Kinetic Study on the Thermal Dehydration of $CaCO_3 \cdot H_2O$ by the Master Plots Method

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Thermal dehydration process of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, was reinvestigated from a viewpoint of reaction kinetics. On the basis of data of thermogravimetry, kinetic analysis was performed under nonisothermal conditions using an integral composite procedure, which includes a integral isoconversional method and an integral master plots method. The results of the integral isoconversional method of TGA data at various heating rates suggested that dehydration of $CaC_2O_4 \cdot H_2O$ followed a single step with an activation energy of 99.02 ± 2.61 kJ/mol, and from the master plots method, the reaction was described by an R_n model. Finally, it was estimated that the pre-exponential factor $A = (2.82 \pm 1.81) \times 10^9\ s^{-1}$, and the kinetic exponent $n = 2.3 \pm 0.2$. The results of nonisothermal kinetic analysis of the thermal dehydration reactions of $CaC_2O_4 \cdot H_2O$ suggested that the integral composite procedure be very successful in evaluating kinetic parameters and describing kinetic model of solid-state reactions.

Keywords: TGA, nonisothermal kinetic analysis, master plots method, $CaC_2O_4 \cdot H_2O$

Introduction

Thermal analysis is a very convenient technique of measuring the kinetic data for the solid-state reaction, which provide us with all the required data for kinetic calculation. Thermal dehydration of calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$, is one of the most frequently investigated cases. Ambiguity accompanies the interpretation of kinetic data produced from various thermal analysis measurements. It originates partly from experimental shortcoming and partly from the use of inadequate computational methods. Elder has reported that dehydration of $CaC_2O_4 \cdot H_2O$ appear to conform to three-dimensional (3-D) diffusion (Ginstling-Brounshtein D_4) model.[1] Anderson et al. summarized the results of the process measured in 13 European laboratories using the *n*th-order model.[2] Gao et al. suggested that the process was described by means of accomodated R_n model,[3] the same model was suggested by Liqing[4] and Chunxiu,[5] respectively. Kinetic parameters for a certain solid-state reaction evaluated by different workers widely deviates from one another. This fact implies the absence of well-accepted procedure for deducing the reaction mechanism.

Theoretically, one could expect that a single experiment in nonisothermal regime could give all the kinetic triplets,[1] namely, kinetic model, activation energy and pre-exponential factor. However, the estimations based on fitting data to single-step kinetic models work poorly, and tend to be misleading, especially when these estimates are obtained from nonisother-

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mal measurements.[6] As an alterative, one may make use of model-free approaches represented by various isoconversional methods to give excellent results of dependencies of the activation energy on the extent of conversion of nonisothermal experiments. Analysis of the activation energy dependency will provide important clues about reaction mechanism.[7-10] Also, the ability of isoconversional methods to reveal the reaction complexity is, therefore, a crucial step toward the ability to draw mechanistic conclusions from kinetic data. However, the knowledge of activation energy alone does not permit adequate interpretation of kinetic data, and it is very important that kinetic triplets are evaluated fully.[11]

Several attempts have been made to determine the physic-geometric mechanism of solid-state reactions by using the so-called "master plot" methods.[12,13] Theoretical master plots are reference curves depending on the kinetic models but generally independent of kinetic parameters of the process. Experimental master plots constructed on the basis of experimental data are independent from the temperature schedules. Comparing experimental master plots with theoretical ones allows us to choose the appropriate kinetic model of the process under investigation, at least, of the type of appropriate kinetic models, without doubt.[12] The knowledge of kinetic model, deduced from such a simple graphical method, is very helpful for further detailed kinetic analysis by avoiding a probable miscalculation of kinetic parameters due to wrong model being assumed. In this work, kinetics of thermal dehydration of $CaC_2O_4 \cdot H_2O$ is systematically studied by means of an integral composite procedure, which is carried out as following steps. An integral isoconversional method is used to estimate the activation energy related to different extent of conversion. Based on the knowledge of activation energies dependency, the experimental master plots are constructed. The master plot method allows us to unmistakably recognize the kinetic model of the reaction process. Also, the pre-exponential factor and the exact kinetic model are finally evaluated.

