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COMPARATIVE METHOD TO EVALUATE RELIABLE KINETIC TRIPLETS OF THERMAL DECOMPOSITION REACTIONS

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Abstract

Reliable kinetic information for thermal analysis kinetic triplets can be determined by the comparative method: (1) An iterative procedure or the KAS method had been established to obtain the reliable value of activation energy E_a of a reaction. (2) A combined method including Coats–Redfern integral equation and Achar differential equation was put forward to confirm the most probable mechanism of the reaction and calculate the pre-exponential factor A. By applying the comparative method above, the thermal analysis kinetic triplets of the dehydration of $CaC_2O_4{\cdot}H_2O$ were determined, which apparent activation energy: 81±3 kJ mol^{-1}, pre-exponential factor: $4.51{\cdot}10^6$–$1.78{\cdot}10^8$ s^{-1}, the most probable mechanism function: $f(\alpha)=1$ or $g(\alpha)=\alpha$, which the kinetic equation of dehydration is $\mathrm{d}\ \ /\mathrm{d}t=A\mathrm{e}^{-E_a/RT}$.

Keywords: calcium oxalate monohydrate, comparative method, dehydration, kinetic triplets, non-isothermal kinetic

Introduction

In the field of thermal analysis kinetic, one of the main targets of researchers is to find the probable mechanism of the solid-state reaction and to determine the kinetic parameters E_a and A simultaneously. The conventional single scan method, which cannot detect the complex nature of the solid-state reaction, has been replaced by multiple scan method or iso-conversional method. Among the iso-conversional methods, Ozawa method [1] and Kissinger–Akahira–Sunose (KAS) method [2, 3] have been widely used to estimate activation energies regardless of the rate expressions of the reactions. But both these two methods are based on the assumption concerning the temperature integral, which will bring the homologous error. This paper describes a comparative method to investigate the reliable kinetic triplets. The first step was to obtain the reliable value of activation energy E_a by an iterative procedure [4, 5] or the KAS method. The second step is to use a combined method, including Coats–Redfern

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integral equation [6, 7] and Achar differential equation [8] to determine the most probable mechanism function of a reaction and calculate the pre-exponential factor *A*. Typical thirty-one kinds of kinetic model of the thermal decomposition [9] were applied in these two equations, respectively. The dehydration of oxalates is interesting for kinetics study because the basic advantage of oxalates as precursors is low temperature of decomposition [10, 11]. On the basis of many thermoanalytical studies on the dehydration processes [10–15], many crystal salt hydrates are well known as a type of $M_aX_b{\cdot}nH_2O$. These hydrates lose crystalline water by a type of dissociation reaction, i.e., dehydration reaction [16]. In this experiment $CaC_2O_4{\cdot}H_2O$ was selected to be studied by the proposed method using differential scanning calorimetry (DSC) and the result is satisfactory.

Theoretical

Calculation of activation energy E_a

Thermal decomposition of solid-state material is subjected to general Eq. (1):

$$\frac{\mathrm{d}}{\mathrm{d}t} \quad A\mathrm{e}^{-E_a/RT} f(\quad) \tag{1}$$

where $f(\alpha)$ is differential expression of kinetic function, α is the reaction fraction of decomposition, E_a and A are so-called activation energy and pre-exponential factor, respectively, and R is the gas constant.

By the usual change of the variable time into temperature, Eq. (1) becomes

$$\frac{\mathrm{d}}{\mathrm{d}T} \quad \frac{1}{\quad}A\mathrm{e}^{-E_a/RT} f(\quad) \tag{2}$$

where $\beta=\mathrm{d}T/\mathrm{d}t$ is the heating rate. In most experiments the heating rate is kept constant. Rearranging Eq. (2), one obtains:

$$\frac{\mathrm{d}}{f(\quad)} \quad \frac{1}{\quad}A\mathrm{e}^{-E_a/RT}\mathrm{d}T \tag{3}$$

From Eq. (3), Ozawa equation and KAS equation are deduced.

