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Note

COMPARISON BETWEEN A CLASSICAL METHOD AND TWO NEW METHODS TO EVALUATE NON-ISOTHERMAL KINETIC PARAMETERS

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This note gives a critical analysis of some results obtained by applying three methods to evaluate non-isothermal kinetic parameters of solid–gas decomposition namely the Coats–Redfern method [1], a modified Coats–Redfern method [2] and an iterative method [3]. The results concerning the thermal decomposition of the following polynuclear coordination compounds are compared

A $[\mathrm{DyNi(Bz.ac)_5}] \cdot 5\mathrm{H_2O}$

B $[\mathrm{HoNi(Bz.ac)_5}] \cdot 6\mathrm{H_2O}$

C $[\mathrm{SmNi(Bz.ac)_5}] \cdot 7\mathrm{H_2O}$

D $[\mathrm{NdNi(Bz.ac)_5}] \cdot 4\mathrm{H_2O}$

E $[\mathrm{Nd_2Ni(Bz.ac)_8}] \cdot 9\mathrm{H_2O}$

where Bz.ac is the anion of benzylic acid.

The non-isothermal kinetic parameters of the kinetically workable decomposition steps, calculated using the Coats–Redfern method, have been reported in a previous note [4]. To facilitate the examination of the results, the labelling of compounds with capital letters and the numbering of the reactions are the same as in the previous note.

The results are summarized in Table 1.

The inspection of this table shows that the two variants of the Coats–Redfern method lead to the same values of the non-isothermal kinetic parameters only for reaction (X). For the other kinetically workable decomposition steps, the differences between the values of non-isothermal kinetic parameters are variable and significant. Nevertheless, if the obtained values of the non-isothermal kinetic parameters are used to calculate the value of the rate constant for a given temperature, the values obtained according to the two variants of the Coats–Redfern method exhibit quite satisfactory agreement. As far as the iterative method is concerned, this was applied only

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TABLE 1

Values of non-isothermal kinetic parameters for workable decomposition steps of compounds A–E determined according to three methods

Compounds	Heating rate (K min^{-1})	Reaction temperature interval (°C)	Non-isothermal kinetic parameter values			
				Coats–Redfern method	Modified Coats–Redfern method	Iterative method
A	5.7	(III)	n	1	1	
		150–330	E(kcal mol^{-1})	17.4	23.7	
			A(s^{-1})	1.3×10^4	6.2×10^6	
			r	0.996	0.990	
			k(s^{-1})(290 °C)	2.29×10^{-3}	3.81×10^{-3}	
	3.0	(III)	n	1	1	
		150–330	E(kcal mol^{-1})	17.9	25.5	
			A(s^{-1})	1.0×10^4	1.6×10^7	
			r	0.989	0.989	
			k(s^{-1})(290 °C)	1.11×10^{-3}	1.98×10^{-3}	
	1.6	(III)	n	1	1	
		150–330	E(kcal mol^{-1})	19.0	40.8	
			A(s^{-1})	2.9×10^4	9.2×10^{12}	
			r	0.996	0.992	
			k(s^{-1})(290 °C)	1.21×10^{-3}	1.33×10^{-3}	
B	5.1	(IV)	n	0.8	0.8	0.8
		145–340	E(kcal mol^{-1})	16.2	24.1	19.6
			A(s^{-1})	3.1×10^3	5.7×10^6	7.2×10^4
			r	0.993	0.992	–
			k(s^{-1})(290 °C)	1.58×10^{-3}	2.33×10^{-3}	1.77×10^{-3}
	3.0	(VI)	n	1.2	1.2	1.2
		145–340	E(kcal mol^{-1})	17.9	26.2	26.4
			A(s^{-1})	4.1×10^4	4.0×10^7	9.1×10^8
			r	0.981	0.995	–
			k(s^{-1})(290 °C)	4.57×10^{-3}	2.69×10^{-3}	5.12×10^{-2}
C	5.6	(IX)	n	0	0	
		150–270	E(kcal mol^{-1})	20.9	35.9	
			A(s^{-1})	6.2×10^5	1.2×10^{12}	
			r	0.993	0.992	
			k(s^{-1})(240 °C)	7.72×10^{-4}	5.76×10^{-4}	
		(X)	n	1	1	
		275–330	E(kcal mol^{-1})	53.0	53.2	
			A(s^{-1})	9.9×10^{17}	1.3×10^{18}	
			r	0.988	0.981	
			k(s^{-1})(300 °C)	5.80×10^{-3}	6.34×10^{-3}	
D	3.2	(XIII)	n	0	0	
		120–280	E(kcal mol^{-1})	14.8	39.6	
			A(s^{-1})	3.8×10^2	4.2×10^{13}	
			r	0.985	0.994	
			k(s^{-1})(220 °C)	1.01×10^{-4}	1.09×10^{-4}	

TABLE 1 (continued)

Compounds	Heating rate (K $\min^{-1}$)	Reaction temperature interval (°C)	Non-isothermal kinetic parameter values			
				Coats–Redfern method	Modified Coats–Redfern method	Iterative method
E	5.7	(XV)	n	0.8	0.8	
		950–150	E(kcal mol^{-1})	16.7	22.7	
			$A(\text{s}^{-1})$	1.6×10^5	1.4×10^8	
			r	0.982	0.992	
			$k(\text{s}^{-1})$(120°C)	8.24×10^{-5}	3.32×10^{-5}	
		(XVI)	n	1.4	1.4	
		160–250	E(kcal mol^{-1})	12.9	15.3	
			$A(\text{s}^{-1})$	1.0×10^2	1.5×10^3	
			r	0.982	0.992	
			$k(\text{s}^{-1})$(200°C)	1.09×10^{-4}	1.27×10^{-4}	

r is the correlation coefficient.

in the case of reaction (III) given by compound **B** for two heating rates. Because of the lack of convergence in this case, the values of the non-isothermal kinetic parameters given in Table 1 are average values.

It should be noticed that in this case too there are significant differences between the individual values of non-isothermal kinetic parameters evaluated according to the three above-mentioned methods. These differences are "erased" using values of k (s^{-1}), whatever the difference between the values of the "reaction order" for the two applied heating rates, whose common probable value is in fact unity.

Thus in spite of the differences between the values of the non-isothermal kinetic parameters obtained using the three methods, these values describe correctly the thermogravimetric data.

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