Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 76 (7) 1015–1026 (2011)
JSCS–4180

UDC 544.421.032.4:546.32'82+
547.461.2:543.57
Original scientific paper

Thermal decomposition of potassium titanium oxalate

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(Received 15 June, revised 14 December 2010)

Abstract: The thermal decomposition of potassium titanium oxalate (PTO) was studied using non-isothermal thermogravimetry at different heating rates under a nitrogen atmosphere. The thermal decomposition of PTO proceeds mainly through five stages forming potassium titanate. The theoretical and experimental mass loss data are in good agreement for all stages of the thermal decomposition of PTO. The third thermal decomposition stage of PTO, the combined elimination of carbon monoxide and carbon dioxide, were subjected to kinetic analyses both by the method of model fitting and by the model free approach, which is based on the isoconversional principle. The model free analyses showed that the combined elimination of carbon monoxide and carbon dioxide and formation of final titanate in the thermal decomposition of PTO proceeds through a single step with an activation energy value of about 315 kJ mol^{-1}.

Keywords: potassium titanium oxalate; non-isothermal thermogravimetry; decomposition kinetics; model free methods.

INTRODUCTION

Metal oxalates have been the subject for a number of thermogravimetric studies, both from a practical and theoretical viewpoint.[1,2] Duval[3] summarized thermogravimetric (TG) data for the drying and ignition temperature of a large number of metal oxalates. Galwey *et al*.[4] identified and discussed studies on the thermal decomposition of silver oxalate. Studies on the thermal decomposition of cobalt oxalate,[5] and manganese(II) oxalate dihydrate and manganese(II) oxalate trihydrate[6] using TG, DTA and X-ray diffraction techniques were reported. Titanate based ceramics have found many applications in material science for different reasons.[7] Even though potassium titanium oxalate (PTO) has many chemical[8] and pharmaceutical[9,10] applications, no kinetic studies on its thermal decomposition have been reported in the literature.

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doi: 10.2298/JSC100615083M

PTO and similar types of compounds have attracted attention due to their technological importance, for instance as precursors of nanostructured titanates. This compound shows an overall decomposition of the type A → B + C, where A and B are solid phases and C is a gas or gases. Such reactions, typically resulting in highly reactive solid products, have attracted a great deal of research interest due to their theoretical and technical relevance.

The objective of this work was to investigate the thermal decomposition of PTO and to determine whether the third thermal decomposition stage, the combined elimination of carbon monoxide and carbon dioxide, occurs through a single stage and to determine the values of the kinetic parameters of this stage. The third thermal decomposition stage of PTO, corresponding to the combined elimination of carbon monoxide and carbon dioxide and the formation of the final titanate, is very important and industry requires measurements of the kinetic parameter for the accurate design of the installations and the treatment conditions, because augmentation of temperature or elongation of reaction time means more cost. The results of the kinetic investigations can also be applied to problems such as the useful lifetime of certain components, oxidative and thermal stability and quality control.[11]

Reaction kinetics by thermogravimetry

Solid-state kinetic data are of practical interest for a large and growing number of technologically important processes. The most common experimental technique employed to study kinetics of thermally activated reactions is thermogravimetry (TG), under the conditions of isothermal and/or non-isothermal conditions. Kinetic studies of the thermal decomposition of solids are one of the most important applications of thermal analysis. In non-isothermal TG, two methods, model fitting and model free analyses have been used for the evaluation of kinetic parameters. Model fitting methods were among the first and most popular methods for kinetic description, because they require only a single heating rate experiment to calculate the kinetic parameters. However, the popularity of these methods has been declining in favour of the isoconversional method of model free approaches.[12–14]

All kinetic methods assume that the isothermal rate of conversion, $\mathrm{d}\alpha/\mathrm{d}t$, is a linear function of the temperature dependent rate constant, $k(T)$, and a temperature independent function of conversion, $f(\alpha)$, which depends on the mechanism of the reaction, that is:

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha) \tag{1}$$

The temperature dependent function $k(T)$ is of the Arrhenius type, can be considered as the rate constant, k, and is obtained from:

$$\mathrm{d}\alpha/f(\alpha) = A/\beta \mathrm{e}^{-E/RT}\mathrm{d}T \tag{2}$$

which upon integration and taking logarithms yields:

$$\ln g(\alpha) = \ln (AE/\beta R) + \ln p(x) \tag{3}$$

where $p(x) = \int_x^\infty (\exp(-x)/x^2)\mathrm{d}x$ and $x = E/RT$.

