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Thermal degradation of coordination polymer $[Cd(N\text{-Boc-gly})_2(H_2O)_2]_n$

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ABSTRACT

Multi-step thermal degradation of coordination polymer $[Cd(N\text{-Boc-gly})_2(H_2O)_2]_n$ in non-isothermal conditions was studied. The kinetic parameters were determined from the thermal decomposition data using the isoconversion and non-isoconversion techniques. It was shown that the coordination polymer is stable up to 60 °C, when the multi-step process of thermal dehydration, followed by steps of degradation, starts. The kinetic triplet for the step of dehydration was established as $f(\alpha) = 3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$, $E_{inv} = 170.4 \pm 6.4\,kJ\,mol^{-1}$ and $Z_{inv} = 2.6 \times 10^{23}$. The established kinetic model, known as "D3 model", was confirmed by application criteria defined by Màlek, Perez-Maqueda et al. as well as Master plot method. Dehydration step is followed by two steps of dehydrated coordination polymer degradation. On the base of the dependence of Arrhenius parameters (E_a and Z) on conversion degree (α), the mechanisms of degradation were discussed. In this way it was shown that second and third steps of degradation of coordination polymer are complex involving more than one elementary step. The second step corresponds to the loss of two $C_6H_5CH_2O-$ fragments in two parallel steps. The third step of degradation, ascribed to the loss of two $-C(=O)NHCH_2-$ fragments, is complicated by changing kinetically to diffusion control.

1. Introduction

Metal coordination polymers of transition metals containing different organic ligands are new compounds attracting significant attention of many researchers in the past few years. They are in focus of many researches due to their structures which are characterized by high dimensionality, advantageous magnetic, optical and other physical and chemical properties and wide range of applications such as adsorbents, sensors and catalysts [1–5]. These compounds possessing very complex structure, involving often beside organic ligands (polymeric or monomeric) and water molecules in inner as well as outer sphere of complex, are thermally unstable and undergo to stepwise structural transformations involving dehydration and degradation at high temperatures. These processes lead to loss of their advantageous properties limiting their application on the conditions where they retain their favorable structure. In spite the existence of many studies concerning their synthesis, characterization, physical–chemical properties [6–10] there are no many papers dealing with thermal degradation kinetics. Most studies on thermal degradation kinetics are based on determination of thermodynamic parameters [11–15] and kinetic parameters using Coats–Redfern equation [16], Freeman–Carroll and Sharp–Wentworth methods [17–19]. However, only few studies are dealing with thermal decomposition mechanism and determination of most probable kinetic model function [20–22].

Results presented in this manuscript are part of our detailed and systematic multidisciplinary studies concerning synthesis and characterization of new transition metal complexes with *N*-benzyloxycarbonylglycinato ligand [23,24]. Although all these systems belong to the same group of compounds, their individual chemical and crystal structures are different, owing to different coordination of metal ions. Therefore, it is interesting from a fundamental point of view to investigate their physicochemical properties and correlate them with different structures exhibited by each compound. From the practical point of view, as prepared Co(II), Cd(II) and Zn(II) complexes with this ligand showed good antimicrobial and antifungal activity. Thermal degradation of these complexes could lead to deterioration of their favorable properties, which imposes the need for more detailed understanding of their thermal stability and degradation kinetics. In addition, Cd(II) complex stands out because it is the only one to exhibit polymeric structure, which is why we placed particular focus on it.

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2. Material and methods

2.1. Material and techniques

The Cd(II) coordination polymer with the *N*-Boc-gly ligand and formula $[Cd(N\text{-Boc-gly})_2(H_2O)_2]_n$ was prepared in a simple reaction between $CdCl_2{\cdot}2.5H_2O$ and *N*-Boc-glyH (molar ratio 1:2, ethanol–water mixture, pH 5–6), as previously described [23].

Non-isothermal thermal degradation was studied by using an SDT Q600 (TA Instruments) apparatus for simultaneous TG-DTA analysis. TG experiments and simultaneously recorded DTA signals were performed from room temperature to 900 °C at different heating rates (5–20 °C min^{-1}) with sample masses about 6 mg in a dry nitrogen atmosphere (flow rate 100 cm^3 min^{-1}) using Pt crucibles. The Pt crucible with a small amount of Al_2O_3 was used as a reference.

2.2. Solid state kinetics

The kinetics of solid state reactions can be described by equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $f(\alpha)$ is the conversion function concerning the kinetic model [25], $k(T)$ is the Arrhenius rate constant, T is temperature, t is time. For non-isothermal conditions, when temperature varies with time with constant heating rate, $\beta = dT/dt$, Eq. (1) is represented as

$$\frac{d\alpha}{dT} = \left(\frac{Z}{\beta}\right)\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{2}$$

where Z is pre-exponential factor, E is the apparent activation energy and R is the gas constant. Eq. (2), as well as numerous approximations of its integral form

$$g(\alpha) = \left(\frac{Z}{\beta}\right)\int_0^T \exp - \left(\frac{E_a}{RT}\right)dT \tag{3}$$

where $g(\alpha) = \int_0^\alpha d\alpha/f(\alpha)$ is the integral form of the conversion function.

