

HETEROLEPTIC CADMIUM(II) COMPLEX, POTENTIAL PRECURSOR FOR SEMICONDUCTING CdS LAYERS

Thermal stability and non-isothermal decomposition kinetics

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Coordination compounds may be used as efficient precursors for fabrication of semiconducting layers. Thermal stability of such a potential precursor – $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$ – was investigated (*tBu* means *tert*-butyl and *Et* means ethyl). The kinetic study was performed by means of different multi-heating rate methods: isoconversional (Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose and Friedmann) methods associated with the criterion of the independence of the activation parameters on the heating rate. The kinetic triplet of the non-isothermal decomposition of this Cd(II) complex was established.

Keywords: multi-heating rate methods, non-isothermal kinetics, precursor for semiconducting CdS layers

Introduction

Sulfur containing compounds e.g. thiolates or dithiocarbamates are often used as ligands in coordination chemistry and related complexes have been extensively studied for the past decades [1]. Recently they have gained new interest since they can provide a source for metal-sulfur species [2] whose applications vary from molecular biology (simple models of some biomolecules) to material engineering (thin layers). These systems are important because of their possible efficiency as precursors for semiconducting CdS layers fabrication [3, 4]. The films can be obtained by classical coating techniques or by laser deposition, using the Cd(II) coordination compounds as deposition phase/target. After the deposition of the coordination complexes, the semiconducting layers are manufactured by appropriate thermal treatment of the deposited systems.

Up to now, there was not much known about compounds having such two types of ligands as thiolate and dithiocarbamate coordinated simultaneously to the same metallic centre. Moreover, thermal behavior of a few known assemblies [5–7] was not studied in detail. Thermal stability studies are, however, indispensable before attempting any deposi-

tion experiments. In fact, both thermal decomposition study and the evaluation of the kinetic parameters are important in order to obtain the right decomposition product (CdS) which exhibits the desired semiconducting properties.

Experimental data for the kinetic analysis of heterogeneous processes can be obtained under different conditions. Under non-isothermal conditions, for a single heterogeneous process, the reaction rate can be expressed by the Eq. (1):

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-\frac{E}{RT}} \quad (1)$$

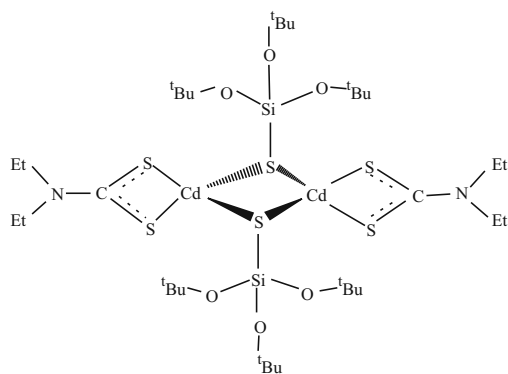
where α is the conversion degree, $(d\alpha/dt)$ is the reaction rate, A is the pre-exponential factor, E is the activation energy, $f(\alpha)$ is the differential conversion function and R is the universal gas constant.

Recent papers have reported on the critical analysis of the single heating rate methods [8–10], suggesting that their use may lead frequently to uncertain values of the activation parameters. That is why the combined kinetic analysis of the experimental data obtained under any temperature profile (isothermal, non-isothermal or SCTA) and by means of multiple temperature regimes is recommended [11].

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Experimental

The neutral $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$ complex (Compound 1) [12, 13] was obtained in the reaction of $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}_2]$ [14] with sodium diethyldithiocarbamate in the presence of a tetraalkylammonium salt.



Compound 1 $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$

Thermogravimetry coupled with IR was carried out in argon flow (purge: 90 mL min^{-1} and protective: 65 mL min^{-1}) using Netzsch Thermobalance TG 209 coupled with a Bruker IFS66 FTIR spectrometer. Approximately, 8–10 mg samples were contained in Al_2O_3 crucibles. The experiments were carried out in the temperature range 20–500°C, for the heating rates of 2, 5, 8 and 10 K min^{-1} . The volatiles evolving from the heated sample were transported to the spectrometer chamber via thermostated pipe in a stream of argon. Differential Scanning Calorimetry measurements were performed with a PerkinElmer DSC7, in similar experimental conditions, for the heating rate of 10 K min^{-1} . The XRD measurements on the crystalline residue were performed at room temperature using X'Pert Philips diffractometer (source radiation: $\text{CuK}\alpha_1$, $\lambda=0.1546 \text{ nm}$, 40 kV, 30 mA).