This is the basic form of equation used for analysis of non-isothermal data. This equation can be readily applied once the form of the function $p(x)$ is established.

For kinetic analyses, the main task is to obtain the solution of the above temperature integral. Several methods are available under different approaches, *viz.*, integral, differential and approximation, for the evaluation of the temperature integral. However, most of the approximation methods neglect the low temperature end of the temperature integral. It has been reported that two-dimensional quantities significantly influence the approximation methods[15] and the solution of the temperature integral is achieved by numerical integration with respect to a dimensionless activation energy variable.[16]

The model fitting method

The function, $p(x)$ given in Eq. (3) is usually expressed as $p(x) = (\exp(-x)/x^2) Q(x)$, where $Q(x)$ is a rational function that depends on the approximation considered. By considering the gross simplification, $Q(x) = 1$, Eq. (3) becomes:

$$\ln (g(\alpha)/T^2) = \ln (AR/\beta) - E/(RT) \tag{4}$$

Therefore, the most probable kinetic function and the corresponding kinetic parameters, namely the activation energy, are determined by plotting $\ln (g(\alpha)/T^2)$ versus $1/T$. Thus, a plot of $\ln (g(\alpha)/T^2)$ *vs.* $1/T$ must be a straight line for the correct mechanism and non-linear for an incorrect mechanism. Hence, by calculating the value of $\ln (g(\alpha)/T^2)$ using the non-isothermal TG trace for the various rate processes mentioned in Table I and plotting them *vs.* $1/T$, the most probable mechanism corresponding to the linear plot can be determined.

The model free methods

Measuring the evolution of the overall physical properties of a system by thermal methods of analysis provides information on the macroscopic kinetics. Macroscopic kinetics is inherently complex because they include information about multiple steps that are occurring simultaneously. Unscrambling complex kinetics presents a serious challenge that can only be met by kinetic methods that provide means of detecting and treating multi-step processes. Isoconversional methods, based on multiple heating programmes, are the most popular methods that can meet this challenge.[17]

As part of the ICTAC Kinetics Project, M.E. Brown *et al.*[18] performed kinetic analysis of isothermal and non-isothermal data sets provided on a hypothetical simulated process as well as on some actual experimental results for the thermal decompositions of ammonium perchlorate and calcium carbonate. They applied a variety of computational methods and found that isoconversional and multi-heating rate methods were particularly successful in correctly describing the multi-step kinetics used in the simulated data.

Isoconversional kinetics rest upon evaluating the dependence of the effective activation energy on conversion or temperature and using this dependence for making kinetic predictions and for exploring the mechanism of thermal processes. These methods are based on the single step kinetic equation, Eq. (2), of non-isothermal decomposition and are the quickest way to derive kinetic parameters for complex reactions involving multiple processes.[19] According to the isoconversional principle, at a constant extent of conversion, the reaction rate is a function only of temperature so that:

$$\mathrm{d}(\ln(\mathrm{d}\alpha/\mathrm{d}t))_\alpha/\mathrm{d}T^{-1} = E_\alpha/RT \tag{5}$$

the subscript α designates the value related to a given value of conversion.

The values of the activation energy can be calculated by different methods based on the isoconversional principle. The isoconversional method suggested by Flynn–Wall–Ozawa[20] uses the approximation of the integral equation, which leads to a simple linear equation for the evaluation of activation energy. This method assumes that the conversion function does not change with alteration of the heating rate for all values of α, *i.e.*, measurement of the temperature corresponding to fixed values of α at different heating rate is required. Considering the Doyle approximation of $p(x)$, *i.e.*, $\ln p(x) = -5.3305 - 1.052\ E/(RT)$, Eq. (2) becomes:

$$\ln\beta = \ln(AE/R) - \ln g(\alpha) - 5.3305 - 1.052\ E/(RT) \tag{6}$$

Therefore, when plotting $\ln\beta$ *versus* $1/T$, a straight line with slope $-1.052E/R$ was obtained.

