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Coupled thermogravimetric-IR techniques and kinetic analysis by non-isothermal decomposition of Cd^{2+} and Co^{2+} vinyl-phosphonates

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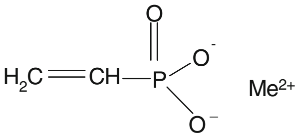
Abstract The thermal behavior of Cd^{2+} and Co^{2+} vinyl-phosphonates was studied using two different experimental strategies: the coupled TG–EGA (FTIR) technique by decomposition in nitrogen, respectively, air, and the kinetic analysis of TG data obtained in dynamic air atmosphere at four heating rates. The both compounds exhibited a good thermal stability: in nitrogen, only an endothermic dehydration step was observed. In air the Cd^{2+} salt presents the same dehydration step whereas by the Co^{2+} salt two simultaneous processes take place dehydration, respectively, thermooxidative destruction of the vinyl group. The kinetic analysis of the TG data was performed with the Flynn–Wall–Ozawa, Friedman's, and modified non-parametric kinetic methods. By means of the coupled techniques, some spectroscopic arguments on the reaction mechanism were obtained. The values of the activation energy by the three methods are in good agreement and support the two different suggested mechanism.

Keywords Coupled TG–EGA · Non-isothermal kinetics · Vinyl-phosphonates

Introduction

The salts of vinyl-phosphonic acid (I) are important as intermediates due to their bifunctionality: the double bond is able to polymerization, respectively, the ionic $(P–O^-)_2Me^{2+}$ bond is of interest for ion exchangers, non-linear optical material and/or photochemically active materials [1].

I



The possible structures by polymerization are of a wide variety: one-dimensional chains [2–4] layered structures [5–7] and three-dimensional micro-porous frameworks [8, 9].

The aim of the present work is to perform a study on the thermal behavior of two vinyl-phosphonates (I): of Cd^{2+} and Co^{2+}. This work folow our recent paper on the thermal behavior of some phenyl-vinyl-phosphonates [10].

The thermal behaviour was studied using a coupled thermogravimetric–evolved gas analysis (TG/EGA) followed by a kinetic analysis of the non-isothermal data.

Experimental

Synthesis

A solution of vinyl-phosphonic acid:metal nitrates:urea:water in a molar ratio of 1:1:1:250 was prepared, the pH was adjusted at 2.8 with a 0.1 M solution of NaOH and then heated 72 h at 70 °C. The resulted crystals of the

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corresponding salts were filtered and dried in air. Data of the structure of these compounds were recent reported [11].

Thermal analysis

The thermoanalytical curves TG, DTG and Heat Flow were obtained on a Perkin-Elmer Diamond device, using Al crucibles. The experiments were performed in dynamic atmosphere (100 cm^3 min^{-1}) of nitrogen, respectively, air, at heating rates of 10, 12, 15 and 20 °C min^{-1}.

FTIR spectra

The FTIR Spectra were drawn up with a Perkin-Elmer Spectrum 100 device. For the solid samples, i.e., before and after the thermal treatment, the U-ATR technique was used. For the EGA, the corresponding gas cell of the Spectrum 100 was coupled to the thermobalance gas exit by means of a Transfer Line. Both the gas cell and transfer line were heated at 250 °C, in order to avoid condensation as far as possible. The evolved gases were identified using a Gas Vapour Library (Sadtler Spectral Databases).

Results and discussions

The thermoanalytical curves of the studied compounds, obtained in nitrogen and air, respectively, are presented in Fig. 1 and 2. Apparently the thermal behavior was the same for the both compounds, in nitrogen as well as in air, i.e., one endothermic mass loss process in the range 150–250 °C.

In fact the thermal behavior is different, first of all due to the reaction atmosphere: in nitrogen it is possible only a thermodegradation (thermally induced destruction of the molecular architecture), whereas in air the thermooxidative processes would be preferred. The arguments are furnished by EGA.

Indeed, in nitrogen, the evolved compounds is water (see an example in Fig. 3). A supplementary argument is brought by the FTIR spectra of the sample before and after the thermal treatment in nitrogen. As it is clearly evidenced in Fig. 4, after the thermal treatment until 300, respectively, 550 °C, the peaks at 3400–3500 cm^{-1}, corresponding to the crystallization water, are completely disappeared. In the same Fig. 4, it is an evidence on the thermal stability in nitrogen at 300 °C of the dehydrated salts, i.e., the maintenance of the peaks for C=C (1620 cm^{-1}) and P=O (1,100, 960, respectively, 750 cm^{-1}).