Experimental

Thermal decomposition of $CaC_2O_4{\cdot}H_2O$ (Analytic grade, sieved to the 100 mesh fraction) was carried out in a thermogravimetric analyzer (Setaram Setsys TG/DTA/DSC-16, France). The sample was loaded in an open alumina crucible and γ-alumina was used as reference. The furnace temperature, which was controlled by a thermocouple, rose linearly according to the preset linear temperature schedules. The sample temperature was measured using another thermocouple located between sample crucible and reference crucible. Sample temperature had been calibrated using standard metals including indium, lead, aluminum, silver, and gold. Data were collected by using software within the Setaram system.

The selected heating rates were 5, 10, 15 and 20 $K \cdot min^{-1}$. Purge gas was nitrogen gas of 99% purity, flowing at 20 $mL \cdot min^{-1}$. Weight of samples was about 3.00 mg. Sampling interval of time for recording sample weight loss was kept at 1 s. The temperature of furnace was programmed to rise from room-temperature (20°C) to 350°C at various heating rates. After an initial period of nonlinear heating, the programmed linear rates were achieved. The real heating rates were derived from the recorded temperature T and time t values. The actual values of heating rates for the temperature region of dehydration were estimated to be 5.50, 11.40, 17.36, and 23.42 $K \cdot min^{-1}$. The TG curves of dehydration of $CaC_2O_4{\cdot}H_2O$ at different heating rates are shown in Figure 1.

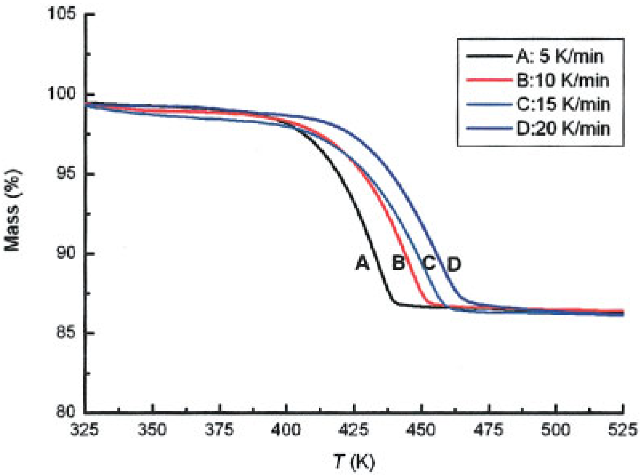

Figure 1. TG curves of dehydration of $CaC_2O_4{\cdot}H_2O$ at different heating rates.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Results and Discussion

Model free analysis

In this work, thermal dehydration of $CaC_2O_4{\cdot}H_2O$[14] can be described as the decomposition of a solid

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{gas}$$

Kinetic analysis of a solid-state decomposition is usually based on a single-step kinetic equation. The rate of nonisothermal decomposition of this type reaction is expressed as

$$d\alpha/dT = (A/\phi)\exp(-E/RT)f(\alpha) \qquad (1)$$

where T is the absolute temperature, α is the extent of conversion, ϕ is the linear heating rate, $f(\alpha)$ is the reaction model depending on the kinetic process, A is the pre-exponential factor, R is the gas constant and E is the activation energy. The reaction models, which are derived by assuming simply idealized models, may take various forms, and some widely used models in solid-state reactions are listed in Table 1.[15]

Rearranging Eq. 1 and integrating both sides of the equation, following expression is obtained

$$g(\alpha) = (A/\phi)\int_{T_0}^{T}\exp(-E/RT)dT \approx (A/\phi)\int_{0}^{T}\exp(-E/RT)dT$$
$$= (AE/\phi R)P(u) \qquad (2)$$

where $P(u) = \int_{\infty}^{u} - (e^{-u}/u^2)\,du$, and $u = E/RT$. Generally, thermal decomposition reactions are very slow at subambient temperatures so that the lower limit of the integral on the righthand side of Eq. 2, T_0, can be approximated to be zero.

