

National Project 2017, Acronym MET-AV, Contract number: 112PCE/2017; Project Manager: Ph. D. Petru Budrugaec

Advanced methodology for the kinetic analysis of complex heterogeneous processes with application in prediction of thermal behavior of materials and their thermal lifetime, Acronym MET-AV

Project Registration Code: PN-III-P4-ID-PCE-2016-0088

Contract number: 112PCE/2017

Name of the Program in PN III: Program 4 - Fundamental and Border Research

Project Type: Exploratory Research Projects

Financing: Public budget

Total amount of the contract: 850.000 lei

Of which, by financing sources:

Source 1 – public budget: 850.000 lei

Source 2 – own budget: 0 lei

Contract duration: 12.07.2017 - 31.12.2019

Contracting Authority: Executive Agency for Higher Education, Research, Development and Innovation Funding (UEFISCDI)

Contractor: NATIONAL INSTITUTE FOR RESEARCH AND DEVELOPMENT IN ELECTRICAL ENGINEERING ICPE-CA BUCHAREST (INCDIE ICPE-CA)

Abstract:

Research teams:

Project objectives:

Project stages:

Expected results:

Contact:

Stage I, Stage II, Stage III (in progress)

Abstract:

The critical analysis of the actual used methods of kinetic analysis of heterogeneous processes by using the thermal analysis data (thermogravimetry, differential thermal analysis, differential scanning calorimetry) and some physical-chemical methods (IR spectroscopy, X-Ray diffraction, etc.) will be performed, putting in evidence the following open problems that will be tried solving: improving the accuracy of isoconversional methods by suggestion of an original method, assessment of errors in the evaluation of activation energy by model-free nonlinear methods, elaboration of a general algorithm for evaluation of the kinetic scheme (mechanism) and corresponding kinetic parameters for a complex heterogeneous process. The

theoretical results will be checked for the following experimental data: non-isothermal and isothermal data corresponding to decomposition and/or thermo-oxidation of some polymers and polymeric materials, and the thermal decomposition of calcium carbonate. The general algorithm for evaluation of kinetic scheme and corresponding kinetic parameters of decomposition or /and thermo-oxidation of a material will be used for improving the procedures of prediction of thermal lifetime of materials that is an important parameter in designing of devices and equipments, or the prediction of duration of decomposition in industrial conditions of raw material in order to obtain a compound or intermediate in chemical synthesis. A procedure for rapid prediction of thermal lifetime of a material by using thermal analysis methods and based on kinetic analysis of heterogeneous processes, will be elaborated. In comparison with Standardized method (IEC 216), this procedure has the following advantages: it could be applied for materials that exhibit of single-step thermal deterioration process, and also to materials that exhibit a complex thermal deterioration process; a less time consuming.

Research teams:

Coordinator CO - INCDIE ICPE-CA Bucharest

1. **PhD Chim Budruga Petru – CSI, Project manager**
2. PhD Chim. Cucos Andrei – CSII, Key person
3. PhD. Chim. Ștefănescu Carmen – CSII, Research team member
4. PhD Ing. Sbârcea Beatrice Gabriela, Research team member
5. Ing. Mitrea Sorina Mitrea – IDTI, Research team member
6. Ing. Chiose Ileana Laura, Research team member
7. Masterand Dascălu Radu-Cristian - Research team member

Project objectives:

The main objectives of the project are:

- a. The use of thermal analysis methods (thermogravimetry (TG or TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC)) and some physical-chemical methods (IR spectroscopy (FTIR), X-Ray diffraction (XRD), etc.) for investigation of non-isothermal decomposition and/or thermo-oxidative degradation of solid compounds or materials
- b. The improving of the methods for kinetic analysis of complex heterogeneous processes by suggestion and checking of an original isoconversional method, solving the problem of assessment of errors in activation energy evaluated by isoconversional non-linear methods, elaboration and checking for simulated and experimental data of a general algorithm

(methodology) for evaluation of kinetic scheme and corresponding kinetic parameters of decomposition or/and thermo-oxidation of a material.

c. The use of the general algorithm (methodology) for evaluation of kinetic scheme and corresponding kinetic parameters of decomposition or/and thermo-oxidation of a material for improving the procedures of prediction of thermal lifetime of materials or the prediction of decomposition duration in industrial conditions of a raw material in order to obtain a compound or intermediate in chemical synthesis.

d. Elaboration of a procedure for rapid prediction of thermal lifetime of a material by using thermal analysis methods, which is also applicable for prediction of the duration of decomposition of a raw material.

Project stages:

Stage I

Stage name: Methods of kinetic analysis of experimental data obtained by thermal analysis of materials characterized structurally by physical-chemical methods (IR spectroscopy, X-ray diffraction, etc.)

Activity type: Fundamental research

Stage duration: 12.07.2017 – 15.12.2017

Stage II

Stage name: Solve a problem regarding non-linear isoconversional methods and elaboration of a general algorithm for kinetic analysis of non-isothermal and isothermal data corresponding to heterogeneous processes

Activity type: Fundamental research

Stage duration: 16.12.2018 – 14.12.2018

Stage III

Stage name: Improving the procedures for prediction of the thermal life of the materials and the duration of decomposition of a raw material under industrial conditions

Activity type: Fundamental research

Stage duration: 15.12.2018 – 31.12.2019

Expected results

- Documentary study;
- Physical-chemical characterization of materials, including the determination of their thermal and thermo-oxidative stabilities
- The improving of methods of kinetic analysis of heterogeneous processes (processes with participation of a solid compound or material), including the elaboration and

checking of a general algorithm (methodology) for evaluation of kinetic scheme and corresponding kinetic parameters of decomposition or/and thermo-oxidation of a material ;

- The use of the general algorithm (methodology) for evaluation of kinetic scheme and corresponding kinetic parameters of decomposition or /and thermo-oxidation of a material for improving the procedures of prediction of thermal lifetime of materials or the prediction of duration of decomposition in industrial conditions of a raw material
- Scientific works communicated at national and international scientific events;
- Scientific papers submitted for publication in ISI rated journals.

