TITANIUM(IV)–EDTA COMPLEX
Kinetics of thermal decomposition by non-isothermal procedures

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This work aims the evaluation of the kinetic triplets corresponding to the two successive steps of thermal decomposition of Ti(IV)–ethylenediaminetetraacetic acid (EDTA) in the solid-state. Applying the isoconversional Wall–Flynn–Ozawa method on the DSC curves, average activation energy: $E=172.4\pm9.7$ and $205.3\pm12.8$ kJ mol$^{-1}$, and pre-exponential factor: $\log A=16.38\pm0.84$ and $18.96\pm1.21$ min$^{-1}$ at 95% confidence interval could be obtained, regarding the partial formation of anhydride and subsequent thermal decomposition of uncoordinated carboxylate groups, respectively.

From $E$ and $\log A$ values, Dollimore and Málek methods could be applied suggesting PT (Prout–Tompkins) and R3 (contracting volume) as the kinetic model to the partial formation of anhydride and thermal decomposition of the carboxylate groups, respectively.

Keywords: activation energy, kinetic model, non-isothermal kinetics, Ti(IV)–EDTA, TiO$_2$

Introduction

Solid Ti(IV)–EDTA complex

Despite the fact the great number of complexes between ethylenediaminetetraacetic acid (EDTA) and metals ions described in literature, there are few studies regarding to the complexes of Ti(IV)–EDTA in the solid-state. Sawyer and McKinnie [1] suggested the formation of the solid TiOH$_2$EDTA$\cdot$H$_2$O and they observed, through infrared spectra, that the TiO$^{2+}$ ion was covalently bonded to only two carboxylate groups of the ligand.

The TiO(EDTAH$_2$)$\cdot$H$_2$O compound was obtained by Kristine et al. [2] by mixing the stoichiometric amounts of disodium EDTA salt and TiO$^{2+}$ ions in solution after adjustment the pH to 1.5. The structural nature of TiO(EDTA)$^2^-$ in solution and its reaction with H$_2$O$_2$ forming TiO$_2$(EDTA)$^2^-$ was studied at pH 2.0–5.2.

Fackler et al. [3] suggested, through X-ray diffraction, the formation of the pentacoordinated compound [Ti(EDTA)(H$_2$O)] with a geometric structure of a pentagonal-bipyramid.

Studies concerning the thermal behavior and mainly the obtainment of the kinetic triplet to thermal decomposition reaction had not been reported.

Kinetics aspects

The rate law for a solid-state process can be expressed by a simple differential kinetic equation [4]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (1)$$

where $A$ is the preexponential factor, $E$ is the activation energy, $R$ is the gas constant and $f(\alpha)$ is an algebraic expression of kinetic model as a function of fractional conversion $\alpha$ ($0 < \alpha < 1$). The Arrhenius parameters should not depend on the temperature $T$ and the fractional conversion $\alpha$ [4]. For dynamic data obtained at a constant heating rate, $\beta = dT/dt$, this new term is inserted in the Eq. (1) to obtain the transformation [5]:

$$\frac{d\alpha}{\beta} = A \exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

This rather trivial transformation presents a great physical meaning. It implicitly assumes that the change in experimental conditions from isothermal to non-isothermal does not affect the reaction kinetics. Intuitively, this assumption feels quite reasonable, at least as long as we are dealing with a single-step process. Non-isothermal heating resolved a major problem of the isothermal experiment, which is that a sample requires some time to reach the experimental temperature undergoing some transformations that are likely to affect the results of the following kinetic analysis. This problem especially restricts the use of high temperatures in isothermal experiments [6]. The kinetic analysis through isoconversional methods support the principle that reaction rate at a constant extent of conversion $\alpha$ is only function of temperature [6]. The isoconversational method of Flynn, Wall and Ozawa for evaluating the activation energy uses the integral form of Eq. (2) to obtain the transformation [5–7]:

$$g(\alpha) = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\beta R} p(x) \quad (3)$$
where \( x=(E/RT) \). For \( p(x) \), where 20\( \leq x \leq 60 \), we can use the Doyle’s approximation of the integral temperature [5, 7, 8]:

\[
\log p(x) \approx -2.315 - 0.4567x
\] (4)

However, a simpler expression has been developed by the substitution of Eq. (4) into Eq. (3) to obtain [5, 7]:

\[
\log g(\alpha) \equiv \log \frac{AE}{R} - \log \beta - 2.315 - 0.457 \frac{E}{RT}
\] (5)

