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# Kinetics of thermal decomposition of lanthanum oxalate hydrate

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**Abstract:** Lanthanum oxalate hydrate  $La_2(C_2O_4)_3$ ·10H<sub>2</sub>O, the precursor of  $La_2O_3$  ultrafine powders, was prepared by impinging stream reactor method with PEG 20000 as surfactant. Thermal decomposition of  $La_2(C_2O_4)_3$ ·10H<sub>2</sub>O from room temperature to 900 °C was investigated and intermediates and final solid products were characterized by FTIR and DSC–TG. Results show that the thermal decomposition process consists of five consecutive stage reactions. Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods were implemented for the calculation of energy of activation (*E*), and the results show that *E* depends on *a*, demonstrating that the decomposition reaction process of the lanthanum oxalate is of a complex kinetic mechanism. The most probable mechanistic function,  $G(\alpha)=[1-(1+\alpha)^{1/3}]^2$ , and the kinetic parameters were obtained by multivariate non-linear regression analysis method. The average *E*-value that is compatible with the kinetic model is close to value which was obtained by FWO and KAS methods. The fitting curve matches the original TG curve very well.

Key words: lanthanum oxalate decahydrate; TG-DSC; thermal decomposition; multivariate non-linear regression analysis

# **1** Introduction

Sustainable technological development is strongly dependent on new materials with particular mechanical, chemical, electrical, magnetic, or optical properties. In order to address this challenge, interdisciplinary research technologies, to develop new materials, especially inorganic materials, to impart new functional properties and to provide new processing methods for the formation of useful objects are under intense focus [1,2].

Within the class of inorganic materials, oxides perform various functions [3]. The oxide ceramics are well known materials for technical applications, particularly in electronic and structural areas. The purity of these materials is extremely important. In the oxide class, lanthanum oxide ( $La_2O_3$ ) is one of the most widely studied oxide over the years. Lanthanum oxide has been widely applied to many industrial applications. For example, it is an important component of automobile exhaust-gas conversion [4], as a catalyst support in the formation of gas conversion catalyst [5] and as a catalyst of oxidative coupling of methane [6]. It is also used as a refractory oxide for calcium lights, optical glass [7] and in the formation of ceramics as a core for carbon arc electrodes [8]. However, as the raw material in these fields, synthesis of lanthanum oxide with good quality is very important [9]. The rare earth oxide can be prepared by oxalate thermal decomposition, but its characteristics on a great degree depend upon the calcining conditions. So monitoring of the process of oxalate thermal decomposition is an important issue [9].

BALBOUL et al [5] had reported that the characteristic of thermal decomposition of  $La_2(C_2O_4)\cdot 10H_2O$  to the onset of  $La_2O_3$  could be measured by thermogravimetry (TG) and different thermal analysis (DTA). The characteristics of the lanthanum oxalate decahydrate and the activation energy of the observed thermal processes were obtained by means of IR-spectroscopy, X-ray diffractometry and N<sub>2</sub>-adsorption isotherm, but kinetic of thermal analysis of various compounds is of major importance because of

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their frequent applications in calcination metallurgy and in the production of sorbents and catalysts with large-surface materials [10]. Unfortunately, most literatures rested on the understanding of the activation energy of the thermal processes and few people paid attention to the kinetics and the most probable model of thermal decomposition.

Compared with other methods, thermal decomposition process has many advantages, such as more effective control of size and shape of the particle, shorter preparation time and fewer impurities in the final product [11,12]. Thermal decomposition methods were preferably used to prepare the nanostructure ceramic materials [13,14]. In the future, the exploitation of such lanthanide oxide architectures by thermal decomposition may provide an opportunity of producing innovative ceramic materials with novel and tunable magnetic, electronic, or catalytic properties [15].