Contact

Coordinator CO: INCDIE ICPE-CA Bucharest

Project manager: PhD Petru Budrugaec

Phone: +40213467231, e-mail: petru.budrugaec@icpe-ca.ro

Stage I. Methods of kinetic analysis of experimental data obtained by thermal analysis of materials characterized structurally by physical-chemical methods (IR spectroscopy, X-ray diffraction, etc.)

Abstract

A critical documentary study concerning the methods of kinetic analysis of thermo-analytical data corresponding to complex heterogeneous processes has been presented. The open problems concerning the assessment of kinetic scheme and corresponding kinetic parameters have been put in evidence.

It has been suggested a simple and precise isoconversional method applicable for evaluation of activation energy dependence on the conversion degree. For the validation of the method the data obtained by thermal analysis of calcium carbonate, PVC and HDPE were used. There was a very good concordance between the activation energy values determined by the simple method proposed with those obtained by the "advanced isoconversion" and "incremental iterative" methods, which are much more laborious.

For calcium carbonate, high density polyethylene (HDPE) and vinyl polychloride (PVC), structural characterization was determined by X-ray diffraction and X-ray photoelectron spectroscopy (XPS). Also, for HDPE and PVC, TG / DTG + DTA or DSC simultaneous thermal analyses coupled with FTIR were performed both under inert atmosphere and oxidizing atmosphere, in order to determine the volatile products as result of progressive heating. The data obtained were used for the validation of the proposed isoconversion method,

but will be used also in the next stages of the present project which have as main objectives the elaboration of a general algorithm of kinetic analysis of the complex heterogeneous processes and the elaboration of a procedure for rapid determination of the lifetime thermal properties of materials and the duration of heterogeneous processes.

Dissemination of the results

- Submission of the following paper to *Thermochimica Acta* (ISI journal): „**A simple and precise differential incremental isoconversional method to kinetic analysis of heterogeneous processes under arbitrary temperature programs**”, author Petru Budrugaac
- Oral communication „**General algorithm for evaluation of the kinetic scheme and corresponding kinetic parameters of heterogeneous processes. Applications.**” author Petru Budrugaac, presented at international conference “**4th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC4)**”, Chişinău – Republica Moldova, *28 August 2017 - 31 August 2017*
- Invited conference “**Non-isothermal model-free prediction for assessment of conversion vs. time curves for complex processes under arbitrary temperature programs – advantages and limitations**”, author P. Budrugaac”, presented at international conference “**13th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta 2017)**”, Loano – Italy, *24 September 2017 – 27 September 2017*

Stage II (in progress)

Stage name: Solve a problem regarding non-linear isoconversional methods and elaboration of a general algorithm for kinetic analysis of non-isothermal and isothermal data corresponding to heterogeneous processes

Activity type: Fundamental research

Stage duration: 16.12.2018 – 14.12.2018

Activity 2.1. Solving the problem of error determination of activation energy determination by non-linear isoconversion methods

An original method for evaluation of the error in activation energy determined by non-linear isoconversional (model-free) methods was elaborated and checked for some non-isothermal data. For this purpose, several linear and nonlinear isoconversional methods were applied for non-isothermal data corresponding to crystallization of $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ (4 constant heating rates), decomposition of ammonium perchlorate (6 constant heating rates), decomposition of poly(vinyl chloride) (PVC) (5 constant heating rates) and simulated data (12 constant heating rates). For each set of non-isothermal data, the linear and nonlinear isoconversional methods were applied for evaluation of activation energy (E). It has been considered some pairs “linear isoconversional method + nonlinear isoconversional method” (“differential isoconversional method suggested by Friedman + nonlinear differential method”; each “integral pair” corresponds to a certain approximation of the temperature integral). The comparison of the errors of activation energy evaluated by a linear method ($\Delta_L E$) with the Fisher confidence intervals evaluated by the corresponding nonlinear method ($\Delta_F E$) shows that the relation $\Delta_L E = b \times \Delta_F E + c \times (\Delta_F E)^2$ (b and c are parameters that not depend on the pair of isoconversional method) exhibits a very good accuracy of $\Delta_L E$ vs. $\Delta_F E$ fitting when $\Delta_F E$ is evaluated for confidence level of 95%. Consequently, the errors in E evaluation by nonlinear methods could be determined by using the above equation and $\Delta_F E$ values determined for the confidence level of 95%. This procedure was also checked for non-isothermal data corresponding to thermal decomposition of HDPE, which were not used for evaluation of b and c parameters.

Activity 2.2 . Determination of thermal degradation curves of a kind of epoxy resin at minimum 3 constant heating rates

The thermal behavior of an epoxy resin (D010S+D110S cured with phthalic anhydride, reinforced with alumina powder), used as electro-insulating material, was performed by the

following the thermal analysis methods: differential scanning calorimetry (DSC), and simultaneous thermogravimetry (TG) + differential thermogravimetry (DTG) + differential thermal analysis (DTA).

The glass transitions of the resin characterized by temperature of 120⁰C, was determined by DSC analysis performed using DSC 204F1 Phoenix apparatus produced by Netzsch – Germany, in the following conditions: temperature: range 25⁰C – 300⁰C, heating rate of 10 K.min⁻¹, nitrogen flow (20 ml.min⁻¹), and aluminum pan.

The heating curves TG + DTG + DTA and FTIR spectra of gaseous products were recorded using STA 490C apparatus produced by Netzsch – Germany, coupled with FTIR Brucker –Germany, in the following conditions: temperature range 25⁰C – 1000⁰C, heating rates of 3 K .min⁻¹, 5 K .min⁻¹, 10 K .min⁻¹, 15 K .min⁻¹, and 20 K .min⁻¹, nitrogen flow (30 ml.min⁻¹), and Pt-Rh crucible. It was obtained that the material exhibits two successive endothermic processes characterized by mass losses, and peaks in DTG and DTA curves. The parameters of these processes depend on the heating rates.

Activity 2.3. Determination of thermal degradation isotherms of a kind of epoxy resin.

The temperature programs in which the degradation quasi-isotherms of epoxy resin were determined by analyzing the non-isothermal data obtained in step 2.2. These programs were used for determination of the corresponding thermal degradation curves.