Ozawa equation:

$$\ln \quad \ln\frac{0.0048AE_a}{g(\quad)R} \quad 1.0516\frac{E_a}{RT} \tag{4}$$

KAS equation

$$\ln\frac{}{T^2} \quad \ln\frac{AE_a}{g(\quad)R} \quad \frac{E_a}{RT} \tag{5}$$

where $g(\alpha)$ is integral expression of kinetic function. These two methods of plotting a linear regressive curve at the same fractional conversion α, different heating rates β are the so-called isoconversional methods. The plots of $\ln\beta$ *vs*. $1/T$ in Eq. (4) and $\ln(\beta/T^2)$ *vs*. $1/T$ in Eq. (5) have been proved to give the activation energies. In practice, mechanism of the reaction cannot be considered in the isoconversional methods for calculating of activation energy. Moreover these equations are both based on the assumption concerning the temperature integral, which will make the result unreliable.

Iterative procedure is used to calculate the approximate value of E_a approach to the exact value, the equation is [5]:

$$\ln\frac{\quad}{H(x)} \quad \ln\frac{0.0048AE_a}{g(\quad)R} \quad 1.0516\frac{E_a}{RT} \tag{6}$$

$$\ln\frac{\quad}{h(x)T^2} \quad \ln\frac{AE_a}{g(\quad)R} \quad \frac{E_a}{RT} \tag{7}$$

where $x=E_a/RT$, β is the heating rate of a linear temperature-programmed process.

The iterative procedure is as follows.

- Supposing $h(x)=1$ or $H(x)=1$ to estimate the initial value of the activation energy E_{a1}. The conventional isoconversional methods stop calculating at this step.
- Using E_{a1} to calculate $H(x)$ or $h(x)$, then from Eq. (6) or Eq. (7) to calculate a new value E_{a2} for the activation energy from the plot of $\ln[\ /H(x)]$ *vs*. $1/T$ or $\ln[\beta/h(x)T^2]$ *vs*. $1/T$.
- Repeating step 2, replacing E_{a1} with E_{a2}. When $E_{ai}-E_{ai-1}<0.01$ kJ mol^{-1}, the last value E_{ai} is the exact value of activation energy of the reaction.

Determination of the most probable mechanism function

Coats–Redfern integral equation [6, 7]

Integrating both sides of Eq. (3), one obtains:

$$\ln\frac{g(\quad)}{T^2} \quad \ln\frac{AR}{\quad E_a} \quad \frac{E_a}{RT} \tag{8}$$

Plotting $\ln[g(\alpha)/T^2]$ *vs*. $1/T$, a straight line is given. The activation energy E_a and pre-exponential factor A can be obtained from the slope $-E_a/R$ and the intercept $\ln(AR/\beta E_a)$.

Achar differential equation [8]

$$\ln\left[\frac{1}{f(\quad)}\frac{\mathrm{d}\quad}{\mathrm{d}T}\right] \quad \ln(A/\quad) \quad E_a/RT \tag{9}$$

The values of E_a, $\ln A$ and the linear correlation coefficients r are calculated from the linear least-squares plot of $\ln\{[1/f(\alpha)][\mathrm{d}\alpha/\mathrm{d}T]\}$ *vs*. $1/T$, which the slope is equal to $-E_a/R$ and the intercept is equal to $\ln(A/\beta)$.

Estimation of the probable mechanism function of reaction and calculation of A

The basic parameters of T, α and $d\alpha/dT$ were obtained from the DSC curves. The basic data and kinetic mechanism functions $f(\alpha)$ and $g(\alpha)$ were inserted into Eqs (8) and (9), respectively. The kinetic analysis was completed with the linear least-squares method. Comparing the kinetic parameters from these two equations, the probable kinetic model may be selected, which the calculated values of E_a and $\ln A$ were close to each other with the better linear correlation coefficient and the activation energies obtained from the two equations above were showing good agreement to those obtained from iterative procedure or KAS method with smaller experimental errors. It can be found that the calculation error of the differential equation is bigger than that of the integral equation. So the pre-exponential factor A can be obtained by calculating the average value of $\ln A(\mathrm{s}^{-1})$ from Eq. (8) for different heating rates.

Experimental

Material

Calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) under investigation was provided by Beijing Chemical Plant (China). Its purity is larger than 99.5%.