At present, the ultra-fine  $La_2O_3$  powder can be prepared by solid phase, hydrothermal synthesis, precipitation, sol-gel and micro-emulsion methods, respectively. Among these methods, precipitation method is used widely for its simplicity. High and uniform super-saturation is the key factor to affect the size of the "ultra fine" solid particles in precipitation. In order to obtain the high and uniform super-saturation, a kind of new reactor, submerged circulative impinging stream reactor (SCISR), was developed [16]. SCISR can do homogeneous micro-mixing. The impingement zone can create high and uniform super-saturation environment for precipitation to yield nuclei in a huge amount, while the non-mixing regions with much lower super-saturation favor helping deactivation of micro-crystal surfaces [16].

In this work, lanthanum oxalate hydrate (precursor) was prepared by SCISR method with PEG 20000 as surfactant. The thermal decomposition of  $La_2(C_2O_4)_3$ ·10H<sub>2</sub>O from room temperature to 900 °C in nitrogen gas was investigated by DSC–TG. Intermediates and final solid products were characterized by FTIR. The kinetics of decomposition was studied by implementing Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods and the most possible conversion function was simulated by the multiple non-linear regression method.

# **2** Experimental

### 2.1 Materials

Lanthanum nitrate hexahydrate  $(La(NO_3)_3 \cdot 6H_2O, 99.9\%, Aladdin, China)$ , ammonium oxalate monohydrate( $(NH_4)_2C_2O_4 \cdot H_2O$ , analytical reagent, Sinopharm Chemical Reagent Co., Ltd, China), and PEG 20000(analytical reagent, Sinopharm Chemical Reagent Co., Ltd, China) were used for the preparation of oxalate.

#### 2.2 Preparation of precursor

The precursor, lanthanum oxalate decahydrate, was prepared in SCISR. The sketch of the submerged circulative impinging stream reactor (SCISR) is shown in Fig. 1.



### Fig. 1 Sketch of SCISR

When the temperature was 40°C and the propellers rotated at 600 r/min, 625 mL of 0.1 mol/ L  $(NH_4)_2C_2O_4$ ·H<sub>2</sub>O solution, and 0.2165 g of PEG 20000 were mixed together and added into the reactor firstly, then 125 mL of 0.1 mol/L La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O solution, was added in drop. After 30 min, white precipitate of precursor was formed, filtrated and then washed with distilled water and absolute alcohol, respectively. After being dried in a vacuum oven at 70 °C and grinded in agate mortar, lanthanum oxalate decahydrate powder was obtained. The TEM (JEM–100CX II, Japan Electronics Co., Ltd., Japan) micrograph of La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O is shown in Fig. 2.



Fig. 2 TEM image of La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O

Figure 2 illustrates that many needle-shaped particles are in the size range of 5–100 nm. The obtained precursor was then heated at different temperatures ranging from room temperature to 900 °C. Intermediates and final solid products were characterized by FTIR (Thermo Nicolet 380, Thermo Scientific, America).

### 2.3 Thermal analysis

DSC-TG analyses (NETZSCH STA409PC, NETZSCH, Germany) of lanthanum oxalate were carried out at heating rates of 10, 15, 20, and 30 °C/min, from room temperature to 900 °C in a dynamic atmosphere of nitrogen (60 mL/min). The sample mass was about 5.5 mg. All records were corrected by the baseline subtraction (a run without pans under the same conditions).

## 2.4 FTIR analysis

FTIR spectra were obtained at a resolution of  $4 \text{ cm}^{-1}$  over the range of  $4000-400 \text{ cm}^{-1}$ . The spectra of intermediates and final products were obtained from thin (>20 mg/m<sup>2</sup>), lightly loaded (<1%) KBr-supported (KBr, Jasco, spectroscopy grade) discs.

### 2.5 XRD analysis

The products obtained at different temperatures were determined at room temperature using a powder X-ray diffractometer (XD–5A, Shimazu, Japan) with a scanning step of 0.04° in the  $2\theta$  range of 20°–70° (Cu K<sub> $\alpha$ </sub> radiation).