Activity 2.4. Applying the non-linear regression method and some physical-chemical analysis methods for finding the kinetic scheme and the kinetic parameters corresponding to the heterogeneous process of decomposition of a kind of epoxy resin

Until now (July 2018), “Netzsch Thermokinetics – A Software Module for the Kinetic Analysis of Thermal Measurements” was used for processing of non-isothermal data corresponding to thermal degradation of epoxy resin recorded at heating rates of 3 K.min⁻¹, 5 K.min⁻¹, 10 K .min⁻¹, 15 K .min⁻¹ and 20 K .min⁻¹. The application of this software involves two successive steps, namely, determining the dependence of activation energy on the degree of conversion by isoconversional methods, and determining the kinetic scheme and the corresponding kinetic parameters by a non-linear regression method. These parameters were used to plan experiments under quasi-isothermal conditions.

Validation of kinetic results obtained by using only non-isothermal was performed by comparing the experimental and theoretical isothermal degradation curves.

Activity 2.5. Dissemination of results through scientific communications presented at Conferences and / or Symposia and by sending articles for publication in ISI journals

1. Published paper

Petru Budruga, **A simple and precise differential incremental isoconversional method to kinetic analysis of heterogeneous processes under arbitrary temperature programs**, *Thermochimica Acta*, 661 (2018) 116-123, doi.org/10.1016/j.tca.2018.01.025

Abstract

A simple and precise linear differential incremental isoconversional (model-free) method for kinetic analysis of heterogeneous processes using thermo-analytical data recorded at arbitrary temperature programs has been suggested. This method has been applied to simulated data corresponding to a single-step process and to a complex process consisting in two consecutive reactions, and experimental data corresponding to thermal degradation of high density polyethylene (HDPE). The obtained results are consistent with those from other isoconversional methods (advanced isoconversional method suggested by Vyazovkin, iterative method suggested by Budruga and differential isoconversional method suggested by Friedman).

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

2. Submission of the following paper to *Thermochimica Acta* (ISI journal)

Petru Budruga, **Estimating errors in the determination of activation energy by nonlinear methods applied for thermoanalytical measurements performed under constant heating rates**

Abstract

Several linear and nonlinear isoconversional methods have been applied for following non-isothermal thermoanalytical data: simulated data for two consecutive first order reactions (12 heating rates), crystallization of $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ (4 heating rates), decomposition of ammonium perchlorate (6 heating rates) and decomposition of poly(vinyl chloride) (PVC) (5 heating rates). It has been considered some pairs “linear isoconversional method + nonlinear isoconversional method”. The “differential pair” is “differential isoconversional method suggested by Friedman + nonlinear differential method”, while each “integral pair”

corresponds to a certain approximation of the temperature integral. The values of activation energy (E), error of E obtained by linear method ($\Delta_L E$) and Fischer confidence interval obtained by nonlinear method ($\Delta_F E$) applying the procedures suggested by V yazovkin and Wight have been determined for each pair of methods, several conversion degrees, and the confidence levels of 68.27%, 80%, 90% and 95%. It has been obtained that, for a certain pair of methods, the values of E determined by linear method are identical with those determined by the nonlinear method. Therefore, it is expected that, in such case, the error in E evaluation by the nonlinear method to be equal with that corresponding to linear method. In the first approximation, for a given confidence limit, the relation between $\Delta_L E$ and $\Delta_F E$ does not depend on both the set of thermoanalytical data and the pair of isocomversional methods. Satisfactory fittings of experimental data have been obtained for the relationships: (1) $\Delta_L E = a \times \Delta_F E$ and (2) $\Delta_L E = b \times \Delta_F E + c \times (\Delta_F E)^2$, here a , b and c are parameters which depend on the confidence limit. These relations have been also checked for high density polyethylene (HDPE) decomposition data that were not used for their derivations. The best accuracy of fitting the experimental data has been obtained for equation (2) and confidence level of 95%. Therefore these equation and Fischer confidence intervals could be used for assessment errors of activation energy determined by a nonlinear method.

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

Received of paper

Thermochimica Acta to bp@icpe-ca.ro

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Successfully received: submission ESTIMATING ERRORS IN THE DETERMINATION OF ACTIVATION ENERGY BY NONLINEAR METHODS APPLIED FOR THERMOANALYTICAL MEASUREMENTS for Thermochimica Acta

Ref: TCA_2018_361

Title: ESTIMATING ERRORS IN THE DETERMINATION OF ACTIVATION ENERGY

BY NONLINEAR METHODS APPLIED FOR THERMOANALYTICAL
MEASUREMENTS, Journal: Thermochemica Acta

Dear Dr. Budrugaec,

Thank you for submitting your manuscript for consideration for publication in Thermochemica Acta. Your submission was received in good order.

To track the status of your manuscript, please log into E-VISE® at: http://www.evise.com/evise/faces/pages/navigation/NavController.jspx?JRNL_ACR=TCA and locate your submission under the header 'My Submissions with Journal' on your 'My Author Tasks' view.

Thank you for submitting your work to this journal.

Kind regards,

Thermochemica Acta

3. Oral communication

Petru Budrugaec. Critical study concerning the use of sinusoidal modulated thermogravimetric data (MTG) for evaluation of activation energy of heterogeneous processes.

It was presented at “12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)”, which happened from 27th to 30th of August 2018, in Brasov –Romania

Abstract

It has been carried out a critical study of the use of isoconversional differential method suggested 48 years ago by Flynn [1] and later by Blaine and Hahns [2] (FBH method) for evaluation of activation energy (E) of a heterogeneous process by using a single conversion degree (α) vs. time (t) curve recorded under a sinusoidal temperature program:

$$T = T_0 + \beta t + A \sin(2\pi\omega t) \quad (1)$$

where: T_0 is the initial temperature, β is the constant heating rate, ω is the frequency and A is the amplitude of the modulation. This method is based on the equation:

$$E = R \frac{T_1 T_2}{T_2 - T_1} \ln \frac{d\alpha_2}{d\alpha_1} \equiv R \frac{T_1 T_2}{T_2 - T_1} L_{2,1} \quad (2)$$

where: R is gas constant, and α_1 and α_2 are two closed values of conversion degree corresponding to temperatures T_1 and T_2 . The derivation of eqn. (2) involves the assumption

$|\ln(d\alpha_2/d\alpha_1)| \gg |\ln(f(\alpha_2)/f(\alpha_1))|$, where $f(\alpha)$ is the differential conversion function (kinetic model). The validity of this assumption has been checked using for the first time several simulated data corresponding to a single step process. It has been obtained that for $\alpha_2 - \alpha_1 = 0.01$ there are some high differences between the values of E determined by FBH method and that used in simulation. Also, unrealistic negative values of E determined by FBH method have been obtained for some simulated programs and relative high values of α .