The molecular content of this crystallization water was determined with the formula:

$$x = \frac{M \cdot a}{18(1-a)} \tag{1}$$

where M is the molecular mass of the salts without water, a—the relative mass loss ($a = \Delta m/\mathrm{mo}$), and x—no. of water molecules/phosphonate molecule. The corresponding data are systematized in Table 1 and it is obvious that the both studied salts are monohydrate.

By decomposition in air, the behavior of these two salts are different:

- the cadmium salt exhibit in air a similar behavior like in nitrogen (compare Fig. 2a, b); the EGA indicate water vapour as the only evolved gas and the mass loss of 7.6% correspond, according to Eq. 1, to one water molecule/phosphonate molecule
- the cobalt salt has apparently a similar curve in air like in nitrogen, but the EGA indicate a mixture of water

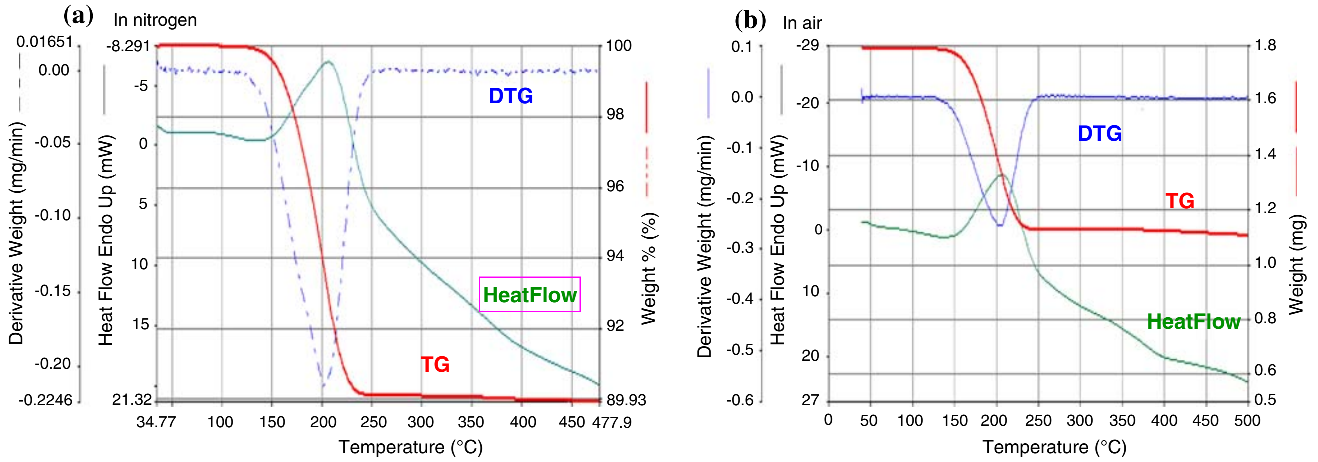

Fig. 1 The thermoanalytical curves at a heating rate of 20 °C min^{-1} of the cobalt salt

