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Thermal behavior of aluminum fluoride trihydrate

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Abstract

The thermal decomposition of aluminum fluoride trihydrate was investigated by TG-DTG. The process was recognized to involve three stages:

$$\mathrm{I}\quad AlF_3\cdot 3H_2O \xrightarrow{108-277^\circ C} AlF_3\cdot 0.5H_2O + 2.5H_2O$$

$$\mathrm{II}\quad AlF_3\cdot 0.5H_2O \xrightarrow{277-550^\circ C} AlF_3 + 0.5H_2O$$

$$\mathrm{III}\quad AlF_3\cdot 3H_2O \xrightarrow{>380^\circ C} Al_2O_3 + 6HF$$

It was found that the apparent activation energy, E, and the preexponential factor, A, for stage I reaction were 41.9 kJ mol^{-1} and $10^{2.49}$ s^{-1}, respectively. For stage II reaction, the value of E was 47.5 kJ mol^{-1} and the most probable differential mechanism function was in the form of $(1-\alpha)$, and magnitude of 80.4 kJ mol^{-1} of E and a function in the form of $3/2(1-\alpha)[-\ln(1-\alpha)^{1/3}]$ were derived for stage III reaction. From the measurements conducted under increasing temperature conditions, contents of fluorine, $C_F(\%)$, on moisture-free basis and water, $C_W(\%)$, on current mass basis contained in the $AlF_3\cdot 3H_2O$ sample were determined and correlation between the temperature range dictated by the quality specification of AlF_3, $C_F \geq 61.0\%$, $C_W < 0.5\%$, and the heating rate were presented. The content of fluorine and water were also determined under isothermal conditions and correlation between the time duration of the treating temperature necessary for the quality specification to be met, and the magnitude of temperature were presented.

Keywords: $AlF_3\cdot 3H_2O$; Isothermal; Kinetic parameters; Non-isothermal; TG-DTG; Thermal behavior

1. Introduction

Anhydrous aluminum fluoride is used in the electrolytic reduction for production of metal aluminum. In the wet process, the anhydrous fluoride is prepared by heating trihydrated aluminum fluoride. Its thermal decomposition behavior has been reported in previous papers [1–4]. Some of the works treated the thermal behavior of $AlF_3\cdot 3H_2O$ in aqueous solution [1]. Istomin et al. [2,3] reported qualitatively the dehydration process of $AlF_3\cdot 3H_2O$ and relevant inferences, and they revealed the rate-limiting stages in the dehydration process of $AlF_3\cdot 3H_2O$. For preparing AlF_3 from $AlF_3\cdot 3H_2O$, with specified quality and reduced energy consumption, the technical parameters are required, however it has rarely been reported. This investigation project intends to reveal the kinetic behaviors of

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dehydration of $AlF_3{\cdot}3H_2O$ and hydrolytic reaction of AlF_3 with water and to determine the values of relevant kinetic parameters.

2. Experimental

2.1. Materials

$AlF_3{\cdot}3H_2O$ used in the experiments was for commercial use, produced by Baiyin Fu Hua Yan Trade Co. Ltd., Baiyin, Gansu, China. The samples were dried in an oven at the temperature of 100–105°C for 2 h and sieved through a 120 mesh sieve before test. MgO used was analytically pure reagent. It was ignited at 900°C for 2 h before use.

2.2. Experimental apparatus and conditions

A thermogravimetry analysis system of TGA7 (Perkin-Elmer Co., USA) was used to study the thermal decomposition process. Inert atmosphere was provided by flowing N_2 of 60 ml min^{-1}. Sample mass of about 6 mg was used in each test. A series of non-isothermal TG-DTG experiments with heating rates of 5, 10, 20, 50, 80 and 130°C min^{-1} were conducted in the program. Another series of isothermal TG-DTG experiments were carried out at the temperature of 500, 550, 600, and 650°C.

3. Results and discussion

3.1. Thermal behavior and decomposition process

Typical curves, at the heating rate of 10°C min^{-1}, for aluminum fluoride trihydrate, $AlF_3{\cdot}3H_2O$ and the system $AlF_3{\cdot}3H_2O/MgO$ are shown in Fig. 1 and the data are listed in Table 1. A three-stage mass loss process is clearly observable from the TG curve for $AlF_3{\cdot}3H_2O$. In the first stage, with the temperature being in the range 108 and 277°C, a mass loss of 32.69% is observed. This value is in good agreement with the calculated one of 32.61% for the loss of 2.5 molecules of water from $AlF_3{\cdot}3H_2O$. In the second-stage, the temperature varied from 277 to 550°C, meanwhile the sample further decomposed. The value of mass loss of 6.96% found from this stage is again in good agreement with the theoretically predicted value of 6.52%, indicating the anhydrous aluminum fluoride result. As the temperature exceeds 380°C the third-stage reaction begins. This stage is a hydrolytic reaction of AlF_3 with water. On the basis of the experiment carried out and the calculated results, the following reactions are suggested for defining the thermal decomposition processes of $AlF_3{\cdot}3H_2O$.