Often, eqn. (2) is applied for adjacent valley (v) and peak (p) of the sinusoidal wave. Eqn. (2) thus reduces to:

$$E = R \frac{(\bar{T}^2 - A^2)}{2A} L_{p,v} \quad (3)$$

where T is the average temperature in the considered range of temperature. The application of eqn. (3) leads to reliable values of E only for quasi-isothermal sinusoidal data ($\beta = 0$ in eqn. 1) and the validity of a assumption that grounds the derivation of eqn. (2). For MTG data recorded at $\beta > 0$, some high differences between E values determined by using eqn. (3) and the value of E used in simulations have been obtained. The cause of these will be discussed.

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

References

- [1] J. H. Flynn, in “Thermal Analysis”, R. F. Schwenker and P. D. Garn, Eds., Academic Press, Budapest, 1969, Vol. 2, p. 1111
- [2] R. L. Blaine, B. K. Hahn, J. Therm. Anal. Calorim., 54 (1998) 695

Abstract acceptance

Dear Petru Budrugaec,

We confirm and acknowledge the acceptance of your abstracts entitled: **“Critical study concerning the use of sinusoidal modulated thermogravimetric data (MTG) for evaluation of activation energy of heterogeneous processes”** as **Oral presentation** at ESTAC12 conference.

This document enables you to attend the 12th European *Symposium on Thermal Analysis and Calorimetry (ESTAC12)*, which will take place from 27th TO 30th of August 2018, in Brasov – Romania.

Andrei ROTARU

Chairman of ESTAC12

President of CEEC-TAC



24th of June 2018

4. Poster

Andrei Cucos, Petru Budrugeac, Thermal behaviour of some electro-insulating materials studied by coupled TG-FTIR technique

It was presented at “12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)”, which happened from 27th to 30th of August 2018, in Brasov –Romania

Abstract

Thermogravimetric analysis coupled with Fourier transform infrared spectrometry (TG-FTIR) was used for investigating the thermal decomposition of some materials used as insulators in electrical devices. Such materials include polymers (PE, PVC) used as dielectric materials and jackets in electric cables, epoxy resins used for coating and encapsulating electrical circuit components, transformer oils used for insulating and cooling electrical oil-filled transformers. Observing by FTIR the volatiles that are released, some insights concerning the processes occurring on heating of these materials were gained. Such studies can be helpful for assessing the hazards linked with the normal or incidental heating of these materials during their usage.

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

Abstract acceptance

Dear Andrei Cucos,

We confirm and acknowledge the acceptance of your abstracts entitled: “**Thermal behavior of some electro-insulating materials studied by coupled TG-FTIR technique**” as **Poster presentation** at ESTAC12 conference.

This document enables you to attend the 12th *European Symposium on Thermal Analysis and Calorimetry (ESTAC12)*, which will take place from 27th TO 30th of August 2018, in Brasov – Romania.

Andrei ROTARU

Chairman of ESTAC12

President of CEEC-TAC



24th of June 2018

5. Poster

Carmen Paraschiv, Gabriela Hristea, Marius Lungulescu, Beatrice-Gabriela Sbarcea, Virgil Marinescu, **Investigation of thermal stability and morphology of zinc oxide-graphene oxide heterostructures obtained by hydrothermal synthesis**

It was presented at “12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)”, which happened from 27th to 30th of August 2018, in Brasov –Romania

Abstract

In the last decade, new hybrid structures combining graphene derivatives and inorganic compounds (metal particles, oxides or sulphides) have been developed for a wide variety of applications, including optics, medicine, solar cells, supercapacitors, (photo)catalysis, (bio) sensors. Among these, zinc oxide-graphene oxide heterostructures are of great interest due to the remarkable affinity of the two materials. Both present hexagonal networks, the good structural compatibility allowing them to be combined into composites with superior properties and performance compared to the individual components [1-3].

Both zinc oxide and graphene are able to form aggregates due to Van der Waals interactions and surface effects. By anchoring zinc oxide particles on the surface of graphene layers, this inconvenience can be eliminated by simultaneous dispersion of ZnO particles as well as preventing agglomeration of graphene layers.

To obtain zinc oxide-graphene oxide heterostructures, we employed the in situ approach, which involves the growth of zinc oxide directly on the graphene structure by mixing the precursors and simultaneously reducing them in solution. The on-site growth allows good control of the morphology, density and orientation of the obtained hybrid structures. It also has the advantage of a more uniform and dense coating.

In the present work we will compare the thermal stability and morphology of zinc oxide-graphene oxide heterostructures synthesized under hydrothermal conditions by varying the reaction parameters.

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

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- [2] R.K. Boroju, P.K. Giri, S. Dharma, K. Imakita, M. Fujii, *ACS Appl. Mater. Interfaces*, 6(2014) 377–387
- [3] T.V. Cuong, V.H. Pham, J.S. Chung, E.W. Shin, D.H. Yoo, S.H. Hahn, *Mater.Lett.* 64(2010) 2479–2482

Abstract acceptance

Dear Carmen Paraschiv,

We confirm and acknowledge the acceptance of your abstracts entitled: **“Investigation of thermal stability and morphology of zinc oxide-graphene oxide heterostructures obtained by hydrothermal synthesis”** as **Poster presentation** at ESTAC12 conference.

This document enables you to attend the **12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)**, which will take place from **27th TO 30th of August 2018**, in Brasov – Romania.

