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ABOUT COMPENSATION EFFECT BY THERMAL DECOMPOSITION OF SOME CATALYST PRECURSORS

T. Vlase[*], Gabriela Vlase, A. Chiriac and N. Doca*

West University of Timişoara, Faculty of Chemistry–Biology–Geography, Str. Pestalozzi No. 16, Timisoara 300115, Romania

In order to obtain catalysts, the thermal decomposition of the precursors is a compulsory step. However, kinetic analysis of the decomposition data obtained under non-isothermal conditions lead very seldom to the intimate reaction mechanism. There is also a lack of information because in non-isothermal kinetics, the compensation effect, is rather a rule and unfortunately a source of debate.

In order to discriminate between these processes, and the influence of conversion, respectively temperature on the reaction rate, the NPK (non-parametric kinetic – Sempere and Nomen) method was used. This method is based on the singular value decomposition algorithm (SVD) applied on the matrix of reaction rate at corresponding conversion and temperature. This method allows a less speculative determination of the conversion functions and of the kinetic parameters.

Keywords: *kinetic analysis, selective activation, vibrational energy transfer*

Introduction

The non-isothermal analysis is frequently used to characterize the thermal decomposition of catalyst precursors. Kinetic analysis of the thermoanalytical, especially the thermogravimetric (TG) data, leads very seldom to the intimate reaction mechanism [1–4].

If the kinetic studies are carried out on a series of similar precursors, one can probe deeper the compensation effect (*CE*), i.e. the linear dependence of activation energy (*E*) and natural logarithm of pre-exponential factor (ln*A*). Unfortunately, the *CE* is a source of continuous debate [5, 6], the reality of this effect being sometimes questioned.

In the classical expression of the *CE*

$$\ln A = bE + c \qquad (1)$$

it is difficult to use *E* or the corresponding isokinetic temperature $T_{\mathrm{iz}}=1/bR$ for any considerations on the mechanism in a studied series of compounds [7].

In a previous work [2] we found quite near values for the T_{iz} from Eqs (1) and (2), respectively, by the non-isothermal decomposition of formates, acetates, propionates and butyrates of d and f metals. The kinetic analysis was performed by the Flynn–Wall [8] and Ozawa [9] integral method. This analysis was continued [3] using the Friedman's isoconversional method and the method of Budrugeac and Segal [10–12], and also a linear relationship between *E* and ln*A* was obtained. Noticeable is that this result, was obtained with the main assumption that *E* and *A* depend on the degree of conversion and do not depend on the heating rate.

In the present paper we continue the kinetic studies by using the non-parametric kinetic method (NPK) for obtaining *A* and *E* parameters.

Results and discussion

The experimental data are presented in Table 1.

Processing of the TG data

The NPK method [13–15] allows the separation of two or more steps of a complex process. It is based on the presumption of the following equation for the reaction rate:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = g(\alpha) f(T) \qquad (2)$$

NPK regards the reaction rate as a surface in a three dimensional space where the axis are the degree of conversion (α), the temperature (*T*) and the reaction rate ($\mathrm{d}\alpha/\mathrm{d}t$ or $\beta\mathrm{d}\alpha/\mathrm{d}T$) with β – the constant heating rate.

This surface is continuous and can be discretised and organized in a $i\times j$ matrix, where the columns account for the temperature T_j (j – 1,m) and the rows reffer to different degrees of conversion α_i ($i-1,n$), i.e.

$$\mathrm{A}=g(\alpha_i)f(T_j) \qquad (3)$$

The NPK method uses the singular value decomposition (SVD) [16] algorithm to decompose matrix A:

$$\mathrm{A}=\mathrm{U}(\mathrm{diag}\ S)\mathrm{V}^{\mathrm{T}} \qquad (4)$$

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[*] Author for correspondence: tvlase@cbg.uvt.ro

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 The studied compounds and the characteristics of the decomposition step [3]