Table 1. Kinetic Model Function $g(\alpha)$ usually Employed for the Solid State Reaction

No	Reaction model	Symbol	$g(\alpha)$	$\Delta^{*,2}$
1.	Avrami-Erofeev, $m = 4$	A_4	$[-\ln(1-\alpha)]^{1/4}$	0.5842
2.	Avrami-Erofeev, $m = 3$	A_3	$[-\ln(1-\alpha)]^{1/3}$	0.5055
3.	Avrami-Erofeev, $m = 2$	A_2	$[-\ln(1-\alpha)]^{1/2}$	0.3407
4.	Avrami-Erofeev, $m = 1.5$	$A_{1.5}$	$[-\ln(1-\alpha)]^{2/3}$	0.1675
5.	Phase boundary reaction, $n = 1$	R_1	α	0.2822
6.	Phase boundary reaction, $n = 2$	R_2	$1-(1-\alpha)^{1/2}$	0.0873
7.	Phase boundary reaction, $n = 3$	R_3	$1-(1-\alpha)^{1/3}$	0.0932
8.	One-dimensional diffusion	D_1	α^2	0.4359
9.	Two-dimensional diffusion	D_2	$[(1-\alpha)\ln(1-\alpha)]+\alpha$	0.8701
10.	Three-dimensional diffusion	D_4	$1-2\alpha/3-(1-\alpha)^{2/3}$	1.1142
11.	Jander's type diffusion	D_3	$[1-(1-\alpha)^{1/3}]^2$	1.7303
12.	Power law, $n = 1/4$		$\alpha^{1/4}$	0.6699
13.	Power law, $n = 1/3$		$\alpha^{1/3}$	0.6252
14.	Power law, $n = 1/2$		$\alpha^{1/2}$	0.5388
15.	Power law, $n = 3/2$		$\alpha^{3/2}$	0.1053
16.	1st order	A_1, F_1	$-\ln(1-\alpha)$	0.3411
17.	2nd order	F_2	$(1-\alpha)^{-1}-1$	2.2711
18.	3rd order	F_3	$1/2\lfloor(1-\alpha)^{-2}-1\rfloor$	9.7333
$19^{*,1}$.		$R_{2.3}$	$1-(1-\alpha)^{1/2.3}$	0.0739

$^{*,1}g(\alpha) = 1-(1-\alpha)^{1/n}$ $(n = 2.3)$

$^{*,2}\Delta$: the average square of the deviation between $P(u)/P(u_{0.5})$ calculated on the base of experiment and $g(\alpha)/g(0.5)$

$P(u)$ cannot be analytically solved. In this article, an accurate approximate formula[16] for $P(u)$ is applied

$$-\ln P(u) = 0.377739 + 1.894661 \ln u + 1.001450u \quad (3)$$

Equation 3 is introduced into Eq. 2, and taken the logarithm of both sides; Eq. 4 is given

$$\ln(\phi/T^{1.894661}) = \ln[AE/Rg(\alpha)] + 3.635041 - 1.894661 \ln E - 1.001450E/RT \quad (4)$$

Assuming that the reaction model, $g(\alpha)$, must be invariant for all considered runs, we plot $\ln(\phi/T^{1.894661})$ vs. $-1/T$. A group of paralleled lines (shown in Figure 2) was obtained. The E were calculated by numerical fitting the experimental data in the range of decomposition degrees $0.2 \leqslant \alpha \leqslant 0.8$ with Eq. 4 by using least-square fitting procedure implemented in the computer program MATLAB 6.5. Also, the E at various α was obtained from the slope of the regression lines. E-α plots is shown in Figure 3. For the region of $\alpha = 0.2 \sim 0.8$, the average value of E is 99.02 ± 2.61 kJ/mol. Little dependence of E on α is observed, which indicates that there exists a high probability for the presence of a single-step reaction.[17,18] Therefore, it allows to estimate the most probable kinetic model.