Andrei ROTARU

Chairman of ESTAC12

President of CEEC-TAC



20th of June 2018

6. Poster

Radu-Cristian Dascălu, Andrei Cucos, Cătălin Maxim, Delia-Laura Popescu, Marius Andruh, Comparative Thermal Studies of Polynuclear Coordination Compounds with Organostannic Knots

It was presented at “12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)”, which happened from 27th to 30th of August 2018, in Brasov –Romania

Abstract

Three new polynuclear complexes with triphenyltin(IV) assembling blocks have been synthesized. All compounds have been characterized in solid state using standard spectroscopic techniques (FT-IR, UV-Vis), elemental analysis, powder and single crystal X-ray diffraction. As a result of single crystal X-ray diffraction has been able to establish molecular formulas as follows: $[(\text{Ph}_3\text{Sn})_2(\mu_3\text{-tma})_2(\text{Ph}_3\text{Sn}(\text{MeOH}))(\text{4-ampH})\cdot\text{MeOH}]_n$ (1), $\{[(\text{Ph}_3\text{Sn})_2(\mu_3\text{-tma})]_2[\text{Ni}(\text{ampy})_2(\text{H}_2\text{O})_2]_3\}_n$ (2) and $[\{\text{Ni}(\text{ampy})_2(\mu_2\text{-BPDC})\text{SnPh}_3\}_2(\mu_2\text{-BPDC})] \cdot \text{H}_2\text{O}$ (3). The compound 1 and 2 are monodimensional coordination polymers and the compound 3 is a tetranuclear complex.

The thermal and thermo-oxidative stabilities of compounds have been determined by simultaneous TG/DTG + DTA methods coupled with Fourier transform infrared spectrometry (FTIR) performed in gaseous atmosphere (N_2 and O_2), in the temperature range $30\text{ }^\circ\text{C}$ - $1200\text{ }^\circ\text{C}$ and heating rate of 10 K/min .

As a result of TG-FTIR analysis of the compound 1 in N₂, it was observed that the material is thermal stable up to 175°C, and then it will lose weight in three successive steps. In case of the same compound, in O₂, it was observed that it is thermal stable up to 175 °C, and then it will lose weight in three successive steps. The TG-FTIR analysis of the compound 2 in N₂ showed that it is thermal stable up to 90 °C, and then it will lose weight in three successive steps. The same compound, in O₂, is thermal stable up to 90 °C, and then it will lose weight in three successive steps. The compound 3 in N₂ is thermal stable up to 195°C, and then it will lose weight in three successive steps as in previous cases. Also, in O₂, for compound 3 it has been observed that it is thermal stable up to 195°C, and then it will lose weight in two successive steps. Some correlation between the structure of the compounds and their thermal behaviors have been made and discussed.

Acknowledgements. The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research project MET-AV, PN-III-P4-ID-PCE Nr. 112/2017.

Abstract acceptance

Dear Radu Cristian Dascălu,

We confirm and acknowledge the acceptance of your abstracts entitled: **“Comparative Thermal Studies of Polynuclear Coordination Compounds with Organostannic Knots”** as **Poster presentation** at ESTAC12 conference.

This document enables you to attend at the *12th European Symposium on Thermal Analysis and Calorimetry (ESTAC12)*, which will take place from *27th TO 30th of August 2018*, in Brasov – Romania.

Andrei ROTARU

Chairman of ESTAC12

President of CEEC-TAC



24th of June 2018

Web page: <http://www.icpe-ca.ro/eng/projects/national-projects/met-av.htm>

Stage III (in progress)

Stage name: Improvement of the processes for predicting the thermal life of the materials and the duration of decomposition in industrial conditions of a raw material used to obtain a product or an intermediate compound necessary for chemical synthesis

Activity type: Fundamental research

Stage duration: 16.12.2019 – 14.12.2019

Activity 3.1. Determination of the thermo-oxidative degradation curves of a sort of epoxy resin at least 3 constant heating rates

The thermal behavior of “composite material based on epoxy resin (D010S+D110S cured with phthalic anhydride, reinforced with quartz flour)”, used as electro-insulating material, was performed by simultaneous thermogravimetry (TG) + differential thermogravimetry (DTG) + differential thermal analysis (DTA).

The heating curves TG + DTG + DTA were recorded using STA 490C apparatus produced by Netzsch – Germany, in the following conditions: temperature range 25⁰C – 1000⁰C, heating rates of 4,99 K.min⁻¹; 10,04 K.min⁻¹ and 20.62 K.min⁻¹, oxygen flow (30 ml.min⁻¹), and Pt-Rh crucible. It was obtained that the material exhibits four successive global processes (I, II, III and IV) characterized by mass losses, and peaks in DTG curves and exothermic peaks in DTA curves. The parameters of these processes depend on the heating rates.

Activity 3.2. Determination of the thermo-oxidative degradation isotherms of a sort of epoxy resin (in progress)

The quasi-isothermal determinations were performed with the STA 490C apparatus produced by Netzsch - Germany, in oxygen flow (30 ml.min⁻¹; oxygen purity 99.999%), the sample masses being 6.66 mg and 6.86 mg, and the isothermal portions of the temperature programs being 290⁰C and 295⁰C. For each temperature program, the sample mass vs. time dependence was determined.

Activity 3.3. Application of nonlinear regression method and physical-chemical methods for finding the kinetic scheme and kinetic parameters corresponding to the heterogeneous process of thermo-oxidative degradation of a sort of epoxy resin

The applied kinetic analysis of data obtained by thermal analysis corresponding to the process I + process II put in evidence in nonisothermal TG curves involves the following successive steps:

- (1) application for data recorded at constant heating rates of isoconversional methods to determine the dependence of apparent activation energy on the degree of conversion;

- (2) processing data recorded at constant heating rates by using a non-linear regression program (we used “Netzsch Thermokinetics” program) to determine the kinetic scheme and the corresponding kinetic parameters.

To evaluate the dependence on the degree of conversion (α) of the apparent activation energy (E) of the thermo-oxidative degradation function as a function, the Friedman (FR) and Ozawa-Flynn-Wall (OFW) isoconversional methods. It was obtained that the apparent activation energy depends on the degree of conversion, and for $\alpha \geq 0.55$, the errors of evaluation of E are large. These results show that the heterogeneous process investigated is complex.