If the values of activation energy (E) determined for various values of α, are almost constant, then certainly the reaction involves only a single step. On the contrary, a change in E with increasing degree of conversion is an indication of a complex reaction mechanism that invalidates the separation of variables involved in the Ozawa, Flynn and Wall analysis.[21] These complications are serious, especially in the case where the total reaction involves competitive reaction mechanisms.[22]

Model free kinetics rests on evaluating the E_α dependence.[23] This dependence is adequate for both theoretical and practical purposes of kinetic predictions. Normally, model free kinetics are not concern with evaluating A and $g(\alpha)$ or $f(\alpha)$ because they are not needed for performing kinetic predictions. In addition, these values are hardly suitable for theoretical interpretation because of the strong ambiguity associated with them. However, these values can be determined within the frameworks of model free kinetics.

EXPERIMENTAL

Materials and instrumentation

AnalaR grade potassium titanium oxalate (PTO) from Merck was recrystalized, dried, the particle size fixed in the range; 90–125 μm mesh and kept in a vacuum desiccator. The thermogravimetric analyses of PTO were performed on a T. A. thermal analyzer, model TGA Q50 V20.2 build 27 in an atmosphere of flowing nitrogen (flow rate 40–60 ml min^{-1}), sample mass: 10 mg, sample pan: alumina, at four different heating rates, *viz*, 5, 10, 15 and 20 K min^{-1}. Duplicate TG runs were performed under similar conditions and the data was found to overlap with each other, indicating satisfactory reproducibility.

Kinetic analyses of the TG data

The non-isothermal thermogravimetric data of PTO were fitted to all the models given in Table I and the kinetic parameters were evaluated for the model which gave the best linear weighted least squares fit. The kinetic data were also evaluated using the isoconversional (model-free) method.

TABLE I. The different reaction models applied to describe the reaction kinetics

SI No.	Reaction model	f(α)	g(α)
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$\frac{2}{3}\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$0.5\alpha^{-1}$	α^{2}
6	Mampel (first order)	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	$4(1-\alpha)[-\ln(1-\alpha]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
11	Contracting sphere	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting area (cylinder)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Second order	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$

RESULTS AND DISCUSSION

Preview of earlier work on PTO

Broadbent *et al.*[24] reported the results of thermogravimetric and differential thermoanalytical studies on PTO and potassium aluminium oxalate under non-isothermal conditions in air, nitrogen and carbon dioxide atmospheres. They reported that the dehydration of PTO starts at 70 °C and proceeds in several stages until completion at 200 °C. They also observed that the thermal decomposition of PTO was rapid above 275 °C and potassium titanate was formed as the final product. It was shown that PTO is less stable than potassium oxalate.[25] Sairam Patra *et al.*[2] studied the thermal decomposition of anhydrous strontium titanyl oxalate (STO) and found that the thermal decomposition of STO proceeded through a series of complex reactions to form strontium metatitanate at high temperatures. They performed kinetic analysis of the α–t data, obtained by cooled gas pressure measurement under vacuum, of oxalate decomposition in the temperature range 553–593 K and observed that the data fitted the Zhuravlev Equation over almost the entire α-range (0.05–0.92), indicating the occurrence of a diffusion-controlled, three-dimensional rate process, and reported an activation energy value of 164±10 kJ mol^{-1}.