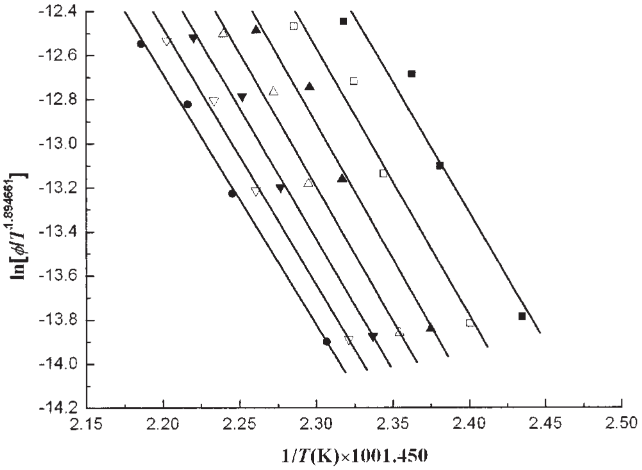

Figure 2. Plots for determination of activation energy of the dehydration of $CaC_2O_4 \cdot H_2O$ at different α: 0.2 (■), 0.3 (□), 0.4 (▲), 0.5 (△), 0.6 (▼), 0.7 (▽), and 0.8 (●).

Solid lines are linear fitting corresponding to different α.

Master-plots method

Using a reference at point $\alpha = 0.5$, and according to Eq. 2, one gets

$$g(0.5) = (AE/\phi R)P(u_{0.5}) \quad (5)$$

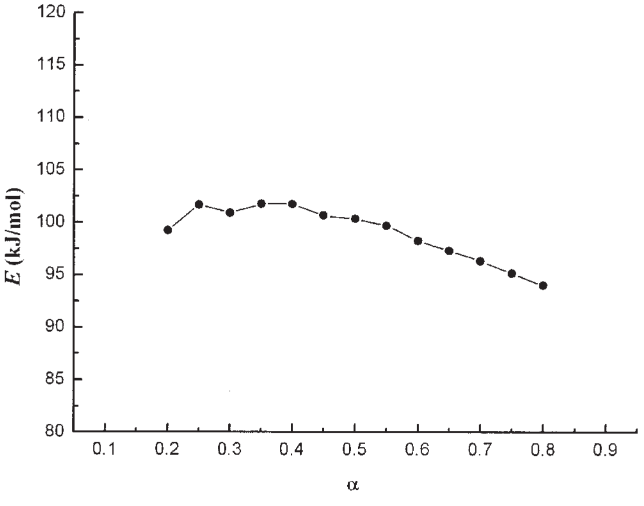

Figure 3. Dependence of the values of E on α.