Results and discussion

Thermal analysis and complementary techniques

Figure 1 shows the TG and DTG curves of the investigated compound recorded at 2 K min^{-1} ; similar curves were obtained for all other heating rates. Between 100 and 220°C, the system loses around 3.5% of its total mass, what most probably corresponds to the adsorbed solvent (toluene or water).

After melting at 246°C, $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$ undergoes endothermic decomposition between 250 and 320°C. The experimental loss of mass ($\Delta m_{\text{exp}}=79.0\%$) corresponds to the theoretical one ($\Delta m_{\text{theor}}=74.67\%$).

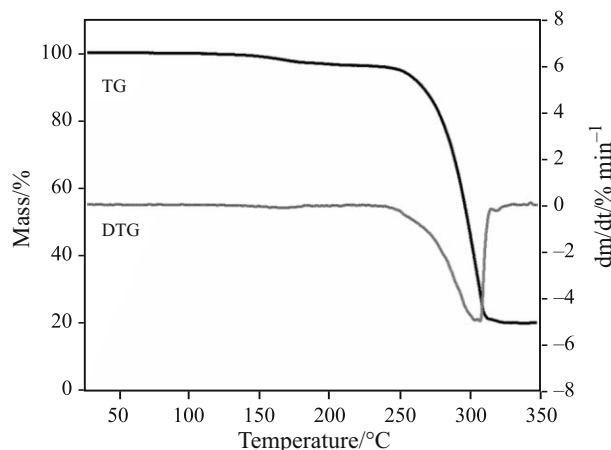


Fig. 1 Thermogravimetric curves of $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$ for the heating rate of 2 K min^{-1}

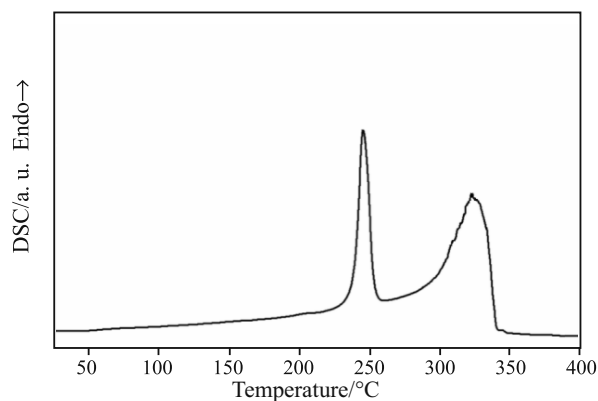


Fig. 2 DSC heating scan curve of $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]$ for the heating rate of 10 K min^{-1}

The DSC curve indicates two heat transfers, corresponding to the melting and decomposition of the investigated compound.

There are two major species in the thermal decomposition products during this process, namely, $\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2$ (which may consist of CS_2 and $\text{N}(\text{C}_2\text{H}_5)_2$ anions [15] with absorption bands at 1542 and 1526 cm^{-1}) and silyl rest with absorption bands at 1074 cm^{-1} . The tri-*tert*-butoxysilyl substituents most probably undergo also decomposition into gaseous products possessing both Si–OH ($\nu_{\text{Si-O}}=1074 \text{ cm}^{-1}$) and Si–O–*t*Bu ($\nu_{\text{C-O}}=1190 \text{ cm}^{-1}$) fragments. It is evidenced by the presence of bands arising from symmetric and

Table 1 DSC thermal parameters for the heating rate of 10 K min^{-1}

Change	Maximum temperature $T_{\text{max}}/^\circ\text{C}$	Temperature range $T_i-T_f/^\circ\text{C}$	Transferred heat $\Delta H/\text{kJ kg}^{-1}$
Melting	246	238–248	64.0
Decomposition	325	290–340	89.2

asymmetric scissor-bending vibration modes characteristic for *tert*-butyl substituent (1391 and 1368 cm^{-1}) as well as skeleton vibration of *t*-Bu rest as a whole (1241 cm^{-1}). In the FTIR spectra of the off-gases, a small amount of ethyl isothiocyanate ($\text{C}_2\text{H}_5\text{NCS}$) with absorption bands at 2072 and 2050 cm^{-1} can be detected. The existence of alkylisothiocyanate has been confirmed in the decomposition processes of other dialkyldithiocarbamate complexes [15].

After the decomposition, a yellow crystalline powder is obtained. The experimental mass of the residue points toward CdS as final reaction product. The X-ray pattern of the residue indicates only the presence of α -CdS wurzite-type crystallites. For characterization and qualitative analysis the results were compared with standard data from the International Centre for Diffraction Data [16].