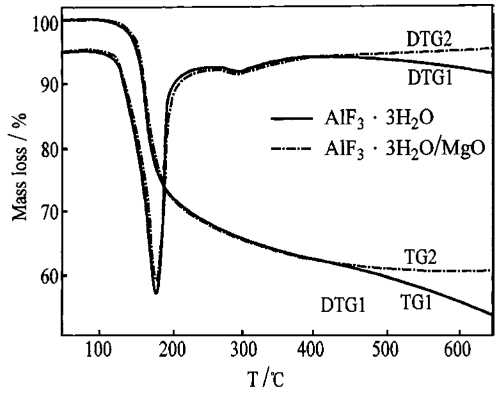

Fig. 1. TG-DTG curves of $AlF_3{\cdot}3H_2O$ and system $AlF_3{\cdot}3H_2O/MgO$ at a heating rate of 110°C min^{-1}.

$$AlF_3\cdot 3H_2O \overset{108-277^\circ C}{\rightarrow} AlF_3\cdot 0.5H_2O + 2.5H_2O$$

$$AlF_3\cdot 0.5H_2O \overset{277-550^\circ C}{\rightarrow} AlF_3 + 0.5H_2O$$

$$2AlF_3\cdot 3H_2O \overset{>380^\circ C}{\rightarrow} Al_2O_3 + 6HF\uparrow$$

3.2. Kinetic parameters determined from the first-stage dehydration reaction

In order to determine the kinetic parameters that is the apparent activation energy, E, and preexponential factor, A, of the first-stage dehydration reaction for the title compound, a multiple heating method (Kissinger's method [4]) was employed. As shown in

Table 1
Mass loss vs. temperature for $AlF_3{\cdot}3H_2O$

Stage	Temperature range (°C)	Mass loss (%)	
		Exp.	Theory
First-stage	108–277	32.69	32.61
Second-stage	277–550	6.96	6.32
Third-stage	>380		

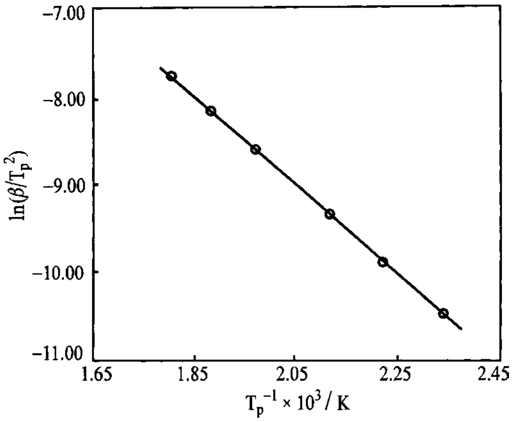

Fig. 2. Kissinger's plot of the first-stage dehydration reaction peak temperature deduced from DTG curves.

Fig. 2, the relationship of $\ln(\beta/T_p^2)$ versus T_p^{-1} presents a straight line, where β is the heating rate, T_p is the maximum peak temperature applied during the reaction mentioned above. From the experimental data in Fig. 1, the calculated value of apparent activation energy is determined to be 41.9 kJ mol^{-1} and of the preexponential factor to be $10^{2.49}$ s^{-1}. The correlation coefficient is 0.998.

3.3. Apparent activation energy and mechanism function of the second-stage reaction for the title compound

Based on the total mass loss in the temperature range, 277–550°C, of the second-stage dehydration reaction of $AlF_3{\cdot}0.5H_2O$, the mass loss fraction, α, in various temperature intervals are calculated by referring to the TG curve shown in Fig. 1. The calculated data are shown in Table 2. In accordance with Phadnis' method [5], substitution of the data of α into the formulas of g(α), 20 in total, listed in Ref. [6] results in the value of E of 47.5 kJ $mol^{-1}$and the most probable differential mechanism function, $(1-\alpha)$, by the method of logical choices.