### 2.6 Thermal and kinetic analyses

The influence of different temperature regions upon the thermal behavior of chemical compounds can provide kinetic parameters indicating change in the reaction pathway. The complexity of a stage can be expressed from the activation energy (*E*) dependent on the extent of conversion ( $\alpha$ ). The activation energy can be obtained by isoconversional method. If *E* does not depend on  $\alpha$ , the investigated process is a simple one and should be described by a unique kinetic triplet. If not, the process is complex. In this work integral isoconversional methods were used to analyze the non-isothermal kinetics of the lanthanum oxalate.

The extent of conversion,  $\alpha$ , is defined by the following equation:

$$\alpha = (m_0 - m)/(m_0 - m_f) \tag{1}$$

where *m* is the mass of the sample at a given time *t*;  $m_0$  and  $m_f$  refer to masses at the beginning and the end.

The rate of solid-state non-isothermal decomposition reactions is expressed as [17–23]:

$$d\alpha/dT = (A/\beta) \exp[-E/(RT)]f(\alpha)$$
(2)

where *T* is the temperature;  $\beta$  is the linear heating rate;  $f(\alpha)$  is the reaction model depending on the reaction mechanism; *A* is the preexponential factor; *R* is the gas constant.

Rearranging Eq. (2) and integrating both sides of the equation lead to the following expression [24]:

$$g(\alpha) = (A/\beta) \int_{T_0}^T \exp[-E/(RT)] dT \approx (A/\beta) \int_0^T \exp[-E/(RT)] dT = AE/(\beta R)P(u)$$
(3)

Here,  $P(u) = \int_{\infty}^{u} -(e^{-u}/u^2) du$  and u = E/(RT).

Flynn-Wall-Ozawa method [25–30] was derived from the integral method. The technique assumes that A,  $f(\alpha)$  and E are independent of T while A and E are independent of  $\alpha$ , and then Eq. (3) is integrated to give the following equation:

$$\lg g(\alpha) = \lg(AE/R) - \lg \beta + \lg P[E/(RT)]$$
(4)

Using Doyle's approximation [31-34] for the integral which allows for *E/RT*>20, Eq. (3) can be simplified as:

lg 
$$\beta = lg[AE/(Rg(\alpha))] - 2.315 - 0.4567E/(RT)$$
 (5)

where  $g(\alpha)$  is considered a constant value. Thereupon, lg  $\beta$  has a linear relationship with 1/T and the activation energy can be obtained from the slope.

Kissinger-Aksahira-Sunose method [35–37] is an integral isoconversional method similar to the FWO method.

$$\ln(\beta/T^2) = \ln[AE/(Rg(\alpha))] - E/(RT)$$
(6)

The dependence of  $\ln(\beta/T^2)$  on 1/T, calculated for the same  $\alpha$  values at the different heating rates  $\beta$ , can be used to calculate the activation energy. TG data were selected under the different  $\beta$  and the same  $\alpha$ ,  $\lg(\beta/T^2)$ — 1/T curve was plotted, line slope was calculated by least square method and activation energy *E* was obtained from the slope.

# **3 Results and discussion**

### 3.1 Thermal decomposition process

DSC-TG curves corresponding to the thermal mass losses of the precursor at different heating rates, are shown in Fig. 3. All curves are approximately in the same shape, indicating that the mass loss is independent of the heating rate. It could be seen that there are five mass loss stages in the decomposition process.

At the first stage, a weak decomposition occurs in the temperature range of 25–226.2 °C ( $t_{max}$ =139.6 °C). The experimental mass loss (14.5%) of the first stage is very close to the theoretical mass loss (14.9%), which could be attributed to the evolution of six water molecules. The second stage beginning at about 226.2 °C and ending at 295.2 °C with a mass loss about 4.9% can be assigned to the loss of two water molecules with the increased temperature. The third stage occurs between 295.2 °C and 372.4 °C ( $t_{max}$ =329.2 °C) with a mass loss about 5.03%, indicating that the last two water molecules of lanthanum oxalate decahydrate are lost. The previous three stages of thermal decomposition process are expressed as follows:

$$La_2(C_2O_4)_3 \cdot 10H_2O \longrightarrow La_2(C_2O_4)_3 \cdot 4H_2O + 6H_2O$$
(7)

$$La_2(C_2O_4)_3 \cdot 4H_2O \longrightarrow La_2(C_2O_4)_3 \cdot 2H_2O + 2H_2O$$
(8)

$$La_2(C_2O_4)_3: 2H_2O \longrightarrow La_2(C_2O_4)_3 + 2H_2O$$
(9)

FTIR spectra of  $La_2(C_2O_4)_3$ ·10H<sub>2</sub>O and the intermediates heated at 140 and 250 °C are shown in Fig. 4. It can be seen that these three spectra are very similar, demonstrating that only water molecules are lost at the previous three mass loss stages [5].