Instrumental

DSC analysis was performed on a Mettler-Toledo DSC822^e (Co., Switzerland). Samples (3.45–3.55 mg) were placed in the aluminum pans with lids which were all

Table 1 Temperatures corresponding to conversion degrees at various heating rates (5, 6, 7, 8, 10 K min^{-1})

Conversion degree/α	Heating rate/K min^{-1}				
	5	6	7	8	10
			T/K		
0.10	425	427	429	432	436
0.20	436	439	442	445	449
0.30	444	447	450	453	458
0.40	450	453	456	459	464
0.50	454	458	460	464	469
0.60	458	462	464	468	473
0.70	461	465	468	471	476
0.80	464	468	471	474	479
0.90	467	471	474	477	482

made hole. The temperature was recorded from 375 to 550 K, with heating rates of 1, 2, 4, 5, 6, 7, 8, 10, 15, 20, 25 K min^{-1}, respectively, under the nitrogen flow of about 20 mL min^{-1}.

Experimental data

The basic data collected from the DSC curves of the dehydration of calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$) at different heating rates are shown in Tables 1, 2.

The DSC curves of the dehydration of $CaC_2O_4{\cdot}H_2O$ at different heating rates and the curves of temperatures corresponding to the same conversion degrees under various heating rates are shown in Figs 1 and 2, respectively.

Table 2 The basic data of α, *T* and dα/d*T* obtained from one DSC curve at the heating rate of 5 K min^{-1}

α	*T*/K	dα/d*T*·10^{-2}
0.10	425	0.006441
0.20	436	0.011012
0.30	444	0.015360
0.40	450	0.019853
0.50	454	0.024434
0.60	458	0.028780
0.70	461	0.032586
0.80	464	0.035209
0.90	467	0.034448

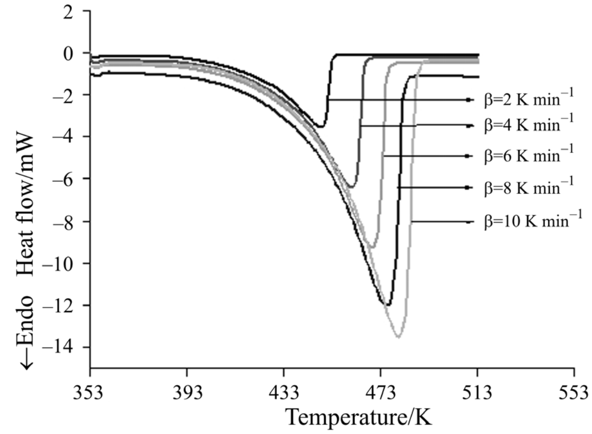

Fig. 1 DSC curves of the dehydration of calcium oxalate monohydrate at different heating rates

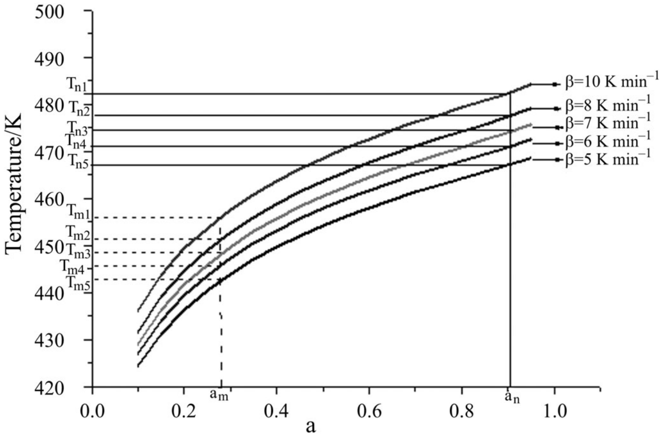

Fig. 2 The curves of temperatures corresponding to the same conversion degrees at various heating rates

Result and discussion

Calculation of activation energy E_a

The basic parameters in Table 1 were inserted into the Eqs (2), (5)–(7). Then the activation energies of the dehydration of $CaC_2O_4 \cdot H_2O$ were obtained. The results are listed in Table 3.