Thermal decomposition pattern of PTO

The thermogravimetric curve for PTO at a heating rate of 10 K min^{-1} in a nitrogen atmosphere is shown in Fig. 1. Similar curves were obtained at all other heating rates (not shown). It was observed that PTO decomposed through five stages as per the scheme given below. The theoretical and experimental mass loss data are in good agreement for all stages of the thermal decomposition of PTO (Table II) as reported earlier.[26,27] Several authors[2,3,7,9] observed this type of phenomena in the decomposition of other titanyl oxalates, *e.g.*, barium titanium oxalate (BTO) and STO:

$$K_2TiO(C_2O_4)_2.2H_2O \rightarrow K_2TiO(C_2O_4)_2 + 2H_2O \qquad \text{(up to 450 K)}$$

$$2K_2TiO(C_2O_4)_2 \rightarrow K_4Ti_2O_2(C_2O_4)_3CO_3 + CO \qquad \text{(450–520 K)}$$

$$K_4Ti_2O_2(C_2O_4)_3CO_3 \rightarrow K_4Ti_2O_5CO_3.CO_2 + 2CO_2 + 3CO \qquad \text{(520–720 K)}$$

$$K_4Ti_2O_5CO_3CO_2 \rightarrow K_4Ti_2O_5CO_3 + CO_2 \qquad \text{(720–870 K)}$$

$$K_4Ti_2O_5CO_3 \rightarrow 2K_2TiO_3 + CO_2 \qquad \text{(above 870 K)}$$

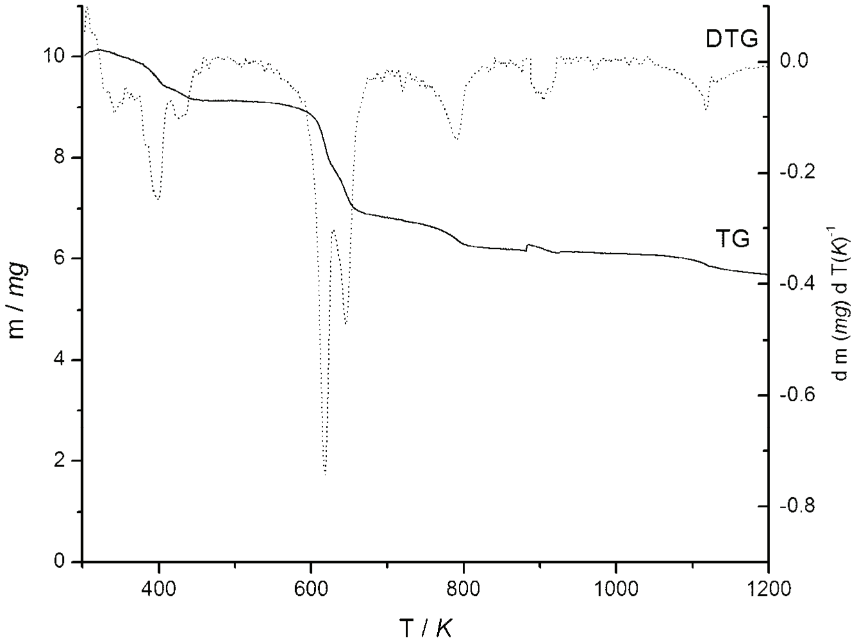

Fig. 1. TG and DTG curve for PTO at a heating rate of 10 K min^{-1}.

TABLE II. Theoretical and experimental mass loss data (%) for the thermal decomposition of PTO at different heating rates

Stage	Decomposition process	Theoretical mass loss %	Heating rate, K min^{-1}			
			5	10	15	20
I	Dehydration	10.17	10.02	10.06	10.11	10.14
II	Elimination of CO	3.95	3.99	3.85	3.91	3.92
III	Elimination of CO and CO_2	24.29	24.01	22.91	24.53	24.16
IV	Elimination of CO_2	6.21	6.12	6.18	6.05	6.25
V	Elimination of CO_2	6.21	6.32	6.22	6.11	6.04

Thermal decomposition and kinetics

It was observed that the thermal decomposition of PTO showed two stages corresponding to the elimination of carbon monoxide in the temperature range 450–490 K and carbon dioxide in the temperature range 690–870 K in addition to three steps corresponding to dehydration (ambient–410 K) and combined elimination of carbon monoxide and carbon dioxide (520–720 K) and the formation of the final titanate (870–1130 K). Elimination of the last molecule of CO_2 was accompanied by melting of potassium titanate (final product), onset around 823 K and a peak around 844 K. The further mass loss observed (Fig. 1) was due to vaporization of potassium titanate. Values of the onset and peak temperatures of the differential TG (DTG) for the different stages of thermal decomposition of PTO at a heating rate of 10 °C min^{-1} are given in Table III. Values of the onset and peak temperatures of the DTG for the third thermal decomposition stage of PTO at different heating rates are given in Table IV.

