The Study Of Thermal Stability And Decomposition In Cadmium Oxalate Single Crystals

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ABSTRACT

Cadmium Oxalate Single crystal grown using well known technique of crystal growth i.e gel technique. The grown crystal characterized using thermal technique. Their thermal behaviour is investigated using thermo analytical techniques (TGA,DTA, DSC). The thermogram reveals that the anhydrous oxalate is formed by liberating three molecules of water in the first step of transition gives the same reaction in both air and nitrogen atmosphere .The second phase transition results in CdO in air atmosphere while Cd is formed in nitrogen atmosphere at 385°C. Based on the data obtained from thermograms, different mechanic and non-mechanic equations are used to calculate kinetic parameters such as activation energy, order of reaction, frequency factor and entropy of the grown crystal.

Key words: Gel method, crystal growth,cadmium oxalate, characterisation

INTRODUCTION:

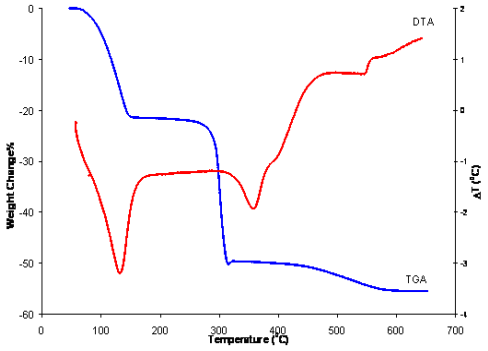
The thermal methods of investigations are generally referred to as thermo analytical techniques. This is an important experimental method for characterizing a system by measuring the changes in physico chemical properties as functions of increasing temperature with time. Cadmium oxalate crystals are obtained by diffusion of cadmium ions through silica hydrogel impregnated with oxalic acid at room temperature. The study of thermal analysis is significant for knowing the different phases and stages of stability and hence the grown crystals have been subjected to thermal treatments in air and nitrogen atmosphere using gravimetric thermal techniques. The methods used in the present analysis are thermogravimetry (TG) and Differential Thermal Analysis (DTA) and DSC. Our aim to do thermal analysis is to measure the temperature of transition, reliability of crystal for particular application, compositional analysis, stability of substance and other dynamic properties.

EXPERIMENTAL

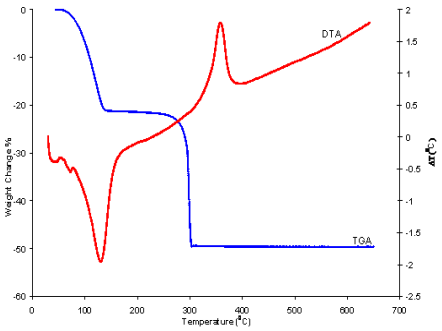
The thermogravimetric analysis (TGA) is carried out using 'Perkin Elmer' analyzer at ambient temperature respectively. The sample is heated at 10 °C/min. in the temperature range 50°C–900°C. The thermograms have been used for evaluation of some important kinetic parameters in respect of the decomposition phases of cadmium oxalate crystals. The DTA analysis is performed on 'Mettler 2000 C' system. During the analysis, thermal energy is added or subtracted from the sample and the reference material at the same temperature. A difference between temperatures of reference material and sample yields a direct calorimetric measurements of the transition energy. The DSC analysis is performed on 'Perkin Elmer' DSC – I Instrument . DSC is carried out only in nitrogen .

RESULTS AND DISCUSSIONS

From the curves obtained from TGA, DTA and DSC one can say that the decomposition in air atmosphere consists of two steps only while in the nitrogen atmosphere that has three steps, which is because in air atmosphere the final product is the metal oxide and do not reach to the metal.



TGA – DTA Curve at heating rate of 10 ^{0}C/min in N_2 atm.



TGA – DTA Curve at heating rate of 10 ^{0}C/min in N_2 atm..