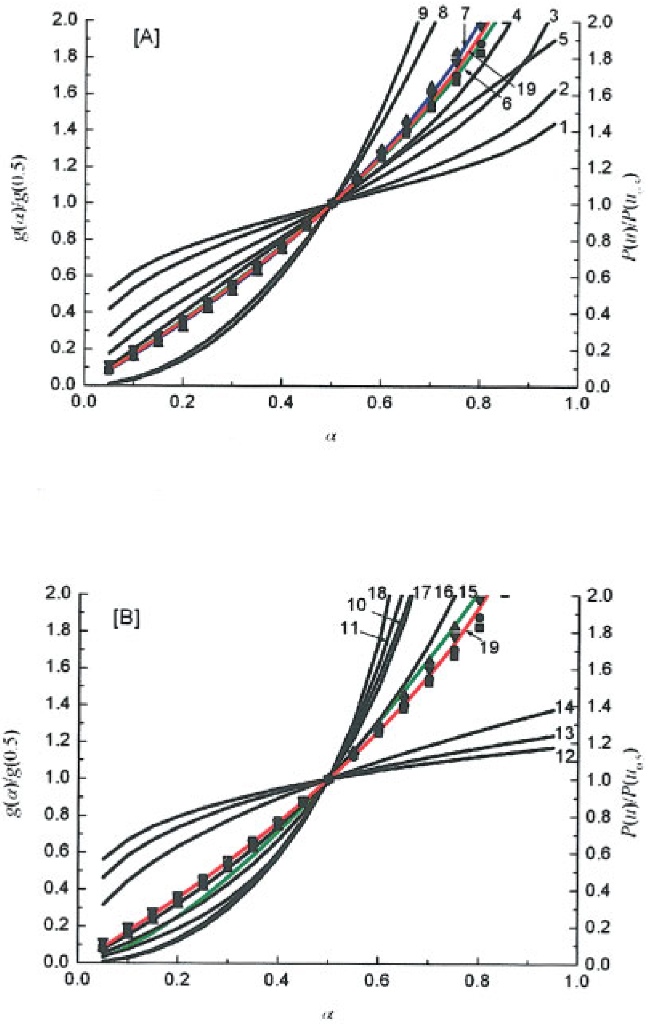

Figure 4. Master plots of theoretical $P(u)/P(u_{0.5})$ against α for various reaction models (solid curves, as enumerated in Table 1, and curve 19 represents function $g(\alpha) = 1 - (1 - \alpha)^{1/2.3}$), and experimental data for the dehydration of $CaC_2O_4 \cdot H_2O$ at heating rates 5 K · min^{-1} (■), 10 K · min^{-1} (●), 15 K · min^{-1} (▲), and 20 K · min^{-1} (▼).

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where $u_{0.5} = E/RT_{0.5}$. Eq. 2 divided by Eq. 5, following equation is obtained

$$g(\alpha)/g(0.5) = P(u)/P(u_{0.5}) \tag{6}$$

Plotting $g(\alpha)/g(0.5)$ against α corresponds to theoretical master plots of various $g(\alpha)$ functions. To draw the experimental master plots of $P(u)/P(u_{0.5})$ against α from experimental data obtained under various heating rates, the knowledge of temperature as a function of α and the value of E for the process should be known in advance, and $P(u)$ can be calculated directly using numerical Simpson's procedure or some approximate formulas. In this article, an approximate formula of $P(u)$ with high accuracy was used.[19]

$$P(u) = \exp(-u)/[u(1.00198882u + 1.87391198)] \tag{7}$$

The experimental master plots were constructed according to Eqs. 6 and 7. Both of the experimental and the theoretical master plots are shown in Figure 4. Equation 6 indicates that, for a given α, the experimental value of $P(u)/P(u_{0.5})$, and theoretically calculated values of $g(\alpha)/g(0.5)$ are equivalent when an appropriated kinetic model is used. The plots related to different heating rates are practically identical. The comparison of the experimental master plots with theoretical ones indicates that no existed theoretical master plots match the experimental ones perfectly. However, the R_n model, should described the kinetic process for thermal dehydration of $CaC_2O_4 \cdot H_2O$ because the experimental master plots lay between the theoretical master plots R_2 and R_3.

The criterion for selecting acceptable models can also be taken as follows

$$\Delta(k) = \sqrt{\frac{\sum_j^n \sum_i^m [g_k(\alpha_i)/g_k(0.5) - P_j(u_i)/P_j(u_{0.5})]^2}{(n-1)(m-1)}} \tag{8}$$

where m and n are numbers of points and heating rates, respectively. The value of $\Delta(k)$ is the average square of the deviation between $P(u)/P(u_{0.5})$ calculated on the base of experiment and $g_k(\alpha)/g_k$ (0.5), in which k denotes the serial number of model functions listed in Table 1. If a model describes the experimental accurately, it is possible to find a minimum of Δ. The values of Δ are listed in Table 1, in which models R_2 and R_3 show minimum of Δ. This fact also indicates that R_n is the most probable kinetic model.

Evaluating pre-exponential factor and kinetic exponent

The accommodated model[20] of R_n with nonintegral exponent n was used for estimating the kinetic exponent n and A. The expression of R_n is introduced into Eq. 2; Eq. 9 is obtained

$$1 - (1 - \alpha)^{1/n} = \frac{AE}{\phi R} P(u) \tag{9}$$

Table 2. $1 - (1 - \alpha)^{1/n}$ vs. $\frac{E}{\phi R} P(u)$

n	B	$k/10^9$	r
2.0	0.0074	2.6166	0.9958
2.1	0.0045	2.5473	0.9958
2.2	0.0019	2.4807	0.9958
2.3	−0.0003	2.4169	0.9958
2.4	−0.0022	2.3559	0.9957
2.5	−0.0039	2.2974	0.9956
2.6	−0.0053	2.2414	0.9955
2.7	−0.0066	2.1877	0.9954
2.8	−0.0077	2.1363	0.9953
2.9	−0.0086	2.0871	0.9951
3.0	−0.0095	2.6166	0.9950

n is the accommodation factor of the mechanism function of R_n, B is the intercept, k is the slope, and r is linear regression coefficients.