As shown in Table 3, the calculated values of E_a show a considerable accordance nearly for all the methods. The Ozawa method is an exception that gives, in

Table 3 The activation energies for the dehydration of calcium oxalate monohydrate at different heating rates (β=5, 6, 7, 8, 10 K min^{-1}) from different methods

Conversion degree/α	E_a/kJ mol^{-1}			
	KAS method	Ozawa method	$\ln[\beta/h(x)T^2]$ *vs.* $1/T$	$\ln[\beta/H(x)]$ *vs.* $1/T$
0.10	83.03	85.79	83.31	83.31
0.20	79.57	82.45	79.91	79.90
0.30	78.27	81.78	78.59	78.59
0.40	77.89	80.32	78.14	78.15
0.50	77.58	80.83	77.91	77.90
0.60	77.54	80.51	77.91	77.94
0.70	77.42	80.66	77.75	77.76
0.80	77.19	80.52	77.54	77.54
0.90	76.58	79.14	76.94	76.93
average	78.34	81.33	78.67	78.67

comparison with the other methods, considerably higher values of E_a. Then, it can be concluded that the values of activation energy obtained from iterative method or KAS method are more reliable and these methods can be used in the determination of the values of E_a with satisfactory accuracy. So the suggestion that the values obtained from these two methods determine the range of the activation energies is reasonable. While the heating rates are 5, 6, 7, 8, 10 K min^{-1}, within the range α=0.10–0.90, the values of E_a is equal to 81±3 kJ mol^{-1}.

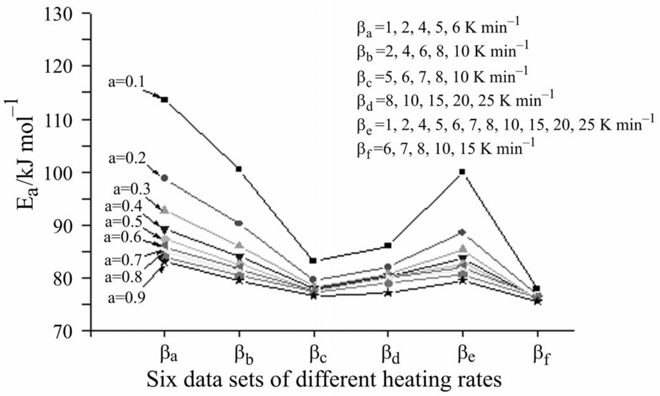

Fig. 3 The influence of different heating rate groups on the values of E_a from KAS method

The influence of the heating rate group on the value of activation energy

In order to discuss the influence of the heating rate group on the activation energy, the data of eleven heating rates were assorted to six groups randomly. The curves of E_a corresponding to the six groups of experimental data within the range of α from 0.10 to 0.90 are shown in Fig. 3. All the values of E_a were obtained from KAS method. Obviously, if the data sets including the minimum value of heating rates (β=1.0 K min^{-1}), the deviation of E_a from the 'real' value is relatively big. In such a way, it is shown that for $0.20 \leq \alpha \leq 0.80$, the values of activation energies calculated from various data sets of heating rates vary small. The values of E_a for the data set (β_d=5, 6, 7, 8, 10 K min^{-1}) are moderate. Left the values with big deviation aside, within the range of α from 0.20 to 0.80, the activation energies obtained from the six groups of heating rates are equal to 81±3 kJ mol^{-1}. Consequently, in this range of heating rates, the moderate value of β is better than the undersize value.

Estimation of the mechanism of reaction

The basic data α, T and dα/dT and the 31 different $f(\alpha)$ and $g(\alpha)$ were inserted into Eqs (8) and (9). The kinetic parameters E_a, A and the linear correlation coefficients r were calculated by the linear least squares method. The results and the relative error to the values of E_a obtained from iterative method are shown in Table 4. Furthermore,

Table 4 Non-isothermal kinetic parameters obtained from Coats–Redfern integral equation and Achar differential equation for =5 K min^{-1}