Kinetic parameters evaluation

The overall kinetic triplet (E , A , $f(\alpha)$) – which describes the time evolution of a physical or a chemical change in a heterogeneous system, unfortunately cannot be always used for the prediction of the system change in time in other conditions than those in which the experiments were performed [10]. Activation parameters should not be evaluated and interpreted without considering the conversion function [17].

The influence of different temperature regimes upon the thermal behavior of the investigated compounds can provide sometimes kinetic parameters indicating change in the reaction pathway. The complexity of a single stage can be expressed from the kinetic triplet dependence on the increasing conversion degree. This can be done using the isoconversional

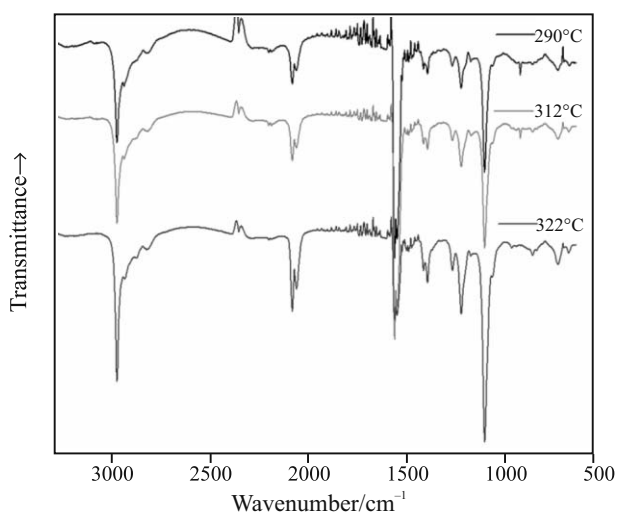


Fig. 3 FTIR spectra of the volatiles evolving during TG analysis of $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNEt}_2)_2]_2$, recorded at several temperatures, for $\beta=2\text{ K min}^{-1}$

methods for the evaluation of the activation energy. If E does not depend on α , the investigated process is a simple one and should be described by a unique kinetic triplet. If E changes with α , the process is complex [18], and in order to discriminate between the occurring reactions, programs were developed, assuming that the overall reaction is the sum of individual reaction steps [19–21].

The investigation of the kinetic triplet has two main purposes: one theoretical and the other practical [22].

Papers reporting on the utility [23] and applications of the kinetic analysis, such as: decomposition of energetic materials [24, 25], flame retardants [26], template removal from porous materials [27], polymer degradation [18], crystallization of glass [28, 29] and life time prediction of explosives [30], have been published over the last years.

In this paper, the kinetic study of the decomposition of the Cd(II) coordination complex was performed using TG and DTG data.

Isoconversional methods

The isoconversional procedures ('model-free kinetics') can be classified as linear (the activation energy is evaluated from the slope of a straight line) [31–36] and non-linear (the activation energy is evaluated from a specific minimum condition) [37–40]. The differential non-linear method [40] leads to results almost similar to the Friedmann (FR) method [35] when the integral non-linear method [37–39] leads to results similar to Kissinger–Akahira–Sunose (KAS) [31, 32] and Flynn–Wall–Ozawa (FWO) [33, 34] methods.

The isoconversional integral linear methods are based on the following integral form of the reaction rate:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^{T_\alpha} e^{-\frac{E}{RT}} dT = \frac{A}{\beta} I(E_\alpha, T_\alpha) \quad (2)$$

where β is the heating rate, $g(\alpha)$ is the integral conversion function and $I(E_\alpha, T_\alpha)$ represents the temperature integral. Substitution of $I(E_\alpha, T_\alpha)$ in the Eq. (2) with Coats–Redfern approximation [41]:

$$I(E_\alpha, T_\alpha) = \frac{RT_\alpha^2}{E_\alpha} e^{-\frac{E_\alpha}{RT_\alpha}}$$

gives Eq. (3) – used by KAS method. Similar substitution with Doyle approximation [42]:

$$I(E_\alpha, T_\alpha) = \frac{E_\alpha}{R} e^{\left(-5.331 - 1.052 \frac{E_\alpha}{RT_\alpha}\right)}$$

gives Eq. (4) – used by FWO method.