The mechanism of each step can be evaluated from the activation energy dependence on the conversion degree. This can be done using isoconversional methods also known as "model-free methods". These methods require determination of the temperature T_α at which an equivalent stage of the reaction occurs for various heating rates [26]. Widely accepted procedure is Kissinger–Akahira–Sunose's (KAS) method [27,28] in the form:

$$\ln\left(\frac{\beta}{T_\alpha^2}\right) = \ln\left(\frac{ZR}{E_a}f(\alpha)\right) - \frac{E_{a,\alpha}}{RT_\alpha} \tag{4}$$

In this sense [27,28], the linear isoconversional relationship of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$ and, describing non-isothermal TG data for different heating rates, can be used to determine the kinetic parameters: apparent activation energies $E_{a,\alpha}$ and intercepts $\ln[(ZRf(\alpha))/E_{a,\alpha}]$ for selected conversion degree according to equation (4), even without the knowledge of the true conversion function. If E_α does not depend on α, the investigated process can be treated as single-step process and should be described by a unique kinetic triplet. If E_α changes with α a process is complex [29–32]. In this case, based on the inter-relationship $E_\alpha = f(\alpha)$, Vyazovkin and Lesnikovich proposed very simple algorithm for discussing the mechanism of complex process [33].

In order to obtain the appropriate conversion function for processes considered as single-step process, we can discriminate between the set of conversion functions [25] by applying the Màlek's method [34], Perez-Maqueda et al. criterion [35] and Master plot procedure [36].

Having determined apparent activation energy, Màlek's method [34] involves the introducing two new functions defined as

$$y(\alpha) = \left(\frac{d\alpha}{dt}\right)\exp\left(\frac{E_a}{RT}\right) \text{ and } z(\alpha) \approx \left(\frac{d\alpha}{dt}\right)T^2 z(\alpha) \approx \left(\frac{d\alpha}{dt}\right)T^2. \tag{5}$$

These two functions can be easily obtained by a simple transformation of experimental data, $d\alpha/dt$, normalized within (0, 1) interval and by using values of E_a from KAS method. In non-isothermal conditions $y(\alpha)$ and $z(\alpha)$ plots are independent from heating rate and they exhibit maxima at α_y^* and α_z^* [34]. These maxima have characteristic values for basic kinetic models [34].

According to the Perez-Maqueda et al. criterion [35], the correct conversion function corresponds to the independence of the activation parameters on the heating rate. By applying any differential or integral model-fitting method, for every heating rate, the true kinetic model should provide both the activation energy as well as the pre-exponential factor. If the Coats–Redfern equation written in the form:

$$\ln\left(\frac{\beta g(\alpha)}{T_\alpha^2}\right) = \ln\left(\frac{Z_j R}{E_a}\right) - \frac{E_{a,j}}{RT_\alpha} \tag{6}$$

is used, where $E_{a,j}$ is activation energy and Z_j is pre-exponential factor and j indices specific model $g(\alpha)$, all the points $\ln(\beta g(\alpha)/T_\alpha^2)$ versus $1/T$ correspond to the same straight line for all applied heating rates for the correct conversion function $g(\alpha)$.

According to Master plod procedure [36], for a single-step process, the following equation is applied

$$\frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}}\frac{\exp(E_a/RT)}{\exp(E_a/RT_{0.5})} = \frac{f(\alpha)}{f(0.5)} \tag{7}$$

where $f(0.5)$ is a constant for given conversion function.

In accordance with IKP method based on the real compensation effect [36,37] the straight lines of $\ln Z_j$ versus E_j dependences should be constructed using the apparent activation parameters obtained by Coats–Redfern method (for all heating rates). These straight lines should intersect in one point corresponding to the true values known as "invariant activation parameters", $\ln Z_{inv}$ and E_{inv} [38].

The invariant kinetic parameters $\ln Z_{inv}$ and E_{inv}, were evaluated by using the super-relation:

$$a_\beta = \ln Z_{inv} - b_\beta E_{inv}. \tag{8}$$

3. Results and discussion

3.1. Thermal stability of the coordination polymer $[Cd(N\text{-Boc-gly})_2(H_2O)_2]_n$

DTA and TG curves of the $[Cd(N\text{-Boc-gly})_2(H_2O)_2]_n$ were recorded at different heating rates (β = 5, 10, 15 and 20 °C min^{-1}) under dynamic nitrogen atmosphere in the temperature interval of 20–900 °C. All curves are shifted to a higher temperature with an increase of heating rate, verifying that thermal activation steps occur during the degradation. The curves obtained at β = 10 °C min^{-1} are shown in Fig. 1.

Our previous results showed that polymer structure of the complex is stable up to 60 °C when multi-step degradation begins with loss of two molecules of coordinated water (rate maximum at 94.1 °C for β = 5 °C min^{-1}) [24]. Further, in the range 123–269 °C dehydrated coordination polymer loses two $C_6H_5CH_2O$– fragments (rate maximum 178.6 °C for β = 5 °C min^{-1}). The ligand chain degradation continues in temperature range 269–461 °C (rate maximum