TABLE III. Onset and peak temperatures (K) of the DTG for different thermal decomposition stages of PTO (heating rate: 10 °C min^{-1})

Decomposition stage	Onset	Peak
I	376	397
II	416	435
III	603	618
IV	764	792
V	1106	1118

The energetic and kinetics of the third thermal decomposition stage, *viz.*, combined elimination of carbon monoxide and carbon dioxide, of PTO in the temperature range 520–720 K was studied and the typical α–T curve for this stage of decomposition (of PTO) is shown in Fig. 2. Similar curves were obtained for all other samples of PTO (not shown). The observed mass loss for this stage is in good agreement with the theoretical value in all cases.

The method of model fitting

The α–T data of the third thermal decomposition stage of PTO was subjected to weighted least squares analysis for all the reaction models given in Table I. All the plots showed random data points and gave poor correlations. However, reaction models 4,7,8,9,12 and 13 gives comparatively better correlation (> –0.99) for the thermal decomposition of PTO at heating rates of 5, 10, 15 and 20 K min^{-1}. The values of activation energy and correlation coefficient obtained from least squares plots (for all reaction models) are given in Table V.

TABLE IV. Onset and peak temperatures (K) of DTG for the third thermal decomposition stage of PTO at different heating rates

Heating rate, °C min^{-1}	Onset	Peak
5	601	618
10	602	617
15	603	618
20	604	618

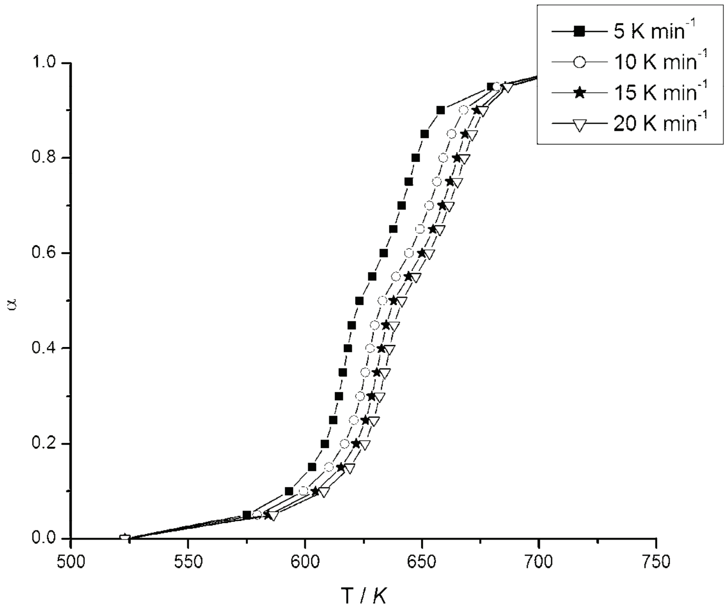

Fig. 2. *α–T* Plots for the third thermal decomposition stage of PTO at different heating rates.

Examination of Table V reveals that the activation energy values obtained for all models at different heating rates vary widely from 12.6 to 305.2 kJ mol^{-1}. Models which give higher correlations, *i.e.*, models 4, 7, 8, 9, 12 and 13, also showed a huge variation in the value of *E* (from 32.9 to 305.2 kJ mol^{-1}). However, reaction model 13 gave values of *E* in the range 298 to 305.2 kJ mol^{-1}. All other models give lower values, which is unacceptable because at this range of temperature a reaction with a low value of *E* is not feasible. On the other hand, the values of *E* obtained by using this model are closer to the values obtained from isoconversional methods (301–324 kJ mol^{-1}, Table VI).