The fourth stage locates approximately between 372.4 °C and 600 °C ( $t_{max}$ =410.2 °C) with a mass loss about 27.2%, which could be assigned to the decomposition of La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> into La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. The decomposition process is as follows:



Fig. 3 TG–DSC plots for precursor at different heating rates: (a) 10 K/min; (b) 15 K/min; (c) 20 K/min; (d) 30 K/min



Fig. 4 IR spectra of precursor and powders heated at different temperatures: (a) Precursor and intermediate; (b) Intermediate

$$La_2(C_2O_4)_3 \longrightarrow La_2O_2CO_3 + 3CO\uparrow + 2CO_2\uparrow$$
(10)

FTIR spectra of solid phases heated at 500 and 600 °C are shown in Fig. 4.

The broad absorption band peaks at 1501, 1450, 1357 and 851 cm<sup>-1</sup> are the indication of characteristic absorption peaks of the monoclinic IA system La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [10].

The fifth stage locates at approximately 600 and 745.6 °C ( $t_{max}$ = 708.3 °C) with a mass loss about 6.5%, which is account for the conversion of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> to La<sub>2</sub>O<sub>3</sub>. The decomposition reaction is as follows:

$$La_2O_2CO_3 \longrightarrow La_2O_3 + CO_2\uparrow$$
(11)

It can be seen from the FTIR spectra of 700 and 800 °C that the characteristic absorbance bands at about 649 cm<sup>-1</sup> is the La—O stretching vibration. The broad absorption band at about 3604 cm<sup>-1</sup> corresponding to hydroxyl stretching vibration is present, which may be due to the surface adsorbed water by nascent state La<sub>2</sub>O<sub>3</sub>.

Figure 5 indicates that the powders of  $La_2(C_2O_4)_3$ ·10H<sub>2</sub>O decomposed into different products after calcining at different temperatures for 3 h. Products calcined at 390 and 500 °C are  $La_2O_2CO_3$  powders and at 800, 900 °C are  $La_2O_3$  powders, according to JCPDS cards 54—0212 and 05—0602; while at 600, 700 °C there is no obvious diffraction peak of  $La_2O_2CO_3$  or  $La_2O_3$ . It is possible that at 500–800 °C most  $La_2O_2CO_3$  decomposed into  $La_2O_3$  but crystal of  $La_2O_3$  had not grown well.



Fig. 5 XRD patterns of powders heated at different temperatures

Based on the results above, thermal decomposition data of  $La_2(C_2O_4)_3 \cdot 10H_2O$  are listed in Table 1. It can be seen that the experimental values are consistent with the theoretical values for all stages.

### 3.2 Thermal decomposition kinetics

3.2.1 Activation energy

Applying Eqs. (5) and (6) on the TG data, plots of  $\lg \beta$  vs 1/T (FWO) and  $\ln(\beta/T^2)$  vs 1/T (KAS)

**Table 1** Thermal decomposition data of  $La_2(C_2O_4)_3 \cdot 10H_2O$ 

Temperature	Mass c	hange/%	Solid residue	
range/°C	Theoretical	Experimental		
e	data	data		
40-226.2	14.9	14.5	Hexahydrate	
226.2-295.2	4.99	4.9	Dihydrate	
295.2-372.4	4.99	5.03	Anhydrous oxalate	
372.4-600	23.8	27.2	$La_2O_2CO_3$	
600-745.6	6.09	6.5	$La_2O_3$	