Then, from the slope of a plot of \( \log \beta \) vs. \( 1/T \) the activation energy can be calculated to fixed values of \( \alpha \) from experiments at different heating rates testing the constancy of \( E \) with respect to \( \alpha \) and \( T \) [5–7]. The pre-exponential factor is evaluated taking into account that the reaction is a first-order one and can be defined as [5]:

\[
A = \frac{BE}{RT_m^2} \exp \left( \frac{E}{RT_m} \right)
\] (6)

**Kinetic model determination**

The rate of the kinetic process \( d\alpha/dt \) through DSC curves is based on the relation:

\[
\frac{d\alpha}{dt} = \frac{\phi}{\Delta H_c}
\] (7)

where \( \phi \) is the heat flow normalized per sample mass and \( \Delta H_c \) corresponds to the enthalpy change associated with this process [4, 9, 10].

The shape of a dynamic DSC curve at a specific heating rate considering any kind of model can be written as [9, 10]:

\[
\phi = \Delta H_c A \exp \left( -\frac{E_c}{RT} \right) f(\alpha)
\] (8)

The test to find the kinetic model proposed by Málek is based on this equation and on the normalized \( y(\alpha) \) and \( z(\alpha) \) functions, that, under non-isothermal conditions, they are given by:

\[
y(\alpha) = \phi \exp \left( -\frac{E_c}{RT} \right) = B_n f(\alpha)
\] (9)

where \( B_n = \Delta H_c A \) is constant and the shape of the \( y(\alpha) \) function is formally identical to the kinetic model \( f(\alpha) \) in which the maximum value is \( \alpha^* \).

\[
z(\alpha) = \phi T \pi \exp \left( -\frac{E_c}{RT} \right) = \Delta H_c \beta f(\alpha) g(\alpha)
\] (10)

where \( \pi (E_c/RT) \) is an approximation of the integral temperature that, in case of the \( z(\alpha) \) function, can be obtained accurately considering the approximation \( \pi \approx RT/E_c \), then:

\[
z(\alpha) = \phi T^2 = C_n f(\alpha) g(\alpha)
\] (11)

where \( C_n = \Delta H_c \beta E_c / R \) is constant and the \( \alpha \) at the maximum of the \( z(\alpha) \), \( \alpha^* \), is characteristic for any kinetic model [4, 9, 10]. The fractional conversion \( \alpha \) can be easily obtained by partial integration of isothermal or non-isothermal TA curve [10].

The kinetic models to some thermal decomposition reactions can also be obtained through Dollimore’s method, which is based on the ‘sharpness’ of the onset \( (T_i) \) and final \( (T_f) \) temperatures of the TG/DTG and its asymmetry. The investigation of some parameters that describe this asymmetry can thereby indicate the probable kinetic mechanism expressed as \( f(\alpha) \). When the thermal decomposition reaction is not complex, the quantitative approach may be obtained using parameters such as \( \alpha_\text{max} \) or \( (d\alpha/dT)_{\text{max}} \), peak temperature \( (T_p) \) and half width from DTG curves [11, 12].

This work aims the kinetic evaluation of \( E, A \) and \( f(\alpha) \) to the partial formation of anhydride and thermal decomposition of the carboxylate groups of Ti(IV)–EDTA complex through the non isothermal methods described, based on the TG, DTG and DSC curves. The kinetic model exercises great influence on the morphological properties to TiO2 obtained at 1200°C like as homogeneity, porosity and surface-to-volume ratio which are fundamental in the gas sensor performance device [13, 14].

**Experimental**

**Chemicals**

The metal, inorganic salts and acids used to prepare the complex were reagent grade. EDTA in acid form and metallic titanium were purchased from Analyticals-Carlo Erba Co. Ammonium carbonate, chloride, nitrate and sulphuric acids were purchased from Merck. Anhydrous ethanol was previously purified in our labor.

**Preparation of the solid titanium(IV)–EDTA complex**

2.729 mmol of metallic titanium was dissolved in a minimum quantity of hot concentrated chloric acid to obtain TiCl3 in the medium HCl which was oxidized to TiOCl2 by further addition of drops of sulphonitric solution. It was added, at room temperature and under constant stirring, to an equimolar aqueous solution of ammonium salt from EDTA maintained at pH 1.5. The system was left still for 1 h at room temperature and the precipitate was filtered, washed in hot distilled water so that anions and ligand excess could be eliminated, dried in an oven at 60°C and stored in a desiccator which contained anhydrous calcium chloride. The obtained