\frac{b}{100}\right)^3}$	. . .	$\frac{a}{3}\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^{n-1}}{\left(1+\frac{b}{100}\right)^{n-1}}$
Initiator AlH_3	$a(1+\frac{b}{100})$	$a\left(\frac{4}{3}+\frac{b}{100}\right)$	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^2}{\left(1+\frac{b}{100}\right)^2}$	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^3}{\left(1+\frac{b}{100}\right)^3}$	. . .	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^{n-1}}{\left(1+\frac{b}{100}\right)^{n-2}}$
Product AlH_3	$a\left(\frac{4}{3}+\frac{b}{100}\right)$	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^2}{\left(1+\frac{b}{100}\right)}$	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^3}{\left(1+\frac{b}{100}\right)^2}$	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^4}{\left(1+\frac{b}{100}\right)^3}$	. . .	$a\frac{\left(\frac{4}{3}+\frac{b}{100}\right)^{n}}{\left(1+\frac{b}{100}\right)^{n-1}}$

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

and so on, until the complete consumption of MH_2 and AlH_3 and producing of a predetermined number of $M(AlH_4)_2$ or AlH_3.

The process is conducted with providing of highly concentrated of AlH_3 at each stage (15-60 g/l) and its excess ($MH_2 : AlH_3 = 1: 1.05 \div 1.3$). 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 $AlCl_3$ 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_2 and $AlCl_3$ based on machine program (Table **2**).

The working program of production of aluminum-based hydrides of alkali-earth metals and aluminum hydride via MH_2 (M = Ca, Sr, and Ba).

In Table **3**, the number of dosage of CaH_2 and $AlCl_3$ 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:

	CaH_2	+	$2AlCl_3$	$\rightarrow$	$2AlH_3$	+	$3CaCl_2$	
mole	0.52		0.35		0.40		0.16	(2)
g	21.84		46.70		12		56.50	

(0.0145 share of the 8th step, Table **2**).

When the volume of the reaction mixture is 300 ml the given concentration of AlH_3 is 12/0.3 = 40 g/l. Table **3** shows the amounts of etherate $AlCl_3$ of the reaction solution at the initiation process, the reaction solution after dosing of $AlCl_3$, and the concentration of AlH_3 at the initiation – and after administration of $AlCl_3$.

The sequence of operations during the synthesis

Preparation of etherate $AlCl_3$: Dissolve 46.7 + 1.57 = 48.27 g in 280 ml Et_2O. $C_{AlCl_3} = \frac{48.27}{280} = 0.1723$ g/ml.

Preparation of initiator: 1.49 (0.039 mole) $LiAlH_4$ was pour to the flask (10 per cent excess) in 20 ml Et_2O and dosed to 9.1 ml (1.57 g, 0.012 mole) $AlCl_3$, which is $\frac{1.416 \cdot 100}{12} = 11.8$ % $AlH_3$of synthesized.

1st step. To the initiator contribute 0.9 (0.022 mole) CaH_2 and the mixture is stirred intensively (initiation process). 11.3 mL (1.94 g, 0.015 mole) of etherate $AlCl_3$ is dosage. The mixture was stirred.

2nd step. 1.17 g (0.028 mole) CaH_2 was introduced to the reaction mass. The mixture was stirred intensively (autoinitiation process). 14.6 ml (2.52 g, 0.019 mole) $AlCl_3$ etherate while stirring.

3rd step. 1.53 g (0.037 mole) CaH_2 was introduced to the reaction mass. The mixture was stirred. 19.1 mL (3.3 g, 0.025 mole) $AlCl_3$ etherate dosed while stirring.

4-8 steps. CaH_2 and AlCl3 were successively added to the reaction mass in the amounts given in Table **3**.

Table 2: The Machine Program for the Synthesis of 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	1st reagent MH	2nd reagent $AlCl_3$	Total amount of 1st reagent	Total amount of 2nd 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 AlH_3nEt_2O in the 8th step crystallized non-solvated AlH_3 by the kinetic method. By other way at the 8th step simultaneously with $AlCl_3$ Et_2O is dosed in the reaction mass since the achievement of dilution of 4-8 g/l by AlH_3. From the resulting solution AlH_3 is crystallized in isothermally or kinetic mode.

Particular attention should be paid to the separately administration and dosing accuracy of reagents CaH_2 and $AlCl_3$ (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_3 and $Ca(AlH_4)_2$ through CaH_2 b=10% (0.0145 Portion of Machine Table)

Step No.	CaH_2, mole/g	V ml solution during the interaction of CaH_2 and AlH_3	C_{AlH_3} during the initiation, (g/l)	$AlCl_3$, mole/g	V of $AlCl_3$ etherate, ml	C_{AlH_3} after adding $AlCl_3$, (g/l)	$\sum CaH_2$, mole/g	$\sum AlCl_3$, mole/g	V of solution after adding the $AlCl_3$, ml	Product per n step, mole/g	Δ g
Production of initiator	(10% lab) 0.039 / 1.49	-	-	0.0118 / 1.57	9.1+20 ml Et_2O	49,00	-	0.0118 / 1.57	29.10	0.0475 / 1.42	
1	0.0216 / 0.90	29.10	490	0.0145 / 1.94	11.30	44.90	0.0216 / 0.90	0.0145 / 1.93	40.10	0.0600 / 1.80	0.38
2	0.0280 / 1.17	40.10	44.90	0.0189 / 2.52	14.60	43.90	0.0497 / 2.08	0.0333 / 4.44	54.70	0.0800 / 2.40	0.60
3	0.0366 / 1.53	54.70	43.90	0.0247 / 5.30	19.10	44.70	0.0864 / 3.61	0.0580 / 7.74	73.80	0.1100 / 3.17	0.90
4	0.0478 / 2.00	73.80	44.70	0.0322 / 4.30	24.96	42.50	0.1342 / 5.46	0.0900 / 12.01	98.80	0.1400 / 4.20	0.90
5	0.0622 / 2.61	98.80	42.50	0.0419 / 5.6	32.50	41.10	0.1964 / 8.27	0.1319 / 17.60	131.30	0.1800 / 5.40	1.20
6	0.0811 / 5.40	131.30	41.10	0.0548 / 7.30	42.40	39.70	0.2800 / 11.76	0.1863 / 24.87	173.70	0.2300 / 6.90	1.50
7	0.1056 / 4.45	175.30	39.70	0.0712 / 9.50	55.10	39.30	0.3833 / 15.96	0.0257 / 34.38	228.80	0.3000 / 9.00	2.10
8	0.1379 / 5.79	228.80	39.30	0.0930 / 9.50	72.00	39.90	0.5211 / 21.84	0.3498 / 46.70	300.80	0.4000 / 12.00	3.00
Σ	V	V	-	V	301.1	-	V	V	V	V	V

the high concentration and excess synthesis of AlH_3 at each step. The process is conducted in suspension with high concentration of 40 g/l AlH_3 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_3 production (2nd equation), we do not let in the process of total 25% $AlCl_3$:

$$3MH_2 + {}^6\!/_4 AlCl_3 \rightarrow {}^3\!/_4 M(AlH_4)_2 + {}^9\!/_4 MCl_2 .$$

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

$$3CaH_2 + {}^6\!/_4 AlCl_3 \rightarrow {}^3\!/_4 Ca(AlH_4)_2 + {}^9\!/_4 CaCl_2$$

<u>0.52 0.026 0.13 0.39</u>

21.84 34.7 53.04 173.1

Thus, the synthesis process of aluminum hydride via binary hydrides of alkali-earth metals and AlCl3 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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