corresponding to different  $\alpha$  can be obtained by a linear regress of least-square method, respectively. The FWO and KAS analysis results taken from the four TG measurements of the first endothermic peak are shown in Figs. 6 and 7, respectively. By the same way, the plots of the other peaks can be obtained. The activation energy *E* can be calculated from the slopes of the straight lines. If *E* value is independent of  $\alpha$ , the decomposition may be a simple reaction, otherwise, it is of multi-step reaction mechanism [38]. The average activation energies are calculated at those heating rates via the FWO and KAS methods in the  $\alpha$  range of 0.1–0.9, and tabulated and drawn in Table 2, Table 3 and Fig. 8, respectively.



**Fig. 6** lg  $\beta$ —1/*T* plots for *E* of the first endothermic peak by FWO method



**Fig. 7**  $\ln(\beta/T^2)$ —1/*T* plots for *E* of the first endothermic peaks KAS method

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~	1st		2nd		3rd		4th		5th	
a	$E/(kJ \cdot mol^{-1})$	R								
0.1	81.61	0.9477	83.44	0.9202	153.88	0.9888	230.06	0.9723	166.35	0.9352
0.15	84.49	0.9437	93.39	0.9586	155.52	0.9336	231.37	0.9643	168.11	0.9685
0.2	80.02	0.9186	98.12	0.9605	160.07	0.9970	226.45	0.9092	169.84	0.9257
0.25	76.55	0.9069	101.47	0.9687	163.36	0.9475	227.00	0.9461	169.49	0.9977
0.3	75.77	0.9384	109.69	0.9776	165.66	0.9778	220.73	0.9926	170.88	0.9988
0.35	72.69	0.9489	111.42	0.9838	163.30	0.9553	217.55	0.9042	175.49	0.9929
0.4	70.24	0.9454	115.89	0.9848	161.51	0.9732	206.60	0.9175	177.71	0.9786
0.45	69.38	0.9482	117.63	0.9882	159.27	0.9666	195.68	0.9236	177.94	0.9884
0.5	68.54	0.9463	123.27	0.9951	143.94	0.9326	181.82	0.9377	180.78	0.9847
0.55	67.04	0.9420	126.44	0.9956	141.19	0.9633	175.16	0.9525	183.06	0.9866
0.6	65.45	0.9376	126.38	0.9972	136.52	0.9962	167.28	0.9328	181.95	0.9759
0.65	64.73	0.9390	125.69	0.9967	140.38	0.9845	156.14	0.9228	183.84	0.9430
0.7	63.72	0.9415	127.42	0.9940	124.92	0.9633	146.82	0.9003	186.45	0.9172
0.75	62.65	0.9367	128.81	0.9977	121.56	0.9519	137.52	0.9746	187.51	0.9123
0.8	61.27	0.9301	130.46	0.9998	117.25	0.9200	130.11	0.9721	187.97	0.9094
0.85	59.18	0.9179	132.57	0.9986	121.83	0.9561	120.44	0.9161	191.28	0.9255
0.9	48.54	0.9016	132.80	0.9968	123.06	0.9404	113.65	0.9295	188.38	0.9384
Average	68.94	0.9347	116.76	0.9832	144.31	0.9617	181.43	0.9393	179.24	0.9576

**Table 2** Activation energies (*E*) based on FWO method with various extent of conversion ( $\alpha$ )

Table 3 Activation energies (E) based on KAS method with various extent of conversion (a)