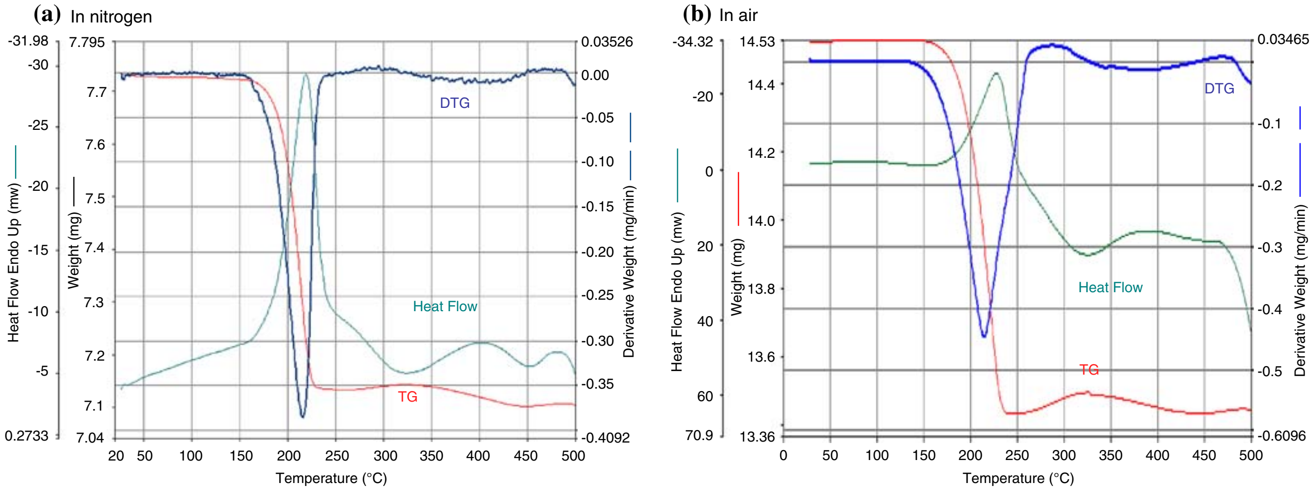

Fig. 2 The thermoanalytical curves at a heating rate of 20 °C min^{-1} of the cadmium salt

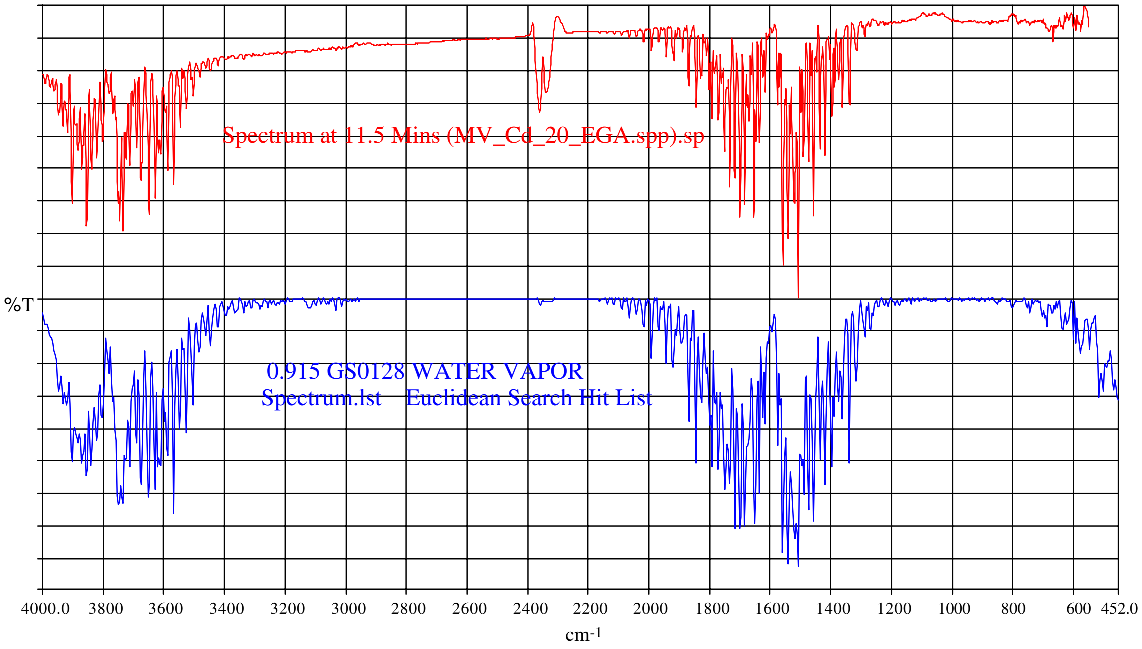

Fig. 3 The evolved gas spectrum corresponding to the TG curve of Cd^{2+} salt in nitrogen, at 230 °C (11.5 min). For comparison also the FTIR spectrum of water vapor is added

vapor and carbon dioxide as evolved gases and the mass loss exceed 30%; this is probably due to a catalytic effect of Co^{2+} which in parallel with the dehydration process, favour the thermooxidative degradation of the organic part into CO_2 and H_2O, simultaneously with the formation of phosphite. More informations about the differences observed by the decomposition in air are expected from the kinetic analysis.