Table 2 Activation energy obtained by means of KAS method

α	$E_{KAS}/\text{kJ mol}^{-1}$	+/-	r	α	$E_{KAS}/\text{kJ mol}^{-1}$	+/-	r
0.15	130.5	1.8	0.9999	0.55	144.8	7.9	0.9985
0.20	131.6	3.0	0.9997	0.60	146.0	6.6	0.9990
0.25	132.6	4.4	0.9994	0.65	147.3	5.3	0.9993
0.30	136.1	5.1	0.9993	0.70	148.6	8.9	0.9982
0.35	139.6	5.7	0.9992	0.75	146.2	5.6	0.9993
0.40	140.2	6.1	0.9990	0.80	148.8	7.6	0.9987
0.45	142.2	6.2	0.9990	0.85	148.2	9.2	0.9981
0.50	143.7	5.2	0.9993	0.90	143.0	5.5	0.9992

Table 3 Activation energy obtained by means of FWO method

α	$E_{FWO}/\text{kJ mol}^{-1}$	+/-	r	α	$E_{FWO}/\text{kJ mol}^{-1}$	+/-	r
0.15	133.0	1.7	0.9999	0.55	146.8	7.6	0.9987
0.20	134.0	2.9	0.9997	0.60	148.0	6.4	0.9991
0.25	135.0	4.2	0.9995	0.65	149.2	5.1	0.9994
0.30	138.4	4.9	0.9993	0.70	150.5	8.6	0.9984
0.35	141.7	5.5	0.9992	0.75	148.2	5.4	0.9993
0.40	142.4	5.9	0.9991	0.80	150.7	7.2	0.9988
0.45	144.3	6.0	0.9991	0.85	150.2	8.7	0.9983
0.50	145.7	5.0	0.9994	0.90	145.3	5.3	0.9993

Kissinger–Akahira–Sunose (KAS method) – integral linear method [31, 32]

This isoconversional integral linear method is based on the Coats–Redfern's approximation [41] of the temperature integral. It was shown that:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(\alpha)} - \frac{E}{RT} \quad (3)$$

Thus, for $\alpha = \text{const.}$, the plot $\ln(\alpha/T^2)$ vs. $(1/T)$ obtained from the experimental thermogravimetric curves, recorded for several heating rates, should be a straight line whose slope could be used for the activation energy evaluation.

Table 2 shows the results obtained using KAS method, as values of the activation energy at various conversion degrees.

Flynn–Wall–Ozawa (FWO method) – integral linear method [33, 34]

This isoconversional integral linear method, suggested independently by Flynn and Wall [33] and by Ozawa [34] uses Doyle's approximation [42] of the temperature integral. This method is based on the equation:

$$\ln \beta = \ln \frac{AE}{Rg(\alpha)} - 5.331 - 1.052 \frac{E}{RT} \quad (4)$$

Thus, for $\alpha = \text{const.}$, the plot $\ln(\beta)$ vs. $(1/T)$ obtained from the experimental thermogravimetric curves, recorded for several heating rates, should be a straight line whose slope could be used for the activation energy evaluation.

Table 3 shows the results of using FWO method, as values of the activation energy at various conversion degrees.

The results obtained by KAS and FWO methods are comparable. The differences between the values of the activation energy obtained by using these two isoconversional integral methods may be attributed to the different approximations of the temperature integral. The mean values of the activation energy for $0.15 < \alpha < 0.90$ are:

$$\bar{E}_{KAS} = 141.8 \pm 6.0 \text{ kJ mol}^{-1}, \quad \bar{E}_{FWO} = 144.0 \pm 5.8 \text{ kJ mol}^{-1}$$

Friedmann (FR method) – differential linear method [35]

The differential linear isoconversional method suggested by Friedmann [35] is the most general isoconversional method which uses the derivative curves. Unlike other methods, this one makes no assumption on the temperature integral. Friedmann modified the general equation of the reaction rate and obtained the following expression:

$$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E}{RT} \quad (5)$$

For $\alpha = \text{const.}$, the plot $\ln(d\alpha/dt)$ vs. $(1/T)$ obtained from the thermogravimetric derivative curves, recorded for several heating rates, should be a straight line whose slope could be used for the activation energy evaluation. Table 4 contains the activation energy values obtained by applying Friedmann method.

The mean value of the activation energy for $0.15 < \alpha < 0.85$ is:

$$\bar{E} = 146.0 \pm 6.7 \text{ kJ mol}^{-1}$$

The kinetic results can be affected by inherent errors arising from $d\alpha/dt$ values (both from the DTG signal obtained directly from the thermobalance or from the numerical differentiation of the TG curve). The noise may be serious when α changes slowly, e.g. at the beginning and at the end of the reaction [36, 43].

There is a good agreement between the integral and differential 'model-free' kinetics. The small differences are the result of the different data involved in the calculations (TG and DTG data).

Perez–Maqueda *et al.* criterion [44]

Based on Criado and Morales' early observation [45], it was suggested [46] that almost any $\alpha = \alpha(T)$ or $(d\alpha/dt) = (d\alpha/dt)(T)$ experimental curve may be relatively correctly described by several conversion functions (integral or differential). For various non-isothermal linear experiments, only one conversion function (kinetic model) from all known heterogeneous reaction mechanisms, fits simultaneously all the data [44].