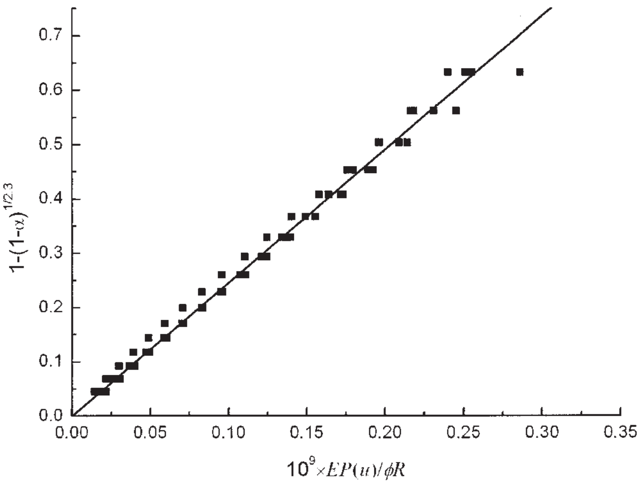

Figure 5. Plotting $[1 - (1 - \alpha)^{1/n}]$ vs. $\frac{E}{\phi R}P(u)$ at $n = 2.3$ for the dehydration of $CaC_2O_4 \cdot H_2O$ at various heating rates and their linear-fitting drawing (solid line).

The probable optimal range of n is 2.0~3.0 because the experimental master plots lay between the theoretical master plots R_2 and R_3. In order to make certain optimal value of n further, we increase n from 2.0~3.0 with increment of 0.1 and plot $[1 - (1 - \alpha)^{1/n}]$ vs. $\frac{E}{\phi R}P(u)$ using linear least square fitting procedure. The most probable value of n is that for which intercept B is closest to zero, and correlation coefficient r is the highest. Results (Table 2) show that $n = 2.3$, $A = 2.42 \times 10^9$ s^{-1} for $E = 99.02$ kJ/mol. The plots of $[1 - (1 - \alpha)^{1/n}]$ vs. $\frac{E}{\phi R}P(u)$ at $n = 2.3$ at various heating rates and their linear-fitting drawing through the zero point are shown in Figure 5, respectively. The value of Δ for $g(\alpha) = -(1 - \alpha)^{1/n}$ $(n = 2.3)$ listed in Table 1 shows the minimum of Δ. The values of n and A are $n = 2.3 \pm 0.2$ and $A = (2.82 \pm 1.81) \times 10^9$ s^{-1}, respectively, when $E = 99.02 \pm 2.61$ kJ/mol. All the values are within the limit of error.

Comparison with early methods

In a Round robin test,[2] dehydration of $CaC_2O_4{\cdot}H_2O$ can be model with an exponent $n = 1/2$ using model F_n from Table 1. That is mathematically analogous to an exponent $n = 2$ for model R_n for a phase boundary reaction. Based on experimental α_{max} values and activation energy estimated from the isoconversional plot,[3] Gao et al. suggested kinetics of dehydration was described by means of accommodated R_n model. Iso-temperature method[4] and comparative method[5] gave the same kinetic model. The results of master plots method indicated that the most probable kinetic model for the dehydration is the R_n model with $n = 2.3 \pm 0.2$. The values of n, E and A are compatible to those reported.

Conclusions

By using the master plots method based on the integral form of the kinetic equation, we have reexamined kinetic aspects of the dehydration of $CaC_2O_4 \cdot H_2O$. It is shown this method can be applied directly to the experimental data obtained under a linear heating rate. The activation energy could be determined from a series of TG curves recorded at different heating rates by using an integral isoconversional method without previous assumptions regarding the kinetic model fulfilled by the reaction. The theoretical plots of $g(\alpha)/g(0.5)$ against α are constructed together with the experimental master plots of $P(u)/P(u_{0.5})$ against α from the experimental data. An appropriate kinetic model can be distinguished by a simple graphical method or a statistical method. Further detailed kinetic analysis is performed based on such a first-find estimation of the appropriate kinetic model.