The determination of the reaction scheme and the corresponding kinetic parameters is done by the nonlinear regression method. The non-isothermal data recorded at the 3 heating rates were used together, the differential equations are numerically solved and the kinetic parameters are numerically optimized. After running the experimental data recorded at the three heating rates used, it was obtained that the thermo-oxidation of the epoxy resin composite material is satisfactorily described by the following kinetic scheme pair - kinetic models A -1 \rightarrow B-2 \rightarrow C-3 \rightarrow D- 4 \rightarrow E - FnFnFnFn, where Fn corresponds to the model of the reaction order; A, B, C, D and E are compounds; 1, 2, 3 and 4 are stages of the mechanism).

Activity 3.4. Development and verification for experimental data of a general algorithm for evaluating the kinetic scheme and kinetic parameters corresponding to the investigated processes

Critical analysis of the procedures for evaluating kinetic parameters from non-isothermal data suggested the algorithm which consists of the following successive stages:

- (1) Physical-chemical characterization of the material
- (2) Application for data recorded at constant heating rates of isoconversional methods to determine the dependence of apparent activation energy on the degree of conversion
- (3) Processing data recorded at constant heating rates by using a linear and/or a non-linear regression program to determine the kinetic scheme and the corresponding kinetic parameters.
- (4) Verification of the validity of the kinetic scheme and the corresponding kinetic parameters for the α vs. t curves recorded at temperature programs, other than those used for kinetic analysis.

In stage (1), the material is characterized by physical-chemical methods. The results obtained by these methods help us to determine the parameters at which the thermal analyzes are performed,

as well as to identify the processes that take place during the progressive heating of the material.

In stage (2), it is determined the dependence of the activation energy on the conversion degree, by applying isoconversional methods. There are two possible cases, namely Case 1. E is independent on a , and Case 2. E is dependent on a . In Case 1, with high probability, the investigated process has a single step, which is characterized from a kinetic point of view by a single kinetic triplet (activation energy (E), pre-exponential factor (A) and conversion function ($f(\alpha)$)).

In step 2 the dependence of the activation energy (E) on the degree of conversion (α) determined by an isoconversion method is determined. There are two distinct cases: Case 1. E is independent of α and Case 2. E is dependent on α . The procedures by which this triplet can be determined are indicated.

The dependence of the activation energy on the conversion degree (Case 2) shows that the investigated process is complex (successive, parallel, reversible reactions; diffusion of the reaction products). In this case, the determination of the reaction scheme and the corresponding kinetic parameters is performed by applying a nonlinear regression method (Stage (3)). It is known that several kinetic schemes with different kinetic parameters can very well fit the experimental data obtained at linear heating speeds. To discriminate the correct kinetic scheme, Stage (4) is performed.

The verification of this algorithm will be presented in the parts of the work corresponding to the activities 3.5 - 3.8.

Activity 3.5. Applying the nonlinear regression method and some physical-chemical methods for finding the kinetic scheme and kinetic parameters corresponding to the thermal decomposition process of a polyethylene sort

The thermal behavior of a kind of low density polyethylene (LDPE) produced by ARPECHIM Pitesti was investigated. The TG, DTG and DTA curves were recorded simultaneously with the STA 490C apparatus produced by Netzsch - Germany, under nitrogen flow (30 ml.min⁻¹; purity of nitrogen 99.999%), in the temperature range 25 - 600⁰C and at heating rates of 2.50 K.min⁻¹, 5.00 K.min⁻¹, 9.91 K.min⁻¹, 14.89 K.min⁻¹ and 19.92 K.min⁻¹. It was obtained that in the progressive heating of the polyethylene two successive processes take place, namely the melting of the polyethylene characterized in the DTA curve by an endotherm and an endothermic process with formation of volatile products.

Kinetic analysis of the volatile product formation process was performed. The activation energy was determined by the FR and OFW methods. Both the values of E determined by the FR method and those determined by the OFW method are dependent on the degree of conversion and the standard deviations of E from the mean value are relatively large. It follows that the process of thermal degradation of polyethylene is complex.

To determine the kinetic scheme and the corresponding kinetic parameters, the program "Netzsch-Thermokinetics" was used, which also includes a nonlinear regression method. After running the experimental data recorded at the five heating rates used it was obtained that the thermal degradation of the polyethylene is satisfactorily described by the following pair kinetic scheme - kinetic models $A-1 \rightarrow B-2 \rightarrow C-3 \rightarrow D - F_n F_n F_n$, where F_n corresponds to the mol. reaction order; A, B, C and D are compounds; 1, 2, and 3 are stages of the mechanism).

Activity 3.6. Determination of thermal degradation isotherms of a sort of polyethylene and calcium carbonate

Determination of the thermal degradation isotherms of a polyethylene sort (in progress)

Determination of the thermal degradation isotherms of calcium carbonate

The thermal decomposition of precipitated calcium carbonate GR p.a. with a purity greater than 99% granulate (particle size of 14 μm), produced by Merck - Germany. Thermogravimetric (TG) curves were recorded with the STA 490C apparatus, produced by Netzsch - Germany, under nitrogen flow 30 $\text{mL}\cdot\text{min}^{-1}$; purity 99.999%, in quasi-isothermal conditions, the sample masses being in the range 5.11 - 5.18 mg.

The quasi-isothermal determinations were performed with the STA 490C apparatus produced by Netzsch - Germany, in nitrogen flow (30 $\text{ml}\cdot\text{min}^{-1}$; nitrogen purity 99.999%), and the final isothermal portions of the temperature programs being 650 $^{\circ}\text{C}$, 660 $^{\circ}\text{C}$, 670 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$. For each temperature program, the sample mass vs. time dependence was determined.