Table 2
Mass loss fraction of the second-stage dehydration of $AlF_3{\cdot}0.5H_2O$ determined from TG curve

Data point	T_i (K)	α_i	Data point	T_i (K)	α_i
1	562.4	0.1185	6	648.8	0.6000
2	572.5	0.1990	7	680.7	0.7000
3	588.3	0.3016	8	716.4	0.8000
4	604.8	0.4005	9	762.2	0.9000
5	625.1	0.5007			

3.4. Kinetic parameters of the hydrolytic reaction of AlF_3 with water

For defining the defluorine process in the hydrolytic reaction of AlF_3 with water in the temperature range 380~615°C, Eq. (1) is used to calculate the fluorine content, C_F, on moisture-free basis preserved at the end of each temperature interval from 380°C to T_i

$$C_{F_i} = 67.88 - (m_i^{A.M.} - m_i^{A})\frac{M_{AlF_3{\cdot}3H_2O}}{M_{AlF_3}} \qquad (1)$$

Where $m_i^{A.M}$ and m_i^{A} are the mass fraction, %, of system AlF_3 ·$3H_2O$/MgO and $AlF_3{\cdot}3H_2O$ preserved at temperature T_i, read from Fig. 1, respectively; $M_{AlF_3{\cdot}3H_2O}$ and $M_{AlF_3}$are molcule mass of $AlF_3{\cdot}3H_2O$ and AlF_3 respectively; and the value of 67.88 is the fluorine content in AlF_3. Data of the defluorine in dehydrolytic process of AlF_3 with water are shown in Table 3. The data are determined in the temperature range 380–615°C, with the defluorine fraction being unity for the whole temperature range.

By substituting the calculated data in Table 3 into the formulas of g(α) mentioned above, the value of E of 80.4 kJ mol^{-1} and the most probable differential mechanism function, $3/2(1-\alpha)[-\ln(1-\alpha)^{1/3}]$ are derived by the method of logical choice.

3.5. Relationships between the content of fluorine and water and temperature

Contents of water, C_W, on current mass basis and fluorine, C_F, are expressed as relationships versus

Table 3
Data of the defluorine reaction in the hydrolytic process of AlF_3 with water

Data point	T_i (K)	α_i	Data point	T_i (K)	α_i
1	673	0.01	7	826	0.50
2	707	0.05	8	836	0.60
3	733	0.10	9	851	0.70
4	767	0.20	10	863	0.80
5	793	0.30	11	876	0.90
6	811	0.40			

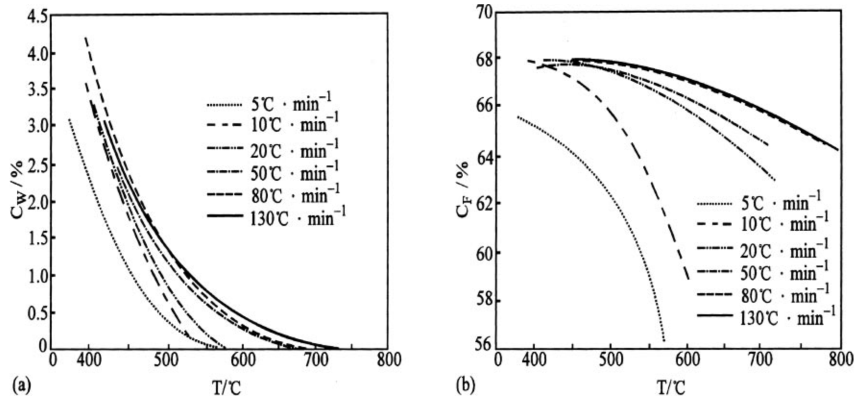

Fig. 3. (a) C_W and (b) C_F vs. T relationships under different heating rate for $AlF_3{\cdot}3H_2O$.

temperature, T, with heating rate, β, as parameters, see Fig. 3 and Table 4. Shown in Fig. 3, the values of C_F and C_W are calculated by using Eqs. (1) and (2)

$$C_W = \frac{m_i^{A.M.} - m_B}{m_i^{A.M.}} \times 100\% \qquad (2)$$

where m_B is the final mass fraction of the system AlF_3 $3H_2O/MgO$, read at the end of the heating process.