Kinetic analysis

The strategy of the kinetic analysis is based on processing the TG/EGA data obtained in air by means of three different isoconversional methods.

(i) The method by Flynn–Wall [12] and Ozawa [13] is an integral method based on the equation:

$$\ln \beta = \ln \frac{A}{R \cdot g(\alpha)} - 1.052 \frac{E}{RT} - 5.331 \qquad (2)$$

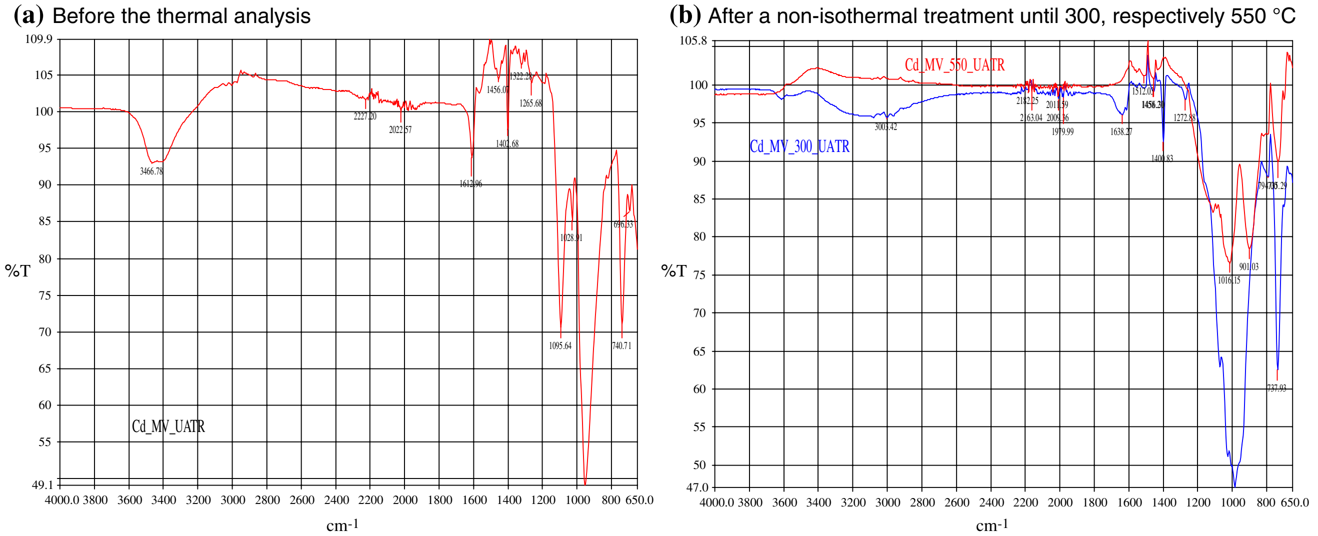

Fig. 4 The FTIR spectra by U-ATR technique of Cd^{2+} salt

Table 1 The dehydration step in nitrogen (in connection with Eq. 1)

Phosphonate of	M (molecular mass)	a (relative mass loss)	x (no. of water molecules)
Cd	218	0.077	1.01
Co	165	0.100	1.02

where α is the degree of conversion, β—the heating rate and

$$g(\alpha) = \int_{\alpha_0}^{\alpha} f(\alpha) \cdot d\alpha \tag{3}$$

is the conversion integral. Being an integral method, the determined value of the activation energy E is in connection with the "history" of the sample. If the variation of E versus α is not significant (see and example in Fig. 5), the mean value of E can be used for the kinetic characterization of the thermal behavior.

(ii) The differential method by Friedman [14] is based on the equation

$$\ln\left(\beta \cdot \frac{d\alpha}{dT}\right)_\alpha = \ln[A \cdot f(\alpha)] - \frac{E}{R \cdot T} \tag{4}$$

This method is more sensitive in respect of the E versus α dependence and is very useful for