No.	Coats–Redfern integral equation				Achar differential equation			
	E_a/ kJ mol^{-1}	ln$A$/ s^{-1}	r	Error	E_a/ kJ mol^{-1}	ln$A$/ s^{-1}	r	Error
1	162.47	36.79	0.9998	1.0652	154.65	34.72	0.9992	0.9658
2	179.83	41.05	0.9997	1.2859	185.77	42.71	0.9985	1.3614
3	201.49	45.70	0.9971	1.5612	223.17	51.61	0.9903	1.8368
4	186.97	41.57	0.9991	1.3766	198.67	44.79	0.9962	0.5254
5	146.44	29.94	0.9989	0.8614	131.81	26.04	0.9971	0.6755
6	250.49	59.55	0.9854	2.1841	296.67	72.06	0.9710	2.7711
7	108.64	23.27	0.9918	0.3810	143.21	32.69	0.9674	0.8204
8	69.96	12.67	0.9913	–0.1107	104.51	22.12	0.9542	0.3288
9	50.60	7.26	0.9905	–0.3568	85.17	16.75	0.9417	0.0826
10	31.26	1.70	0.9892	–0.6026	65.82	11.27	0.9197	–0.1633
11	1.59	–1.21	0.9872	–0.9798	56.15	8.44	0.9017	–0.2861
12	99.81	19.34	0.9958	0.2687	124.83	26.19	0.9773	0.5868
13	97.04	18.82	0.9969	0.2335	118.70	24.77	0.9808	0.5088
14	91.70	17.68	0.9986	0.1656	106.45	21.77	0.9879	0.3531
15	77.52	14.25	0.9998	–0.0146	69.71	12.23	0.9971	–0.1139
16	120.00	25.59	0.9998	0.5254	112.18	23.54	0.9987	0.4260

Table 4 Continued

No.	Coats–Redfern integral equation				Achar differential equation			
	E_a/ kJ mol^{-1}	ln$A$/ s^{-1}	r	Error	E_a/ kJ mol^{-1}	ln$A$/ s^{-1}	r	Error
17	35.04	2.55	0.9995	–0.5546	27.23	0.64	0.9833	–0.6539
18	20.89	–1.60	0.9997	–0.7345	13.07	–3.40	0.9355	–0.8339
19	13.79	–3.83	0.9994	–0.8247	5.99	–3.50	0.7743	–0.9239
20	128.46	28.25	0.9804	0.6329	179.95	42.22	0.9513	1.2874
21	66.06	12.74	0.8453	–0.1603	216.70	53.14	0.9392	1.7545
22	203.09	50.79	0.9382	1.5815	290.20	74.28	0.9229	2.6888
23	56.09	8.60	0.9868	–0.2870	–3.79	–7.53	–0.0815	–1.0481
24	41.40	4.55	0.9598	–0.4736	–77.29	–27.57	–0.6592	–1.9825
25	31.05	1.59	0.9239	–0.6053	–150.79	–47.73	–0.7575	–2.9167
26	224.71	54.47	0.9922	1.8564	259.28	63.86	0.9808	2.2958
27	340.78	85.36	0.9924	3.3318	375.34	94.74	0.9850	3.7711
28	456.84	116.13	0.9925	4.8070	491.42	125.51	0.9871	5.2466
29	42.13	4.37	0.9983	–0.4645	56.89	8.54	0.9700	–0.2769
30	44.79	4.97	0.9963	–0.4307	41.97	4.19	0.9887	–0.4665
31	190.83	43.48	0.9986	1.4257	205.58	47.52	0.9945	1.6132

Table 5 The kinetics parameters from differential method and integral method at the eleven heating rates

β/kJ min^{-1}	Function No.	Coats–Redfern integral equation				Achar differential equation			
		E_a/kJ mol^{-1}	ln$A$/s^{-1}	r	Error	E_a/kJ mol^{-1}	ln$A$/s^{-1}	r	Error
1	15	94.33	19.00	0.9981	0.1991	75.31	13.65	0.9979	–0.0427
2	15	86.46	16.72	0.9991	0.0990	73.13	13.08	0.9977	–0.0704
4	15	80.95	15.20	0.9995	0.0290	70.95	12.57	0.9976	–0.0981
5	15	77.52	14.25	0.9998	–0.0146	69.71	12.23	0.9971	–0.1139
6	15	75.82	13.79	0.9999	–0.0362	69.63	12.22	0.9966	–0.1149
7	15	75.26	13.66	0.9998	–0.0433	68.43	11.93	0.9947	–0.1302
8	15	75.04	13.59	0.9999	–0.0460	68.50	11.95	0.9948	–0.1293
10	15	75.76	13.78	0.9998	–0.0370	69.61	12.26	0.9955	–0.1152
15	15	74.88	13.55	0.9998	–0.0482	67.90	11.85	0.9903	–0.1396
20	15	73.05	13.10	0.9999	–0.0714	65.95	11.39	0.9870	–0.1617
25	15	72.61	13.02	0.9997	–0.0770	63.66	10.86	0.9750	–0.1908