	1st		2nd		3rd	3rd		4th		5th	
α	$E/(kJ \cdot mol^{-1})$	R									
0.1	79.43	0.9343	74.18	0.9625	152.07	0.9822	230.85	0.9238	158.48	0.9193	
0.15	82.33	0.9375	85.72	0.9632	153.72	0.9584	232.13	0.9469	160.30	0.9976	
0.2	77.55	0.9350	90.96	0.9635	158.44	0.9457	226.87	0.9948	162.09	0.9988	
0.25	73.83	0.9294	91.16	0.9639	161.84	0.9103	227.37	0.9339	161.69	0.9924	
0.3	72.96	0.9236	113.10	0.9651	164.19	0.9397	220.69	0.9836	163.12	0.9769	
0.35	69.66	0.9250	113.18	0.9852	161.65	0.9222	217.27	0.9953	167.95	0.9872	
0.4	67.04	0.9277	113.49	0.9929	159.69	0.9572	205.67	0.9091	170.24	0.9828	
0.45	66.09	0.9215	113.59	0.9929	157.28	0.9976	194.10	0.9149	170.47	0.9848	
0.5	65.16	0.9129	113.96	0.9843	141.09	0.9490	179.44	0.9301	173.42	0.9723	
0.55	63.55	0.9967	119.64	0.9846	138.13	0.9963	172.35	0.9462	175.79	0.9341	
0.6	61.84	0.9685	138.66	0.9852	133.17	0.9226	163.98	0.9231	174.59	0.9039	
0.65	61.06	0.9797	138.56	0.9931	137.16	0.9008	152.18	0.9110	176.55	0.9982	
0.7	59.96	0.9253	119.56	0.9934	120.85	0.9107	142.28	0.9846	179.27	0.9947	
0.75	58.80	0.9394	119.59	0.9939	117.25	0.9018	132.40	0.9549	180.35	0.9131	
0.8	57.31	0.9349	119.67	0.9558	112.66	0.9654	124.49	0.9539	180.79	0.9282	
0.85	55.03	0.9051	138.88	0.9143	117.42	0.9982	114.18	0.9947	184.22	0.9496	
0.9	43.64	0.9907	138.85	0.9452	118.67	0.9323	106.89	0.9077	181.11	0.9335	
Average	65.60	0.9404	114.28	0.9728	141.49	0.9465	179.01	0.9476	171.79	0.9628	



Fig. 8 Dependence of apparent value E on  $\alpha$ 

The activation energy values calculated by FWO method are close to the ones obtained by KAS method. And it also could be seen that E depends on  $\alpha$ , demonstrating that the decomposition reaction process of the lanthanum oxalate is of a complex kinetic mechanism [38]. For this multi-step reaction, FWO and KAS methods cannot obtain the accurate mathematical model and kinetic parameters of those thermal decomposition processes. So the most probable model and the kinetic parameters should be obtained by multivariate non-linear regression method [38]. The difference between the values of the activation energy obtained by FWO and KAS methods may be attributed to the different approximations of the temperature integral

### they use [39].

3.2.2 Determination of probable mechanism

For a one-step reaction, the most probable model can be obtained by multivariate linear regression method but for a multi-step reaction, the most probable model should be obtained by multivariate non-linear regression method [38]. Multivariate non-linear regression is based on multiple heating rates by making the assumption that the parameters of the model are identical for measurements at all heating rates [37]. Compared with the single curve analysis, the quality of fit diminishes considerably for the non-applicable reaction types [37]. So the distinguishing ability between the individual reaction types improves drastically. In addition, there are no limitations with respect to the complexity of the model, and consequently it can be applied to multi-step reactions. Nonlinear regression allows a direct fit of the model to the experimental data without a transformation, which would distort the error structure.

The basic hypothesis of this method is that the

kinetic parameters, E and  $\lg A$ , do not change with reaction rate  $\alpha$ , therefore, we can use the hypothetical model to obtain the parameter values (E and  $\lg A$ ) from fitting the original data by multivariate non-linear regression method. Finally, the model, in which the correlation coefficient R is approximate to 1 and E values are comparable to those by FWO and KAS methods, is the most probable mechanism. The entire process, multivariate non-linear regression method, which is one of the multiple scanning methods, is discussed in this paper to obtain the most probable model one by one. As it is very hard to separate the thermal decomposition process of lanthanum oxalate decahydrate that has no obvious mass loss platform in five one-stage processes, the consecutive reaction model  $(A \rightarrow B \rightarrow C \rightarrow D)$  by multivariate non-linear regression method was used for the determination of the most probable model to calculate the kinetic model of Table 4 [40,41]. The calculated values of E, lg A and kinetic model fitted for every stages are presented in Table 5. It can be seen that the thermal