Activity 3.7. Determination of the thermal degradation curves of calcium carbonate at least 3 constant heating rates

Non-isothermal determinations were performed at constant heating rates of 2.5; 5.0; 7.5; 10.0; 12.5 and 14.9 $\text{K}\cdot\text{min}^{-1}$, in nitrogen stream (30 $\text{mL}\cdot\text{min}^{-1}$; purity 99.999%) and temperature range 25-1000 $^{\circ}\text{C}$. It was obtained that at the breakdown of calcium carbonate a single global endothermic process with formation of calcium oxide and carbon dioxide takes place.

Activity 3.8. Application of the general algorithm for evaluation of kinetic scheme and the corresponding kinetic parameters for calcium carbonate decomposition

The elaborated algorithm (Activity 3.4) was applied for kinetic analysis of thermoanalytical data corresponding to decomposition of calcium carbonate

The activation energy was determined by the FR and Iterative (IT) methods. Both the values of E determined by the FR method and those determined by the IT method are dependent on the degree of conversion and the standard deviations of E from the mean value are relatively large. It follows that the process of thermal degradation of calcium carbonate is complex.

To determine the kinetic scheme and the corresponding kinetic parameters, the program "Netzsch-Thermokinetics" was used, which also includes a nonlinear regression method. After running the experimental data recorded at the five heating rates used it was obtained that the thermal degradation of the polyethylene is satisfactorily described by the following pair kinetic scheme - kinetic models $A \xrightarrow{-1} B$; $A \xrightarrow{-2} B \xrightarrow{-3} C$ - $F_n F_n D_3$, where F_n corresponds to the model

of reaction order, and D_3 is the diffusion model (Jander equation: $f(\alpha) = \frac{3(1-\alpha)^{2/3}}{2[1-(1-\alpha)^{1/3}]}$) A, B, C and D are compounds; 1, 2, and 3 are steps of the mechanism). It has been shown that the calculated quasi-isothermal curves are in very good agreement with the experimental ones.

Activity 3.9. Use of data obtained by kinetic analysis for the prediction of thermal decomposition isotherms of polyethylene and calcium carbonate by kinetic scheme method and by isoconversional methods

The "kinetic scheme" method was applied to evaluate the following thermal degradation isotherms:

- thermal decomposition isotherms of LDPE corresponding to temperatures of 400⁰C, 410⁰C, 420⁰C, 430⁰C and 440⁰C;
- thermal decomposition isotherms of calcium carbonate corresponding to temperatures of 600⁰C, 620⁰C, 640⁰C, 660⁰C and 680⁰C.

Applying the isoconversional method for isothermal predictions leads to correct results if the relative errors of evaluation of the activation energy by the isoconversional method are less than 2%, even for small values of the conversion degree. This condition is not met by LDPE and CaCO₃, and, therefore, the isoconversional prediction method does not lead to correct α vs. time curves.

Activity 3.10. Developing a procedure for rapid prediction of the thermal life of a material by using the thermal analysis data, that is also applicable for the prediction of the decomposition time of a raw material (in progress)

Activity 3.11. Dissemination of results through scientific communications presented at Conferences and / or Symposia and by sending articles for publication in ISI journals

I. Published paper

Petru Budrugaec, **Comparison between model-based and non-isothermal model-free computational procedures for prediction of conversion-time curves of calcium carbonate decomposition**, *Thermochimica Acta*, 679 (2019) 178322;

<https://doi.org/10.1016/j.tca.2019.178322>

(Impact Factor: 2,251; yellow zone)

Abstract

The model-based and non-isothermal model-free procedures have been applied for prediction of conversion-time curves of calcium carbonate decomposition. In this purpose, the thermogravimetric (TG) curves corresponding to decomposition of CaCO_3 have been recorded in nitrogen flow in non-isothermal conditions at constant heating rates of 2.5; 5.0; 7.5; 10.0; 12.5 and 14.9 $\text{K}\cdot\text{min}^{-1}$, and in other temperature programs that exhibit the following final isothermal steps: 650°C; 660°C; 670°C and 700°C.

To apply model-based procedure, the most probable kinetic schemes and corresponding kinetic parameters have been determined by using the non-isothermal data, and the isoconversional and “multivariate nonlinear regression” (“Multivar-NLR”) methods. By comparing the experimental and predicted conversion-time curves that exhibit a final isothermal step, it has been obtained that the most probable kinetic scheme consists a reversible reaction of CaCO_3 decomposition followed by diffusion of carbon dioxide. The non-isothermal model free prediction procedure has been also used for assessment of conversion-time curves that exhibit a final isothermal step. Both model-based procedure and non-isothermal model-free procedure lead to satisfactory agreements between experimental and calculated conversion curves corresponding to temperature programs that exhibit a final isothermal step, but the curves predicted by a non-isothermal model-free procedure have a large deviation from the experimental ones than those predicted by model-based procedure.

Paper in progress that will be sent for publication to the journal *Thermochimica Acta*

Petru Budrugaec, **Estimating errors in the determination of activation energy by nonlinear isoconversional methods applied for thermoanalytical measurements performed under arbitrary temperature programs**

Abstract

In a previous paper (Thermochimica Acta, 670 (2018) 1-6) it has been obtained that for thermoanalytical measurements performed under constant heating rates, the error in determination of the activation energy by using nonlinear methods (ΔE) can be evaluated by applying the relation:

$$\Delta E = 0.2447(\pm 0.0005) \times \Delta_F E + 0.00037(\pm 0.00001) \times (\Delta_F E)^2$$

where $\Delta_F E$ is the Fischer confidence interval obtained by nonlinear method ($\Delta_F E$) for confidence level of 95% determined by the procedure suggested by Vyazovkin and Wight (Anal. Chem. 72 (2000) 3171-3175).

This relationship has been verified also for the following sets of thermoanalytical data performed under arbitrary temperature programs: simulated sinusoidal modulated data, experimental TG data obtained in investigating thermal decomposition of HDPE under quasi-isothermal conditions and experimental TG data obtained in investigating thermal decomposition of LDPE under arbitrary temperature programs.

It has been pointed out that for thermoanalytical data performed under any temperature programs, the procedure for evaluation the error of activation energy determinate by a nonlinear isoconversional method consisting in the following two successive steps: the determination of $\Delta_F E$ for confidence level of 95%, and the evaluation of ΔE by using the above relationship between ΔE and $\Delta_F E$.