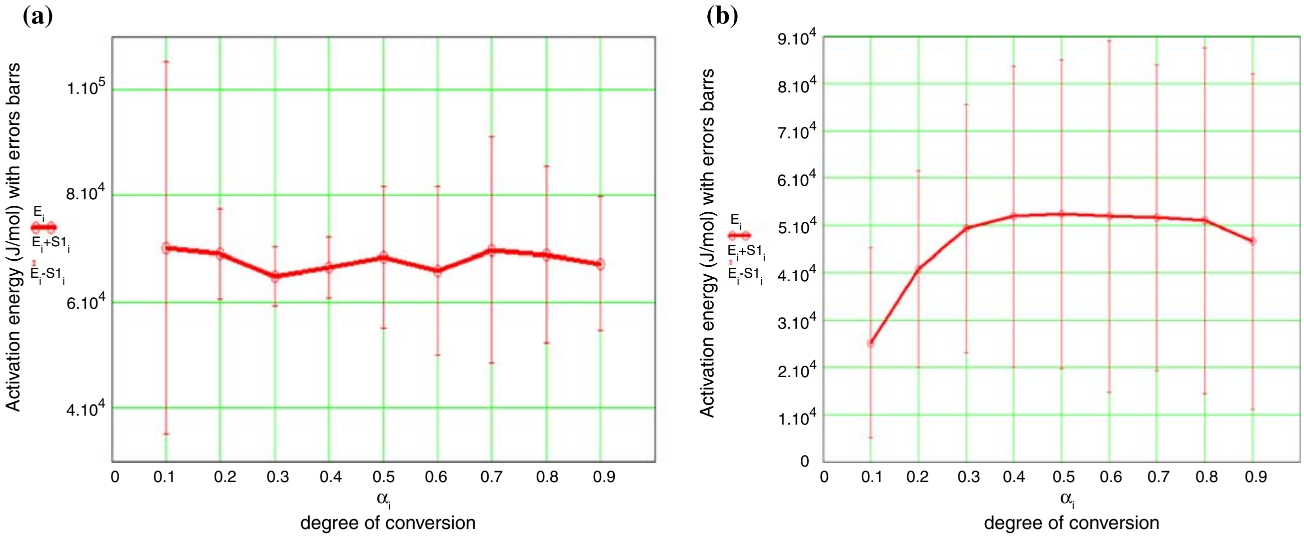

Fig. 5 The dependence of E versus α, according to FWO method, for **a** Co^{2+} and **b** Cd^{2+} salt in air

discrimination between a single step or a complex process. According to Fig. 6, by Cd salt it is certainly such a process.

(iii) The non-parametric kinetic method [15] is based on the assumption that the reaction rate can be expressed as a product of two independent functions f(T) and g(α), so that a square matrix M can be defined, with the element $M_{ij} = f(T_j) \cdot g(\alpha_i)$.
By multi-step processes, for example by two simultaneous processes with the reaction rates of r_1 and r_2, the observed reaction rate is.

$$r = r_1 + r_2 = f_1(T) \cdot g_1(\alpha) + f_2(T) \cdot g_2(\alpha) \tag{5}$$

and the initial matrix will be decomposed in

$$M = M_1 + M_2 \tag{6}$$

The contribution of each step is expressed by the explained variance λ_i, so that $\sum \lambda_i = 100\%$.
This matrix model allows the decomposition of M by the Singular Value Decomposition algorithm [16].

$$M = U(\mathrm{diag} \cdot s)V^{\mathrm{T}} \tag{7}$$

The vector u_1, i.e., the first column of U, is analyzed in order to establish the conversion function; we suggest the Šestak–Berggren equation [17]:

$$g(\alpha) = \alpha^{\mathrm{m}}(1 - \alpha)^{\mathrm{n}} \tag{8}$$

where m and n take into consideration physical, respectively, chemical phenomenon.
A similar vector v_1, corresponding to V, is checked for an Arrhenius type temperature phenomenon.

(iv) The results by these three methods are presented in Table 2.

By inspecting the data in Table 2, a very good agreement between the values of E by FWO, respectively, FR method was observed, especially by the cadmium salts.