TABLE V. Values of the activation energy (E / kJ mol^{-1}) and correlation coefficient (r) obtained for all reaction models at different heating rates

Reaction model	Heating rate, K min^{-1}							
	5		10		15		20	
	E	$-r$	E	$-r$	E	$-r$	E	$-r$
1	21.9	0.9734	20.8	0.9760	20.7	0.9737	21.2	0.9732
2	27.2	0.9772	25.8	0.9795	25.7	0.9774	26.3	0.977
3	35.5	0.9838	33.6	0.9853	33.5	0.9836	34.5	0.9834
4	50.3	0.9940	47.5	0.992	47.4	0.992	48.7	0.9927
5	48.3	0.9852	45.6	0.9817	45.5	0.9825	46.8	0.9835
6	111.1	0.9763	104.8	0.972	104.5	0.9725	107.5	0.9738
7	34.9	0.9924	33.0	0.9923	32.9	0.9911	33.8	0.9913
8	45.0	0.9936	42.6	0.9931	42.4	0.9921	43.6	0.9924
9	63.5	0.9936	60.0	0.9921	59.8	0.9916	61.5	0.9921
10	13.4	0.9376	12.6	0.931	12.6	0.9323	13.0	0.9343
11	27.5	0.989	26.0	0.9861	25.89	0.9862	26.6	0.9871
12	35.8	0.9927	33.8	0.9905	33.70	0.9904	34.6	0.9911
13	305.2	0.9986	298.4	0.9906	298.9	0.9916	301.9	0.9940

TABLE VI. Apparent activation energy (E) obtained for the third thermal decomposition stage of PTO from isoconversional method ($-r$ = 0.9999)

Conversion, %	E / kJ mol^{-1}
10	312.2
20	312.6
30	322.6
40	324.2
50	315.1
60	301.0
70	304.3
80	311.4
90	315.1

The model free approach

The value of the apparent activation energy was also estimated by the isoconversional method suggested by Ozawa, Flynn and Wall[20] for the thermal decomposition of PTO at different percentage conversions by fitting the plots of $\ln \beta$ *vs.* $1/T$ and the obtained values are given in Table IV. Plots of $\ln \beta$ *vs.* $1/T$ under the isoconversional method for the thermal decomposition of PTO at all percentages of conversions gave high values of the correlation coefficient (r = = –0.9999) with activation energy values in the range 301–324 kJ mol^{-1}. Typical isoconversional plots for the thermal decomposition of PTO are given in Fig. 3. The plot of activation energy against conversion for the third thermal decomposition stage of PTO is shown in Fig. 4.

As the apparent activation energy values determined for the various values of α of the third thermal decomposition stage of PTO are almost constant, one can infer that the combined elimination of carbon monoxide and carbon dioxide occurred through a single step.