Atm.	Step	Temp. Range(°C)	Mean Temp.(°C)	Mass Loss %		Reaction
				Obs.	Cal.	
N_2	I	55 -155	105	21.25	21.23	$CdC_2O_4 . 3H_2O = CdC_2O_4 + 3H_2O$
	II	265 -311	339.5	49.58	49.53	$CdC_2O_4 = CdO + CO + CO_2$
	III	400-596	498	55.417	55.8	$CdO = Cd + 1/2O_2$
Air	I	56 --- 145	98	21.25	21.23	$CdC_2O_4 . 3H_2O = CdC_2O_4 + 3H_2O$
	II	264 – 303	283.5	49.58	49.53	$CdC_2O_4 = CdO + CO + CO_2$

Thermal kinetics:

Horowitz - Metzger relation

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{1-n}\right)=\frac{E\theta}{2.303RT_m^2}$$

Where $T-T_m = q$, $n \neq 1$: n = 1/2, 1/4, 2/3, etc. From the plot the activation energy (E) can be calculated from the slope of the graph.

α = Weight loss up to particular temperature / Total weight loss in the step

R = Gas constant = 8.31432 x 10^3 J $K^{-1}$$mol^{-1}$,β = Heating rate (K/min^{-1}) ,T = Temperature (K)

Z = Frequency factor (min^{-1}) ,T_m = Temperature of maximum reaction rate.

Piloyan - Novikova relation

$$\log\left(\frac{\alpha}{T^2}\right)=\log\left(\frac{ZR}{\beta E}\right)-\frac{E}{2.303RT}$$

From the plot log (α/T^2) → 1/T, E can be calculated from the slope and Z from the intercept of the graph obtained.

Coats-Redferm relation

$$\log\left(\frac{2(1-\alpha)^{1/2}}{T^2}\right)=\log\frac{ZR}{\beta E}-\frac{E}{2.303RT}$$

From the plot $\log\left(\frac{2(1-\alpha)^{1/2}}{T^2}\right)$ → ***1/T, E*** *can be calculated from the slope and Z from the intercept of the graph obtained. Hence, the values of entropy S^* are obtained using the following equation:*

$$Z=\left[\frac{kTm}{h}\right]\exp\left[\frac{S^*}{R}\right]$$

Kinetic parameters evaluated from non-mechanistic equations for thermal analysis

Relation used	Atm.	Step	Order of Reaction (n)	Frequency Factor Z	Activation Energy		Entropy S* ($J.K^{-1}mole^{-1}$)
					(eV)	(J/mole)	
H - M	Air	I	½	–	0.599	57724.432	–
P - N			–	1.09×10^{6}	0.609	58688.112	-131.18
C - R			1	1.27×10^{6}	0.651	62735.568	-129.80
Broido			1	–	0.716	68999.488	–
H - M		II	½	–	1.95	187917.60	–
P - N			–	4.07×10^{10}	2.04	196590.72	-47.03
C - R			1	9.09×10^{10}	2.164	208540.35	-40.34
Broido			1	–	2.96	285249.28	–
H - M	N_2	I	½	–	0.6	57820.8	–
P - N			–	4.83×10^{5}	0.582	56086.18	-138.46
C - R			1	8.42×10^{5}	0.635	61193.68	-136.78
Broido			1	–	0.691	66590.29	–
H -M		II	½	–	2.334	224922.91	–
P - N			–	2.17×10^{10}	2.0	192736.0	-52.34
C -R			1	6.5×10^{10}	2.12	204300.16	-43.22
Broido			1	–	2.52	242847.36	–
H -M		III	½	–	0.945	91054.77	–
P - N			–	2.03×10^{5}	0.715	68903.12	-151.23
C -R			1	6.82×10^{5}	0.899	86634.83	-141.16
Broido			1	–	1.177	113425.14	–