For the aluminum fluoride quality specifications, i.e. $C_W<0.5\%$, and $C_F \geq 61.0\%$, to be met by a certain heating rate, allowable temperature range is solved from the equations in Table 4. Values solved are tabulated in Table 5 and expressed with empirical equations, as Eqs. (3a) and (3b). From the point of view of controlling the heating process conditions for preparing the qualified AlF_3 from $AlF_3{\cdot}3H_2O$, these data and equations should be of practical importance.

$$T > 441.89 + 31.12 \ln \beta \quad \text{for } C_W < 0.5\% \quad |r| = 0.9914 \qquad (3a)$$

$$T \leq 308.60 + 134.41 \ln \beta \quad \text{for } C_F \geq 61.0\% \quad |r| = 0.9794 \qquad (3b)$$

3.6. Thermal behavior of $AlF_3{\cdot}3H_2O$ under isothermal conditions

Samples of $AlF_3{\cdot}3H_2O$ were also tested under isothermal conditions with the temperature regulated to 500, 550, 600 and 650°C respectively. The results are shown in Fig. 4.

Fig. 5 depicts the contents of fluorine and water varying with time under constant temperature condition. Table 6 summarizes the relationships of linear regression between the contents of fluorine and water and the time elapsed under specific temperature. Table 7 presents the time duration required to have the quality specification to be met. Eqs. (4a) and (4b) give the regression formulas to predict the required time range.

Table 4
Relationships of T vs.C_W and C_F under different heating rates for AlF_3 $3H_2O$

β (°C min^{-1})	C_W (%)–T (°C)	R^2	C_F (%)–T (°C)	R^2
5	C_W=7.45×10$^{-5}T^2$−8.53×10^{-2}T+24.47	0.9997	C_F=−2.25×10$^{-4}T^2$+17.22×10^{-2}T+32.41	0.9869
10	C_W=7.65×10$^{-5}T^2$−9.55×10^{-2}T+29.34	0.9998	C_F=−2.40×10$^{-4}T^2$+19.82×10^{-2}T+26.50	0.9982
20	C_W=7.38×10$^{-5}T^2$−9.10×10^{-2}T+27.99	0.9944	C_F=−5.06×10$^{-5}T^2$+4.04×10^{-2}T+59.86	0.9984
50	C_W=3.94×10$^{-5}T^2$−5.36×10^{-2}T+18.16	0.9970	C_F=−3.25×10$^{-5}T^2$+2.42×10^{-2}T+63.47	0.9992
80	C_W=4.60×10$^{-5}T^2$−6.32×10^{-2}T+21.70	0.9857	C_F=−3.34×10$^{-5}T^2$+3.09×10^{-2}T+60.55	0.9973
130	C_W=3.48×10$^{-5}T^2$−4.90×10^{-2}T+17.31	0.9960	C_F=−2.48×10$^{-5}T^2$+2.01×10^{-2}T+63.86	0.9986

Table 5
Allowable temperature ranges for the quality specification to be met

β (°C min^{-1})	T (°C) for C_W<0.5%	T (°C) for C_F≥61.0%
5	>495.3	≤521.8
10	>510.5	≤575.9
20	>529.1	≤769.1
50	>570.5	≤838.5
80	>581.5	≤910.3
130	>588.9	≤933.5

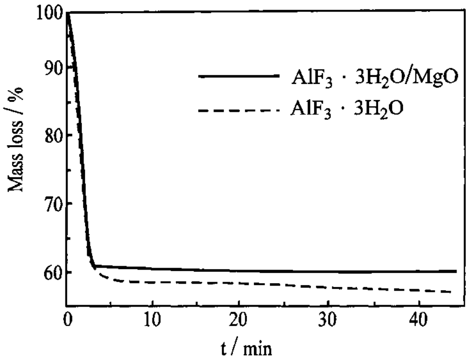

Fig. 4. Typical TG curve of $AlF_3{\cdot}3H_2O$ at 500°C.