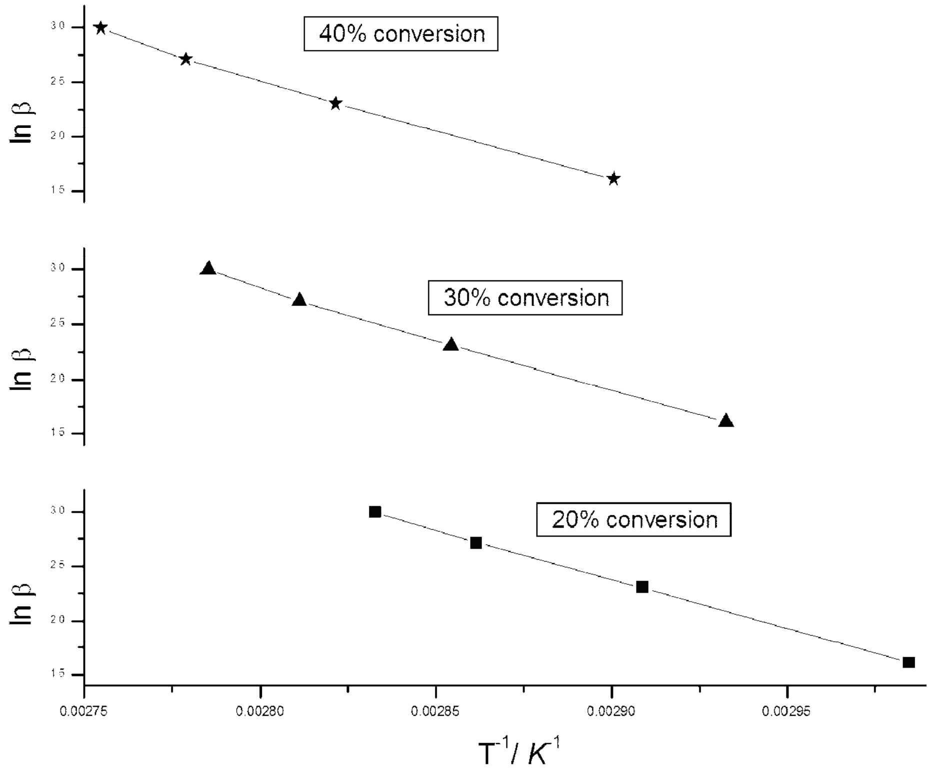

Fig. 3. Typical isoconversional plots for the third thermal decomposition stage of PTO.

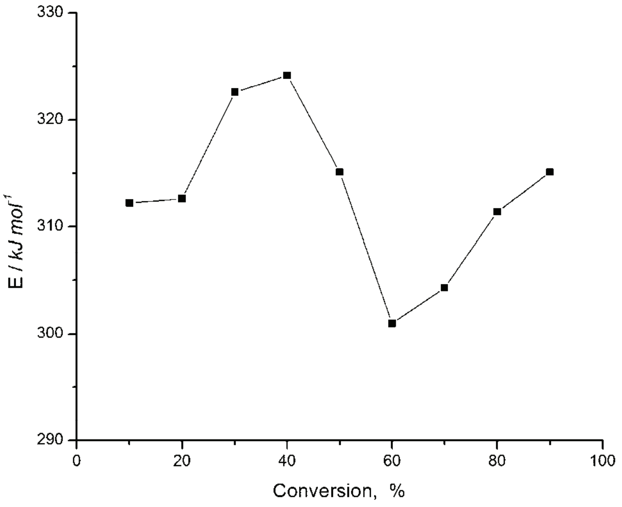

Fig. 4. Plot of activation energy against conversion.

CONCLUSIONS

The kinetic results on the third thermal decomposition stage of PTO showed that the conventional non-isothermal model fitting method gave poor correlations. On the other hand, the correlation was very high for the model free kinetic methods and the value of activation energy showed only negligible variation for different conversions. Reasonably constant values for the apparent activation energy (312±12 kJ mol^{-1}) were obtained over the whole conversion range (10–90 %) for the third thermal decomposition stage by using the isoconversional method. This indicates that the third thermal decomposition stage of PTO, the combined elimination of carbon monoxide and carbon dioxide, proceeds through a single step.

ИЗВОД

ТЕРМИЧКА РАЗГРАДЊА КАЛИЈУМ-ТИТАН-ОКСАЛАТА

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Термичка разградња калијум-титан-оксалата испитивана је неизотермалном термогравиметријом у атмосфери азота при различитим брзинама грејања. Термичка разградња калијум-титан-оксалата одвија се кроз пет ступњева у којима се формира калијум-титанат. Теоријски и експериментални губитак масе су у добром слагању за свих пет ступњева. Трећи ступањ термичке разградње, комбинација елиминације угљен-моноксида и угљен-диоксида, био је предмет кинетичке анализе засноване на два модела – модел фитовања и изоконверзиони модел анализе. Елиминација угљен-моноксида и угљен-диоксида, и стварање титаната при разлагању калијум-титан-оксалата, може се описати јединственим ступњем са укупном енергијом активације која износи 315 kJ mol^{-1}.

(Примљено 15. јуна, ревидирано 14. децембра 2010)

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