when the ‘real’ kinetic model is determined, the activation energies obtained from KAS method or iterative method will conform to those obtained from Eqs (8) and (9) with small relative errors. Comparing the data in Table 4 with those in Table 3, function No. 15, namely, $f(\alpha)=1$ or $g(\alpha)=\alpha$ is the most probable mechanism function of the dehydration of $CaC_2O_4\cdot H_2O$.

Similarly, the results for other heating rates display the same trend. The possible kinetic models and respective kinetic parameters from differential and integral equations at various heating rates are shown in Table 5. We find that the differential form for the dehydration of $CaC_2O_4\cdot H_2O$ is $f(\alpha)=1$ and the integral form is $g(\alpha)=\alpha$, the Mample power law mechanism, in which n is equal to 1. It is not difficult to find that the results obtained by using the method we proposed have the uniqueness.

Calculation of the pre-exponential factor A

As shown in Table 5, the range of A is from 4.51 10^6 to 1.78 10^8 s^{-1}.

Comparison with Popescu method [17]

Popescu method is to investigate the kinetics and mechanism of reactions based on the use of the degree of conversion measured at the same tempertures on curves recorded for a reaction carried out at various heating rates. Two data sets of different heating rates were selected randomly. One typical plot in (α, T) coordinates of the experimental data from Table 6 which the heating rates are 5, 6, 7, 8, 10 K min^{-1} is given in Fig. 4, where α_m, α_n are two different degrees of conversion and T_m, T_n are their corresponding temperatures. Analytical forms of various functions, differential form $f(\alpha)$ and integral form $g(\alpha)$ are listed in Table 7. This method was to estimate the mechanism function by judging the best values of correlation coefficient corresponding to the kinetic functions in Table 7. The results of the two data sets are shown in Tables 8, 9.

Table 6 Conversion degrees corresponding to various temperatures at different heating rates (β=5, 6, 7, 8, 10 K min^{-1})

Temperature/K	Heating rates/K min^{-1}				
	5	6	7	8	10
	α/%				
435	18.6	15.9	14.0	12.0	9.3
440	24.4	20.8	18.4	15.8	12.3
445	31.7	26.9	23.7	20.5	16.1
450	40.7	34.4	30.4	26.3	20.8
455	52.0	43.7	38.6	33.4	26.6
460	66.1	55.5	49.0	42.3	33.6
465	83.0	70.0	61.8	53.3	42.4
470	98.5	87.0	77.1	66.9	53.4

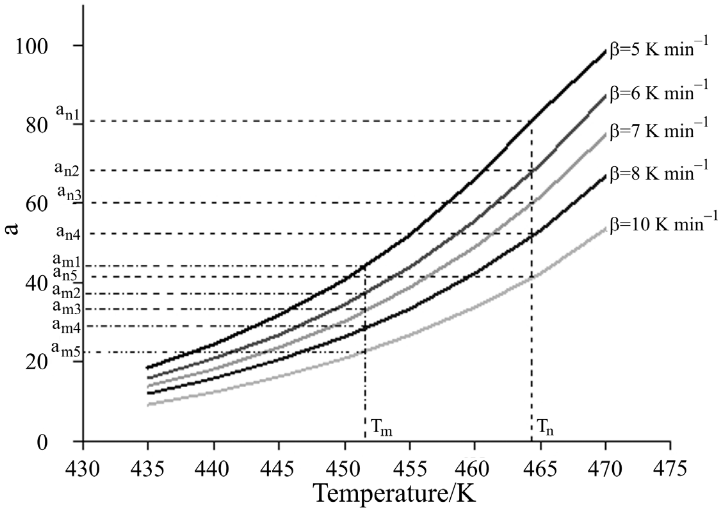

Fig. 4 The α-*T* curves obtained by Popescu method for dehydration of the calcium oxalate monohydrate