l'able 4 Ku	hetic function of $g(\alpha)$ used for present	analysis	
No.	Function name	$g(\alpha)$	Mechanism
1	Parabola law	$\alpha^2$	1-dimensional, 1D
2	Valensi equation	$\alpha + (1+\alpha)\ln(1-\alpha)$	2-dimensional, 2D
3	Ginstling-Brounstein equation	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	3-dimensional, 3D; cylindrical symmetry
4	Jander equation	$[1-(1-\alpha)^{1/3}]^2$	3-dimensional, 3D; spherical symmetry
5	Anti-Jander equation	$[(1+\alpha)^{1/3}-1]^2$	3-dimensional, 3D
6	Zhuralev,Lesokin and Tempelman equation	$[\{1/(1-\alpha)^{1/3}\}-1]^2$	3-dimensional, 3D
7	Avrami-Erofeev equation, <i>n</i> =1	$-\ln(1-\alpha)$	Assumed random nucleation and its subsequent growth
8	Avrami-Erofeev equation, n=1.5	$[-\ln(1-\alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth
9	Avrami-Erofeev equation, <i>n</i> =2	$[-\ln(1-\alpha)]^{1/2}$	Assumed random nucleation and its subsequent growth
10	Avrami-Erofeev equation, <i>n</i> =3	$[-\ln(1-\alpha)]^{1/3}$	Assumed random nucleation and its subsequent growth
11	Avrami-Erofeev equation, <i>n</i> =4	$[-\ln(1-\alpha)]^{1/4}$	Assumed random nucleation and its subsequent growth
12		$1 - (1 - \alpha)^{1/2}$	Contracting sphere(spherical symmetry)
13		$1 - (1 - \alpha)^{1/3}$	Contracting sphere(spherical symmetry)
14	Mampel power law	α	Chemical reaction
15-17	Mampel power law	$\alpha^{1/2}, \alpha^{1/3}, \alpha^{1/4}$	
18	Second order	$(1-\alpha)^{-1}-1$	Chemical reaction
19		$(1-\alpha)^{-1/2}$	Chemical reaction
20		$\alpha^{2/3}$	
21	Exponential law	$\ln \alpha$	
22	Prount-Tomkins	$\ln[\alpha/(1-\alpha)]$	Branching nuclei
23		$[-\ln(1-\alpha)]^2$	
24		$\left[-\ln(1-\alpha)\right]^3$	
25		$\left[-\ln(1-\alpha)\right]^4$	
26	Third order	$[1/(1-\alpha)]^2$	
27		$1 - (1 - \alpha)^{1/4}$	
28		$1 - (1 - \alpha)^2$	
29		$1 - (1 - \alpha)^3$	
30		$1 - (1 - \alpha)^4$	
31		$[1-(1-\alpha)^{1/3}]^{1/2}$	
32		$[1-(1-\alpha)^{1/2}]^{1/2}$	

decomposition process of lanthanum oxalate decahydrate is a kind of five-stage consecutive reaction, which has the same reaction model and the dominant function of the possible mechanism is  $g(\alpha)=[1-(1+\alpha)^{1/3}]^2$  which indicates that the thermolysis mechanism is three-dimensional spherical symmetry diffusion. The kinetic parameters of the first stage are E=65.47 kJ/mol,  $lg(A/s^{-1})=-1.6$ ; the second stage E=

106.9 kJ/mol,  $lg(A/s^{-1})=-0.1$ ; the third stage E=120.9 kJ/mol,  $lg(A/s^{-1})=-0.183$ ; the fourth stage E=177.68 kJ/mol,  $lg(A/s^{-1})=2.27$ ; the fifth stage E=156.4 kJ/mol,  $lg(A/s^{-1})=-2.54$ . The plots fitted with the best model are presented in Fig. 9. The average *E*-values matching with the kinetic model are close to values obtained by FWO and KAS methods. This fitting accuracy is acceptable.