Scientific communications at conferences and / or scientific symposia

1. Oral paper communicated to “**28th Symposium of Thermal Analysis and Calorimetry – Eugen Segal**”, Timișoara, 9 – 10. 05. 2019.

Petru Budrugaec, **On the applicability of incremental model-free methods to determine activation energy corresponding to heterogeneous processes performed under arbitrary temperature programs**

Abstract

The applicability of the following isoconversional (model-free) incremental methods for determining the energy of activation of the heterogeneous processes under arbitrary temperature

programs are discussed: advanced nonlinear isoconversional method (A-NL method), iterative incremental isoconversion method (IT-method) and incremental differential method (Incr-dif method).

It is justified that when a process takes place in some arbitrary temperature programs, always applying the A-NL method considering that dependence T vs. t is linear even for narrow domains of the degree of conversion leads to erroneous activation energy values.

A procedure for applying the A-NL method applicable to any temperature programs (modified A-NL method) has been suggested. This procedure has been verified for simulated sinusoidal modulated data, experimental data obtained by TG analysis of HDPE under quasi-isothermal conditions, and experimental TG data obtained in investigating thermal decomposition of LDPE under arbitrary temperature programs. For this purpose, the values of the activation energy obtained by the modified A-NL, IT and Incr-dif were compared.

Acknowledgements

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2. Oral paper communicated to “2nd Journal of Thermal Analysis and Calorimetry Conference (2nd JTACC+V4 2019)”, June 18-21, 2019, Budapest, Hungary

Petru Budrugaec, **Applicability of incremental isoconversional methods to determine of the dependence of activation energy on the conversion degree corresponding to heterogeneous processes performed under arbitrary temperature programs**

Abstract

The following incremental isoconversional methods can be used to evaluate the dependence of activation energy on the conversion degree of heterogeneous processes occurring in arbitrary temperature programs, including programs with constant heating rates: advanced non-linear isoconversional method (A-NL) [1]; integral incremental isoconversional method (Incr-int) [2];

differential incremental isoconversional method [3]; iterative incremental isoconversional method [4].

A-NL, Incr-int and Incr-dif methods are applicable only if for small intervals of the conversion degree, the dependencies temperature (T) vs. time (t) can be approximated satisfactorily with straight lines. For example, this condition is respected when using constant heating rate programs. However, it also uses temperature programs in which this condition is not desirable, e.g. sinusoidal modulated programs. For such programs, the correct values of activation energy are obtained by the IT method in which the temperature integral is performed numerically. Also, the A-NL method could be applied in these cases if the temperature integral to a determination would be evaluated as the sum of the integers corresponding to each linear portion of the T vs. t curve own to the range of conversion. Applying the procedure involves the initial drawing of the T vs. t for delimiting linear domains. Verification of this procedure was performed for simulated sinusoidal modulated data and experimental data obtained by TG analysis of HDPE under quasi-isothermal conditions. The values of the activation energy thus obtained are compared with those obtained by applying the Incr-int, Incr-dif and IT methods.

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3. Oral paper communicated to “**5th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC5) and 14th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2019)**”, Roma, Italy, 27 -31 August 2019

Petru Budrugaec, **Estimating errors in the determination of activation energy by nonlinear isoconversional methods applied for thermoanalytical measurements**

Abstract

Several linear and nonlinear isoconversional methods have been applied for following non-isothermal thermoanalytical data performed under constant heating rates: crystallization of $(\text{GeS}_2)_{0.3}(\text{Sb}_2\text{S}_3)_{0.7}$ (4 heating rates), decomposition of ammonium perchlorate (6 heating rates) and decomposition of poly(vinyl chloride) (PVC) (5 heating rates) and simulated data for two consecutive first order reactions (12 heating rates). It has been considered some pairs “linear isoconversional method + nonlinear isoconversional method”. Each “integral pair” corresponds to a certain approximation of the temperature integral. The values of activation energy (E), error of E obtained by linear method ($\Delta_L E$) and Fischer confidence interval obtained by nonlinear method ($\Delta_F E$) applying the procedure suggested by Vyazovkin and Wight [1] have been determined for each pair of methods, several conversion degrees, and the confidence level of 95%. It has been obtained that, for a certain pair of methods, (a) $\Delta_F E$ values are substantially greater than $\Delta_L E$ values, and (b) the values of E determined by linear method are identical with those determined by the nonlinear method. The statement (a) is explained by the procedure for $\Delta_F E$ evaluation in which it is assumed that $\Delta_F E$ correspond to maximum value of Fischer distribution function. According statement (b) it is expected that is a relationship between $\Delta_L E$ and $\Delta_F E$. Both statements suggest that the error in E determined by a nonlinear isoconversional method (ΔE) is equal with $\Delta_L E$. It has been obtained the following correlation between $\Delta_L E$ and $\Delta_F E$ valid for all pairs of isoconversional methods and all considered processes:

$$\Delta E \equiv \Delta_L E = 0.2447(\pm 0.0005) \times \Delta_F E + 0.00037(\pm 0.00001) \times (\Delta_F E)^2$$

This relationship has been verified also for the following sets of thermoanalytical data performed under arbitrary temperature programs: simulated sinusoidal modulated data, experimental TG data obtained in investigating thermal decomposition of HDPE under quasi-isothermal conditions and experimental TG data obtained in investigating thermal decomposition of LDPE under arbitrary temperature programs.

For thermoanalytical data performed under any temperature programs, the procedure for evaluation the error of activation energy determinate by a nonlinear isoconversional method consisting in the following two successive steps: the determination of $\Delta_F E$ for confidence level of 95%, and the evaluation of ΔE by using the above relationship between ΔE and $\Delta_F E$.

Acknowledgements

The work was supported by the Romanian “Ministry of Research and Innovation –Executive Agency for Higher Education, Research, Development and Innovation Funding, UEFISCDI” research projects— *Advanced methodology for the kinetic analysis of complex heterogeneous processes with application in prediction of thermal behavior of materials and their thermal lifetime* (MET-AV, PN-III-P4-ID-PCE Nr. 112/2017).

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