It was found that the best values of correlation coefficients corresponding to the kinetic functions by using the different conversion degrees for the two data sets of different heating rates randomly mostly centre at No. 15–19 functions, which are Mample power law with different accommodation factor *n*. The results offered by the proposed method (*n*=1) accord to that used Popescu method in substance. But the mechanism determined by Popescu method is dependent on the correlation coefficients good or not and some values of correlation coefficients were very similar, which would led to the distinguishability low and made the determination of the mechanism function uncertainty.

Table 7 Analytical forms of mechanism functions, differential form $f(\alpha)$ and integral form $g(\alpha)$

Function No.	Mechanism	Integral form $g(\alpha)$	Differential form $f(\alpha)$
8	Avrami–Erofeev equation (*n*=2/3)	$[-\ln(1-\alpha)]^{2/3}$	$3/2(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev equation (*n*=1/2)	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
14	Phase boundary reaction	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$
15	Mample power law (*n*=1)	α	1
16	Mample power law (*n*=3/2)	$\alpha^{3/2}$	$2/3\alpha^{-1/2}$
17	Mample power law (*n*=1/2)	$\alpha^{1/2}$	$2\alpha^{1/2}$
18	Mample power law (*n*=1/3)	$\alpha^{1/3}$	$3\alpha^{2/3}$
19	Mample power law (*n*=1/4)	$\alpha^{1/4}$	$4\alpha^{3/4}$

Table 8 Correlation coefficients corresponding to the kinetic functions from Table 7 for the first data set

Function No.	Correlation coefficient, *r*				
	T_m=435 K T_n=460 K	T_m=435 K T_n=470 K	T_m=440 K T_n=465 K	T_m=445 K T_n=465 K	T_m=445 K T_n=470 K
8	0.9973	0.9966	0.9969	0.9984	0.9988
9	0.9943	0.9875	0.9930	0.9949	0.9927
14	0.9981	0.9878	0.9960	0.9964	0.9869
15	0.9997	0.9964	0.9995	0.9996	0.9953
16	0.9984	0.9976	0.9985	0.9987	0.9985
17	0.9968	0.9904	0.9974	0.9983	0.9918
18	0.9976	0.9929	0.9989	0.9995	0.9960
19	0.9992	0.9965	0.9998	0.9995	0.9988

Table 9 Correlation coefficients corresponding to the kinetic functions from Table 7 for the second data set

Function No.	Correlation coefficient, *r*				
	T_m=439 K T_n=474 K	T_m=445 K T_n=469 K	T_m=451 K T_n=469 K	T_m=456 K T_n=474 K	T_m=445 K T_n=464 K
8	0.9955	0.9973	0.9992	0.9987	0.9985
9	0.9846	0.9931	0.9962	0.9967	0.9958
14	0.9874	0.9962	0.9971	0.9714	0.9984
15	0.9959	0.9994	0.9996	0.9934	0.9996
16	0.9980	0.9997	0.9992	0.9979	0.9996
17	0.9883	0.9974	0.9987	0.9913	0.9977
18	0.9910	0.9991	0.9998	0.9961	0.9990
19	0.9953	0.9998	0.9988	0.9978	0.9998

Conclusions

- The comparative method has been used to evaluate the kinetic model and kinetic parameters for non-isothermal decomposition. Results show that this method is feasible and conventional with good reproducibility.
- Determination of the most probable mechanism of a reaction by using the proposed method has uniqueness and higher distinguishability. The calculated results are relatively in agreement with those obtained by using Popescu method.
- The kinetic triplets can be evaluated from the results obtained by differential and integral equations at only one heating rate with the constraint of the activation energy calculated by iterative method or KAS method.

- The kinetic triplets of the dehydration of $CaC_2O_4 \cdot H_2O$ are the following: E_a=81±3 kJ mol^{-1}; A=4.51·10^6–1.78·10^8 s^{-1}. The kinetic model of this reaction can be described by Mample power law mechanism: $f(\alpha)=1$ or $g(\alpha)=\alpha$.

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