Broido relation: - **lnln(1/y) = (E/(RT)) + constant.** *Here **y** = fraction of the number of initial molecules not yet decomposed.Where W_T = weight of active material at temperature T,W_0 = weight of the material taken initially,W_∞ = weight of the material at the end of reaction, Plotting lnln(1/y) $\rightarrow$ 1/T gives the value of the activation energy by the slope of this plot.Kinetic parameters evaluated from non-mechanistic equations for thermal analysis of CdC2O4 . 3H2O*

Borchardt and Daniels $k = \frac{\Delta T}{(A - a)}$ k = Specific reaction rate constant (min-1),A = Total area of a peak (min $\cdot$ ^{0}C) , ΔT = Peak height at any temperature T (^{0}C), a = Area of the peak at the temperature T (min$\cdot$ ^{0}C)

Piloyan, Ryabchikov and Novikova $\ln\Delta T = C' - E/RT$ The values of ΔT are taken directly from the DTA curve in units of length.Thus by ploting the graph of lnΔT $\rightarrow$ 1/T we have calculated the required activation energy and frequency factor

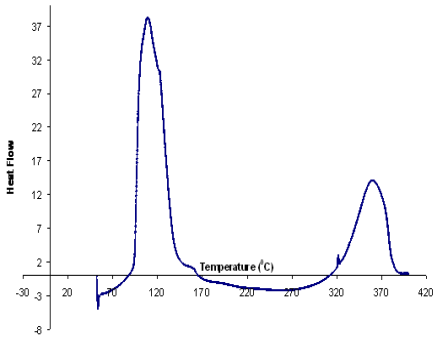
Some kinetic parameters calculated from DTA using different models

Relation used	Atm.	Stage	Activation energy E (eV)	Frequency Factor Z (min^{-1})	Order of reaction (n)	Entropy 'S' ($J.K^{-1}.mol^{-1}$)
P R N	N_2	I	0.686	1.075×10^{9}	1	-74.556
		II	2.04	2.24×10^{16}		62.521
	Air	I	0.683	1.67×10^{10}	1	-51.75
		II	1.83	6.30×10^{14}		32.836
B D	N_2	I	0.779	3.268×10^{8}	1	-84.469
		II	2.33	3.49×10^{16}		66.207
	Air	I	0.672	2.264×10^{8}	1	-87.508
		II	2.064	1.425×10^{15}		39.617

Matusita and Sakka (MS) relation $\log[-\ln(1-x)] = -n\log\alpha - \frac{mE}{2.303\,RT} + constant$

Where E is the activation energy, α is the healing rate, n and m are numerical constant, depend upon the mechanism of crytallization

Some kinetic parameters calculated from DSC thermogram



Peak	Peak Height (mW)	Peak Area (mJ)	Peak Temp.(°C)	ΔH (J/g)	C_p ($Cal.g^{-1}$ °C)	r_{eff} (A°)
I	39.26	7337.92	108.729	587.88	1.521	0.57
II	13.108	2692.72	360.214°	215.728	0.508	1.55

Relation used	Atm.	Stage	Activation Energy E (eV)	Frequency Factor Z (min^{-1})	Order of reaction (n)	Entropy 'S' ($J.K^{-1}.mol^{-1}$)
M S	N_2	I	0.912	9.016×10^{8}	1	-75.562
		II	2.437	5.197×10^{14}		30.512

CONCLUSIONS:

The crystals of cadmium oxalate trihydrate are thermally stable upto 54^0C, beyond which they begin to decompose. implies weak ionic bonds.The decomposition of the grown crystals occurs sequentially, gradually in three stages in nitrogen atmosphere while in two steps in air atmosphere. First, dehydration takes place, when the water molecules are liberated out. Then, the anhydrous material breaks down (the ionic bonding may be breaking), resulting ultimately into

the production of cadmium oxide which is seen not to be stable for high temperatures, upto around 400 ^{0}C.The activation energy (and so also the frequency factor) of the dehydration step is the smallest of all the stages of decomposition implies low energies involved for loosening of the bonded water molecules.

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