Regarding the NPK method, the following observations are noticeable:

- for reasons of significance, only the step with $\lambda = 10\%$ will be considered; so the behavior of the two samples

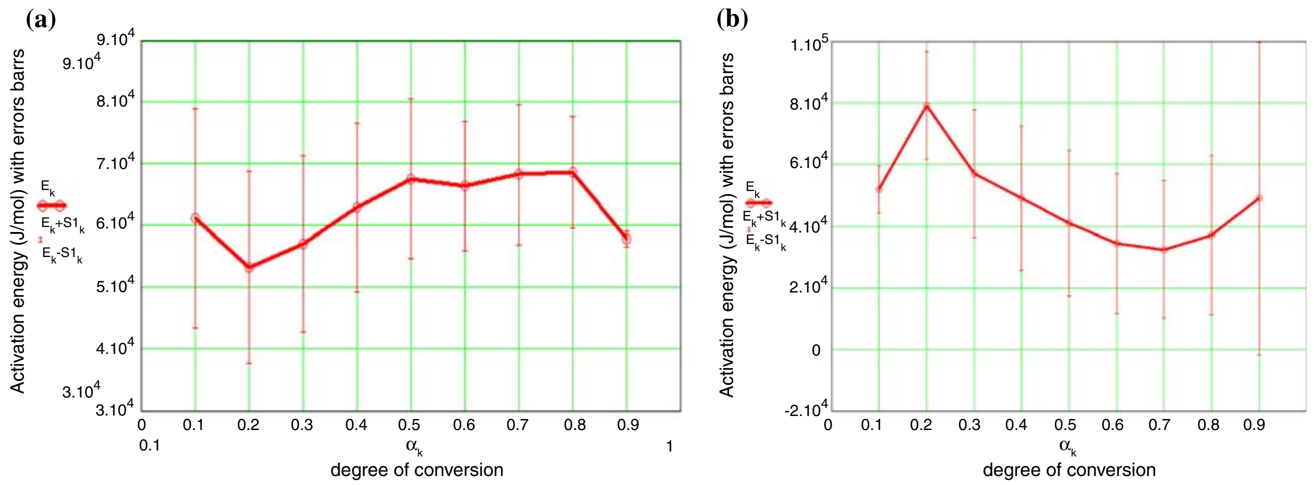

Fig. 6 The dependence of E versus α, according to Friedman method, for **a** Co^{2+} and **b** Cd^{2+} salt in air

Table 2 Comparative data of the kinetic analysis

Phosphonate of	Main value of E (kJ mol^{-1})		NPK method					
	Flynn–Wall–Ozawa	Friedman	E (kJ mol^{-1})	A (min^{-1})	m	n	λ	$\bar{E} = \sum \lambda E$
Cd^{2+}	46.8 ± 16.1	47.8 ± 14.4	48.9 ± 4.6	7.34×10^4	3/2	1	91.2	49.6
			57.4 ± 22.3	1.07×10^6	1	3/2	8.8	
Co^{2+}	67.9 ± 20.4	62.6 ± 5.3	68.0 ± 14.3	1.07×10^7	3/2	1	71.5	68.1
			71.5 ± 11	4.78×10^7	0	1/5	27.2	

seems to be different: by cadmium salt, one step process, whereas by cobalt salt, a two step process;

- the values of E by the first step are also in a very good agreement with the main values by FWO and FR methods;
- the conversion dependence of the first step by both salts is described by the same equation, with $m = 3/2$ and $n = 1$ (see Eq. 7)
- the main value of E by NPK method, i.e. $\bar{E} = \sum\lambda_{\mathrm{i}} \cdot E_{\mathrm{i}}$, is practically the same with the main value of E by FWO method, and this last one is in connection with the thermal "history" of the sample.

By corroborating the data of the kinetic analysis with the TG–EGA data we suggest a thermodegradation of the cadmium phosphonate monohydrate due to a single step dehydration, whereas the thermodegradation of the corresponding cobalt salt is due to a simultaneously two step process: a dehydration and a redox destruction of the organic part with the formation of phosphite.

Conclusions

The data on thermal behavior of cadmium and cobalt phosphonate were obtained using a coupled TG/EGA technique and an adequate kinetic analysis.

Both salts are monohydrate and in dynamic nitrogen atmosphere the dehydration is the only thermal event until 300 °C. In dynamic air atmosphere the behavior of these two salts is different: by the cadmium salt the dehydration is the remarkable thermal event, whereas by the cobalt salt beside the dehydration, a parallel thermooxidative degradation of the vinyl radical take place.

A good agreement of the activation energy values are obtained by three different isoconversional methods used for the TG/DTG data processing.

Supplementary the NPK method allows a discrimination between two and more steps of a complex process and a less speculative separation of the temperature respective conversion influence on the reaction rate.

Only a strategy of kinetic analysis using at least three different methods is able to characterize the thermal behavior in a less speculative manner.

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