In order to obtain the appropriate conversion function, one can discriminate between them by applying the Perez–Maqueda *et al.* criterion. According to this criterion, the correct kinetic model corresponds to the independence of the activation parameters on the heating rate. By applying any differential or integral method which uses only a single heating rate – curve, for every constant heating rate, the true kinetic

model shall provide both the same constant activation energy as well as the pre-exponential factor.

If the Coats–Redfern equation written in the form:

$$\ln \frac{\beta g(\alpha)}{T^2} = \ln \frac{AR}{E} - \frac{E}{RT} \quad (6)$$

is used, for the correct conversion function, the points $\{\ln[\beta g(\alpha)/T^2]$ vs. $1/T\}$ corresponding to all the heating rates lie on the same straight line.

Figure 4 shows the straight line $\{\ln[\beta g(\alpha)/T^2]$ vs. $1/T\}$ for the true conversion function A1.4.

From the parameters of the A1.4 straight line, one obtains:

$$E = 143.9 \pm 1.4 \text{ kJ mol}^{-1}, \ln A = 23.95 \pm 5.1 \text{ ([A] = s}^{-1}\text{)}$$

$$A = 2.5 \cdot 10^{10} \pm 1.6 \cdot 10^2 \text{ s}^{-1}$$

These values are in agreement with those obtained by isoconversional methods.

Obtaining the A1.4 model as the suitable one, as well the other two kinetic parameters, was not the result of a random choice from a pre-established set of conversion functions.

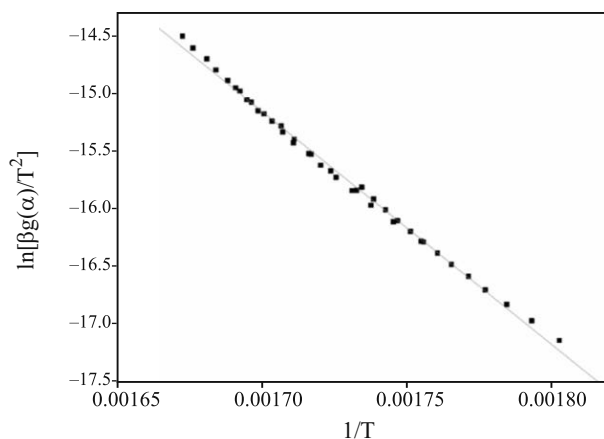


Fig. 4 The Perez–Maqueda *et al.* straight line

Table 4 Activation energy obtained by means of Friedmann method

α	$E_{FR}/\text{kJ mol}^{-1}$	+/-	r	α	$E_{FR}/\text{kJ mol}^{-1}$	+/-	r
0.15	134.4	7.1	0.9986	0.55	146.1	1.9	0.9999
0.20	136.8	4.8	0.9994	0.60	146.7	2.4	0.9998
0.25	145.3	5.4	0.9993	0.65	146.4	2.0	0.9999
0.30	157.4	12.1	0.9976	0.70	146.2	0.1	1
0.35	154.8	6.1	0.9992	0.75	140.9	0.2	1
0.40	152.0	2.4	0.9999	0.80	143.6	2.8	0.9998
0.45	151.9	0.4	1	0.85	137.1	6.0	0.9990
0.50	149.9	0.5	1				

Although the conversion function corresponds to a nucleation model, the description of our experimental data by this function does not necessarily mean that the reaction proceeded according to the mechanism for which the conversion function was originally derived. In fact, A1.4 model belongs to the empirical expression of the conversion function suggested by Šesták and Berggren [47].

Conclusions

Thermal stability of $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNET}_2)_2]$ compound was investigated. The kinetic parameters for the decomposition process of heteroleptic Cd(II) complex with different S-donor ligands were evaluated. The kinetic study by means of the isoconversional methods leads to constant activation energy values during the decomposition process, which are in good agreement with those obtained with Perez-Maqueda *et al.* criterion.

The kinetic results correlated with the thermogravimetric analysis and infrared studies of the evolved gases, lead to the conclusion that the decomposition undergoes in a single step, as a single reaction mechanism. It turned out that A1.4 kinetic model is the most suitable one.

The investigation has confirmed that $[\text{Cd}\{\text{SSi}(\text{O}-t\text{Bu})_3\}(\text{S}_2\text{CNET}_2)_2]$ complex is thermally stable in order to perform a good deposition and is also a new promising precursor for obtaining α -CdS layers.

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DECOMPOSITION KINETICS OF A HETEROLEPTIC CADMIUM(II) COMPLEX

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