Samples	Mass loss calculated Δm_{theor}/mg	Mass loss experimental, Δm_{exp}/mg by different heating rates			
		2.5 K min^{-1}	5 K min^{-1}	10 K min^{-1}	20 K min^{-1}
formates					
$Zn(HCOO)_2$	37	–	34	34	34.5
$Cu(HCOO)_2$	38.5	–	34	37	36
$Ni(HCOO)_2$	17	–	16	17	20
$Co(HCOO)_2$	41	–	40	43	41
acetates					
$Mn(CH_3COO)_2$	45.3	45.5	45	46.6	–
$Zn(CH_3COO)_2$	30.6	–	41	39.5	40.6
$Sm(CH_3COO)_3$	26.4	27.8	25	25.2	–
$Eu(CH_3COO)_3$	25.5	–	23.6	24	26.5
$Cd(CH_3COO)_2$	39.3	37	36.3	37.7	–
propionates					
$Cd(C_2H_5COO)_2$	28.5	30.5	–	27.5	28.5
$Mn(C_2H_5COO)_2$	45.3	–	45.6	45.5	44
$Zn(C_2H_5COO)_2$	66	64	–	71	66
$Ni(C_2H_5COO)_2$	31	30	–	34.8	33.6
$Cu(C_2H_5COO)_2$	58.9	59.5	–	56.8	56.5
butyrates					
$Cu(C_3H_7COO)_2$	56	–	55.9	55.8	56.8
$Ni(C_3H_7COO)_2$	50	–	48	50	50.9
$Sm(C_3H_7COO)_3$	20.4	–	17	22.2	24
$Zn(C_3H_7COO)_2$	70.3	–	71.5	70	70.5

Table 2 NPK parameters for the preponderant process

Compound	λ/%	E/kJ mol^{-1}	A/min^{-1}	n (ec. S-B)	m (ec. S-B)
$Zn(HCOO)_2$	68.7	165.1	$7.589\cdot10^{16}$	1	–
$Cu(HCOO)_2$	99.3	69.29	$3.683\cdot10^{8}$	1	–
$Co(HCOO)_2$	84.1	201.5	$2.52\cdot10^{18}$	2	–
$Mn(CH_3COO)_2$	89.7	47.75	$2.42\cdot10^{4}$	3/2	1
$Zn(CH_3COO)_2$	87.7	87.98	$2.49\cdot10^{8}$	3/2	1
$Sm(CH_3COO)_3$	80.6	145.2	$1.59\cdot10^{13}$	2	–
$Eu(CH_3COO)_3$	67.8	164.0	$1.64\cdot10^{8}$	1	2
$Cd(CH_3COO)_2$	90.0	52.1	$9.97\cdot10^{4}$	2	1
$Cd(C_2H_5COO)_2$	53.4	25.7	72.9	1	3/2
$Mn(C_2H_5COO)_2$	56.6	76.3	$1.30\cdot10^{7}$	3/2	1
$Zn(C_2H_5COO)_2$	97.4	90.5	$7.60\cdot10^{7}$	1/2	–
$Ni(C_2H_5COO)_2$	59.8	108.0	$4.52\cdot10^{10}$	3	–
$Cu(C_2H_5COO)_2$	66.8	103.0	$2.31\cdot10^{10}$	2	1
$Cu(C_3H_7COO)_2$	96.4	108.9	$1.13\cdot10^{11}$	1	–
$Ni(C_3H_7COO)_2$	56.2	12.9	5.49	1	1
$Sm(C_3H_7COO)_3$	76.1	235.2	$1.81\cdot10^{20}$	1	–
$Zn(C_3H_7COO)_2$	56.5	72.3	$1.32\cdot10^{6}$	1	1

If the matrix A has a singular significant value of the vector S, it seems the decomposition reaction takes place by one elementar step.

If the matrix A has two significant values S_1 and S_2, there are two elementar processes, and the discrimination between them depends on the values of the corresponding explained variance λ_1 and λ_2 ($\lambda_1+\lambda_2\approx100\%$).