$\beta/(K \cdot min^{-1})$	Stage	Function	$E/(kJ \cdot mol^{-1})$	$lg(A/s^{-1})$	R
	1st		64.71	-1.45	0.9997
	2nd		100.7	-0.45	0.9999
10	3rd	$g(\alpha) = [1 - (1 + \alpha)^{1/3}]^2$	110.1	-1	0.9999
	4th		173.09	2.14	0.9997
	5th		172	-1.6	0.9999
	1st		66.71	-1.37	0.9997
	2nd		102.3	-0.45	0.9998
15	3rd	$g(\alpha) = [1 - (1 + \alpha)^{1/3}]^2$	122.6	0.07	0.9999
	4th		177.01	2.28	0.9998
	5th		156.9	-2.5	0.9999
	1st		65.45	-1.72	0.9998
	2nd		112.8	0.37	0.9999
20	3rd	$g(\alpha) = [1 - (1 + \alpha)^{1/3}]^2$	125.2	0.21	0.9999
	4th		177.57	2.26	0.9998
	5th		159.1	-2.47	0.9999
30	1st		65.01	-1.85	0.9998
	2nd		111.7	0.13	0.9999
	3rd	$g(\alpha) = [1 - (1 + \alpha)^{1/3}]^2$	125.6	-0.012	0.9999
	4th		183.03	2.4	0.9998
	5th		137.75	-3.6	0.9999
	1st		65.47	-1.6	0.9998
	2nd		106.9	-0.1	0.9999
Average	3rd	$g(\alpha) = [1 - (1 + \alpha)^{1/3}]^2$	120.9	-0.183	0.9999
	4th		177.68	2.27	0.9998
	5th		156.4	-2.54	0.9999

Table 5 Kinetic parameters by different mechanism



Fig. 9 Multiple non-linear regression results of TG curve: (a) Original TG curve; (b) Fitting TG curve

# **4** Conclusions

1) The thermal decomposition process of lanthanum oxalate decahydrate is a kind of five-stage consecutive reaction.

2) The activation energy values calculated by FWO method are close to the ones obtained by KAS method. *E* is depends on  $\alpha$ , demonstrating that the decomposition reaction process of the lanthanum oxalate is of a complex kinetic mechanism.

3) For a multi-step reaction, the most probable model and the kinetic parameter should be obtained by multivariate non-linear regression method. The most probable mechanism function is  $g(\alpha)=[1-(1+\alpha)^{1/3}]^2$ . The kinetic parameters of the first stage are E=65.47 kJ/mol,  $lg(A/s^{-1})=-0.1$ ; the second stage E=106.9 kJ/mol,  $lg(A/s^{-1})=-0.183$ ; the fourth stage E=177.68 kJ/mol,  $lg(A/s^{-1})=-2.27$ ; the fifth stage E=156.4 kJ/mol,  $lg(A/s^{-1})=-2.54$ . The fitting curve matches with the original TG curve very well.

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# 水合草酸镧的热分解动力学

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**摘 要:** 以 PEG 20000 为表面活性剂在撞击流反应器中制备 La<sub>2</sub>O<sub>3</sub> 超细粉体的前驱体十水草酸镧 (La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O)。在室温至 900 ℃ 下研究 La<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O 的热分解过程,通过 FTIR 和 DSC-TG 对其反应 中间物及最终固体产物进行分析。结果表明,该热分解过程由 5 个连续的反应阶段组成。采用 Flynn-Wall-Ozawa (FWO)和 Kissinger-Akahira-Sunose (KAS)法对活化能 *E* 进行求取,结果显示 *E* 值随着 *a* 的变化而变化,说明草酸 镧的分解为复杂的热分解过程。采用多元非线性回归分析法对动力学方程和相关动力学参数进行拟合,得到动力 学模型为 *G*(*a*)=[1-(1+*a*)<sup>1/3</sup>]<sup>2</sup>。采用该动力学模型求得的活化能平均值与采用 FWO 法和 KAS 法计算而得的活化能 平均值十分接近,其拟合曲线与样品的热重分析曲线吻合。

关键词: 十水草酸镧; TG-DSC; 热分解; 多元非线性拟合

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