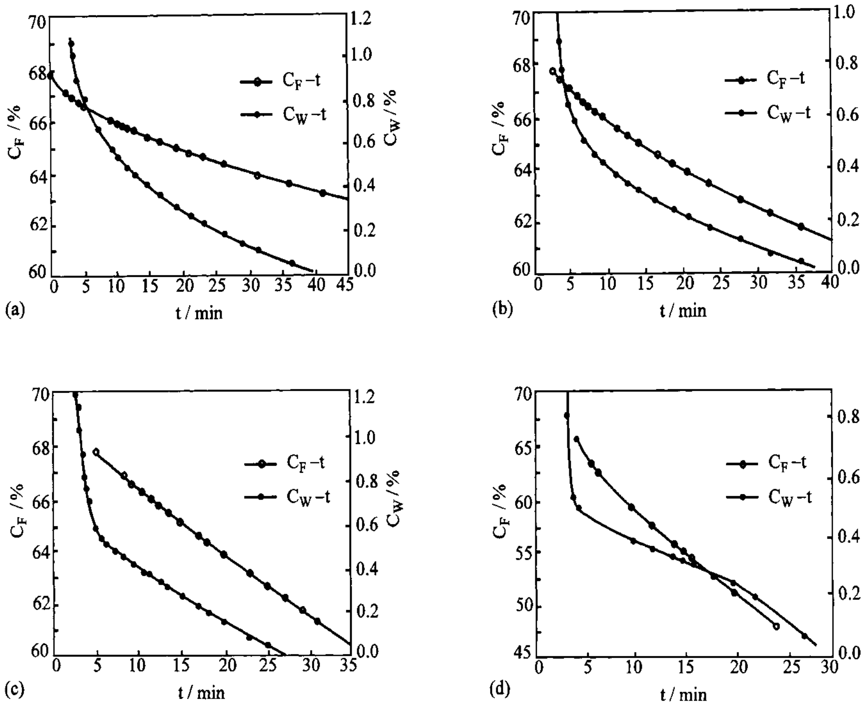

Fig. 5. 'C_F–t' and 'C_W–t' relationships of $AlF_3{\cdot}3H_2O$ at (a) 500°C; (b) 550°C; (c) 600°C; (d) 650°C.

Table 6
'C_F–t' and 'C_W–t' relationships of $AlF_3{\cdot}3H_2O$ under isothermal condition

T (°C)	C_F (%)–t (min)	$\lvert r\rvert$	C_W (%)–t (min)	$\lvert r\rvert$
500	C_F=66.97−9.73t (C_F: 60.0–46.5)	0.9909	C_W=1.53−40.96×10^{-2}ln$t$ (C_W: 0.10–1.20)	0.9979
550	C_F=67.66−17.64×$10^{-2}t$ (C_F: 60.0–67.0)	0.9924	C_W=1.11−29.73×10^{-2}ln$t$ (C_W: 0.10–0.70)	0.9947
			3.76−0.82t (C_W: 0.70–1.50)	0.9999
600	C_F=68.86−25.12×$10^{-2}t$ (C_F: 60.0–67.0)	0.9992	C_W=0.65−2.48×$10^{-2}t$ (C_W: 0.05–0.55)	0.9974
			2.11−0.32t (C_W: 0.55–1.20)	0.9999
650	C_F=68.69−91.78×$10^{-2}t$ (C_F: 50.0–66.0)	0.9959	C_W=0.58−1.83×$10^{-2}t$ (C_W: 0.20–0.55)	0.9849
			2.61−0.55t (C_W: 0.55–0.80)	0.9998

Table 7
The isothermal time necessary for the quality specifications to be met by constant temperature treatment

T (°C)	t (min)	
	for C_W<0.5%	for C_F≥61.0%
500	>12.36	≤61.36
550	>7.78	≤37.75
600	>6.05	≤31.29
650	>4.37	≤8.38

$$t > \exp(5.84 - 6.74 \times 10^{-3}T) \quad \text{for} \quad C_W < 0.5\% \quad |r| = 0.9923 \tag{4a}$$

$$t \leq 224.91 - 0.33T \quad \text{for} \quad C_F \geq 61.0\% \quad |r| = 0.9799 \tag{4b}$$

4. Conclusions

Three stages have been recognized in the thermal decomposition of $AlF_3{\cdot}3H_2O$.

For the first-stage dehydration, the values of E and A have been determined by experiments to be 41.9 kJ mol^{-1} and $10^{2.49}$ s^{-1} respectively.

The value of E and the most probable differential mechanism function for the second-stage dehydration are 47.5 kJ mol^{-1} and $(1-\alpha)$ respectively.

For the hydrolytic reaction of AlF_3, with water, the most probable differential mechanism function is in the form of $3/2(1-\alpha)[-\ln(1-\alpha)^{1/3}]$ and the value of E is 80.4 kJ mol^{-1}.

For the reason that the activation energy for the second-stage is significantly less than that for the third-stage it can be seen that the dehydration rate should be greater than the hydrolytic reaction rate. However, as the temperature further increases, the latter will increase more rapidly than the former.

Based on the TG-DTG measurements the technical conditions for heating $AlF_3{\cdot}3H_2O$ to the qualified AlF_3 have been recommended.

Measurements indicated that greater heating rate was beneficial to dehydration of $AlF_3{\cdot}3H_2O$ and manifested a relative suppression of hydrolytic defluorination. Higher degree of constant temperature resulted in more efficient dehydration of the $AlF_3{\cdot}3H_2O$ and more detrimental to preservation of fluorine.

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