The TG data were interpolated with a logistical function and finally numerical derivated. The surface of the reaction rate was obtained by multivariant regression, and then the matrix A (Eq. (3)) was generated.

After applying the SVD algorithm, two significant S values were obtained, for a preponderant (S_1) respective a secondary (S_2) process. In this case, the matrix A is a sum:

Table 3 NPK parameters for the secondary process

Compound	λ/%	E/kJ mol^{-1}	A/min^{-1}	n (ec. S-B)	m (ec. S-B)
$Zn(HCOO)_2$	30.8	66.36	$6.13\cdot10^{5}$	1	–
$Cu(HCOO)_2$	0.7	721.0	$4.4\cdot10^{92}$	–	2
$Co(HCOO)_2$	11.4	29.7	58.69	3/2	1
$Mn(CH_3COO)_2$	9.9	332.0	$3.97\cdot10^{32}$	1	2
$Zn(CH_3COO)_2$	9.7	315.4	$3.02\cdot10^{30}$	1	3/2
$Sm(CH_3COO)_3$	15.6	169.7	$7.93\cdot10^{14}$	2	2/3
$Eu(CH_3COO)_3$	29.3	213.0	$4.65\cdot10^{19}$	1	–
$Cd(CH_3COO)_2$	7.5	417.0	$2.08\cdot10^{42}$	1	2
$Cd(C_2H_5COO)_2$	41.8	202.3	$3.27\cdot10^{17}$	1	–
$Mn(C_2H_5COO)_2$	38.7	162.0	$1.26\cdot10^{15}$	–	2
$Zn(C_2H_5COO)_2$	2.0	72.74	$3.44\cdot10^{6}$	2	2/3
$Ni(C_2H_5COO)_2$	35.1	478.0	$6.89\cdot10^{47}$	2	2/3
$Cu(C_2H_5COO)_2$	32.5	182.0	$8.37\cdot10^{17}$	–	2
$Cu(C_3H_7COO)_2$	2.4	349.7	$4.93\cdot10^{36}$	1	–
$Ni(C_3H_7COO)_2$	38.9	373.2	$4.03\cdot10^{34}$	1	–
$Sm(C_3H_7COO)_3$	23.2	224.8	$3.83\cdot10^{18}$	1	–
$Zn(C_3H_7COO)_2$	38.2	159.8	$1.21\cdot10^{14}$	1	–

$$\mathrm{A} = \mathrm{A}_1 + \mathrm{A}_2 = u_1 v_1^{\mathrm{T}} + u_2 v_2^{\mathrm{T}} \tag{5}$$

We assume for the temperature dependence (elements of v_1 and v_2 vectors) an Arrhenius function and for the conversion dependence (elements of u_1 and u_2 vectors) a Šesták–Berggren [17] equation.

$$g(\alpha)=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}} \tag{6}$$

Using the above described procedure, the data in Tables 2 and 3 were obtained.

By inspecting the values in Tables 2 and 3, the parallel variation of ln$A$ *vs*. E is observed by each series of carboxylates. In means the presence of a compensation effect.

The isokinetic temperatures, calculated according to Eq. (1), are systematized in Table 4.

The way of the TG data processing avoids any subjective considerations or approximations. Nevertheless, the absence of a noticeable regularity in the variation of T_{iz} values or of E and ln$A$ pairs with the anion type make it difficult to discuss the reaction mechanism.

Table 4 The isokinetic temperature for the preponderant and secondary processes

Compound series	Isokinetic temperature, T_{iz}/K acc. Eq. (1)	
	preponderant process	secondary process
formates	680	396
acetates	582	474
propionates	492	509
butyrates	596	479

Conclusions

- data processing by the NPK methods allows to obtain the kinetic parameters in an objective manner, without any approximations
- the observed compensation effect is therefore a real phenomenon and the corresponding isokinetic temperature is able to have a real significance

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