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Literature Cited

1. Elder JP. The 'E-ln(A)-f(a)' triplet in non-isothermal reaction kinetics analysis. *Thermochimica Acta*. 1998;318:229-238.
2. Anderson HL, Kemmler A, Höhne GWH, Heldt K, Strey R. Round robin test on the kinetic evaluation of a complex solid state reaction from 13 European laboratories. Part 1. Kinetic TG-analysis. *Thermochimica Acta*. 1999;332:33-53.
3. Gao Z, Amasaki I, Nakada M. A description of kinetics of thermal decomposition of calcium oxalate monohydrate by means of the accommodated R*n* model. *Thermochimica Acta*. 2002;385:95-103.
4. Liqing L, Donghua C. Application of iso-temperature method of multiple rate to kinetic analysis Dehydration for calcium oxalate monohydrate. *J of Thermal Analysis and Calorimetry*. 2004;78:283-293.
5. Chunxiu G, Yufang S, Donghua C. Comparative method to evaluate reliable kinetic triplets of thermal decomposition reactions. *J of Thermal Analysis and Calorimetry*. 2004;76:203-216.
6. Burnham AK. Computational aspects of kinetic analysis. Part D: The ICTAC kinetic project-multi-thermal-history model-fitting methods and their relation to isoconversional methods. *Thermochimica Acta*. 2000;355:165-170.
7. Vyazovkin S, Wight CA. Isothermal and nonisothermal reaction kinetics in solids: in search of ways toward consensus. *J of Phys Chem: A*. 1997;101:8279-8284.
8. Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochimica Acta*. 1999;340/341:53-68.
9. Vyazovkin S. Kinetic analysis of reversible thermal decomposition of solids. *Intl J of Chem Kinetics*. 1995;27(1):73-84.
10. Vyazovkin S. A unified approach to kinetic processing of nonisothermal data, *Intl J of Chem Kinetics*. 1996;28(2):94-101.
11. Maciejewski M. Computational aspects of kinetic analysis. Part B: The ICTAC Kinetics Project - the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochimica Acta*. 2000;355:145-154.
12. Gotor FJ, Criado JM, Malek J, Koga N, Gotor FJ, Criado JM, Malek J, Koga N. Kinetic Analysis of solid-state reactions: The universality of master plots for analyzing isothermal and nonisothermal experiments. *J of Phys Chem: A*.2000;104:10777-10782.
13. Perez-Maqueda LA, Criado JM, Gotor FJ, Malek J. Advantages of combined kinetic analysis of experimental data obtained under any heating profile. *J of Phys Chem: A*. 2002;106:2862-2868.
14. Chang H, Huang PJ. Thermal decomposition of $CaC_2O_4 \cdot H_2O$ studied by thermo-Raman spectroscopy with TGA/DTA. *Analytical Chem*. 1997;69:1485-1491.
15. Mamleev V, Bourbigot S, Bras ML, Duquesn*e*c S, Sestak J. Modelling

of nonisothermal kinetics in thermogravimetry. *Phys Chem Chem Phys*. 2000;2:4708-4716.

16. Wanjun T, Yuwen L, Hen Z, Cunxin W. New approximate formula for arrhenius temperature integral. *Thermochimica Acta*. 2003;408(1/2):39-43.
17. Vyazovkin S. Computational aspects of kinetic analysis. Part C: The ICTAC Kinetics project - the light at the end of the tunnel? *Thermochimica Acta*. 2000;355:155-163.
18. Opfermann JR, Flammersheim HJ. Some comments to the paper of J.D. Sewry and M.E. Brown: "Model-free" Kinetic Analysis? *Thermochimica Acta.* 2003;397:1-3.
19. Wanjun T, Yuwen L, Hen Z, Zhiyong W, Cunxin W. New temperature integral approximate formula for non-isothermal kinetic analysis. *J of Thermal Analysis and Calorimetry*. 2003;74:309-315.
20. Tanaka H. Thermal analysis and kinetics of solid state reactions. *Thermochimica Acta.* 1995;267:29-44.

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