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Thermal decomposition kinetics of $PrMO_3$ (M = Ni or Co) ceramic materials via thermogravimetry

F. M. Aquino · D. M. A. Melo · R. C. Santiago · M. A. F. Melo · A. E. Martinelli · J. C. O. Freitas · L. C. B. Araújo

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Abstract Thermogravimetric data using the non-isothermal kinetic models of Flynn and Wall and "Model-free Kinetics" were used to determine the activation energy to study the decomposition kinetics of the ligand groups with system's metallic ions that takes part in the synthesis of $PrMO_3$ (M = Ni or Co). This activation energy was determined for the stage of highest decomposition of the organic matter to establish parameters in synthesis condition optimization and application of the proposed material.

Keywords Ceramic materials · Thermogravimetry · Activation energy

Introduction

Ceramic oxides with ABO_3 perovskite structure (where A and B are generally metallic ions of rare earths and transition metals, respectively) have been used for various types of catalytic reactions [1, 2]. The perovskite-type structure has been exhaustively researched for having interesting physical and chemical properties such as: superconductivity, magnetic and optical properties, and catalytic activity, with possible applications in a wide range of technological areas [3].

In general, these properties are potentially influenced by the synthesis method, the calcination conditions (temperature, time, and atmosphere) and substitutions of the A and/or B sites. There are several methods for obtaining ceramic oxides with perovskite-type structures. Recent studies make use of gelatin as a polymerization agent and this process appears as a new alternative for obtaining materials with high efficiency and low cost [4].

A preliminary thermogravimetric analysis is sufficient for verifying the temperature at which these oxides are stabilized and the thermal behavior of the material studied. Thermogravimetric analysis (TGA) is one of the most commonly used technologies to study of a variety of primary reactions of decomposition of solids and estimate the kinetics parameters of these processes [5].

With data obtained from thermogravimetric analysis, the kinetic study is performed using various mathematical models that have been developed to determine some kinetic parameters. In these studies, the most-used thermal analysis techniques are thermogravimetric analysis (TG) and differential thermal analysis (DTA) [6]. Thermogravimetry is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program. Differential thermal analysis is a technique that involves measuring the temperature difference (ΔT) between the substance and the reference material, as both are subjected to a controlled temperature program [7].

With this purpose, it was necessary to conduct a kinetic study of the thermodecomposition of the new synthesis method for obtaining materials with perovskite-type structure.

The objective of this study is to study the thermal degradation of the ligand groups with the metallic ions of the system using the Flynn and Wall and "Model-free kinetics" methods and evaluate the results in order to establish the activation energy as a parameter to

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F. M. Aquino (✉) · D. M. A. Melo · R. C. Santiago · M. A. F. Melo · A. E. Martinelli · J. C. O. Freitas · L. C. B. Araújo
Laboratory of Catalysis and Refining-NUPRAR, Federal University of Rio Grande do Norte, Av. Senador Salgado Filho, 3000, CEP 59078-970 Natal, RN, Brazil
e-mail: flavyma@hotmail.com

characterize and optimize the synthesis conditions for the applicability of the material.

Kinetic methods

The ASTM E 1641 standard for the determination of kinetic parameters via thermogravimetry is based on the method proposed by Flynn and Wall [8]. The "Model-free kinetics" method is based on the Vyazovkin theory [9–11]. Both methods allow determination of the kinetic parameters of a reaction by thermal analysis—activation energy, for example.

Activation energy via the Flynn and Wall method uses the method of least squares (Linear Regression) to determine the slope, $\Delta(\log\beta)/\Delta(1/T)$. Therefore, the estimated activation energy (E_{ae}) can be calculated with Eq. 1, using the value of the slope, $\Delta(\log\beta)/\Delta(1/T)$, and setting a b value of 0.457 in the first iteration. This is an iterative method, using tabulated values for the b iterations. These values were determined and tabulated by Doyle [12, 13] and comprise a range of $7 \leq E/RT \leq 60$.

$$E_{ae} = -(R/b)^{*}\Delta log(\beta)/\Delta(1/T) \qquad (1)$$

"Model-free kinetics" applies isoconversional techniques for calculating activation energy (E) as a function of the conversion (α) of the chemical reaction $E = f(\alpha)$. Thus, this theory is based on Eq. 2:

$$d\alpha/dt = k(T)f(\alpha) \qquad (2)$$

where t is time, T temperature, and α the extent of conversion, $f(\alpha)$ represents the reaction model and $k(T)$ the Arrhenius reaction rate coefficient,

$$d\alpha/dt = A\,exp(-E/RT)f(\alpha) \qquad (3)$$

and where R is the universal gas constant. Taking Eq. 3 as a base and dividing by the heating rate $\beta = dT/dt$, yields Eq. 4,

$$\frac{d\alpha}{dt} = kf(\alpha) \rightarrow \frac{d\alpha}{dt} = \frac{k}{\beta}f(\alpha) \qquad (4)$$

where $d\alpha/dt$ is the reaction rate and K the rate constant. Substituting Eq. 4 in Eq. 5, we have:

$$\frac{1}{f(\alpha)}d\alpha = A/\beta e^{-E/RT}dt \qquad (5)$$

integrating up to the conversion, α (at temperature T)

$$\int_0^{\alpha}\frac{1}{f(\alpha)}d\alpha = g(\alpha) = \frac{A}{\beta}e^{-E/RT}dt \qquad (6)$$

because $E/2RT \gg 1$, the temperature integral can be approximated by,

$$\int_{T_0}^{T} e^{-E/RT}dT \approx \frac{R}{E}\cdot T^2 \cdot e^{-E/RT} \qquad (7)$$

replacing the temperature integral and rearranging in logarithmic form,

$$\frac{\ln\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \left(\frac{E_\alpha}{R_\alpha}.\frac{1}{T_\alpha}\right) \qquad (8)$$

as follows:

$$\int_0^{\alpha}\frac{1}{f(\alpha)} = g(\alpha) \qquad (9)$$

One of the main advantages of this method is the possibility of isolating the $g(\alpha)$ function of the linear coefficient. The determination of this function in complex processes is difficult to determine [8].

Experimental

Two samples with $PrCoO_3$ and $PrNiO_3$ perovskite-type structure were studied. Perovskites were synthesized using gelatin as a polymerization agent in the reaction. Initially, nickel nitrate or cobalt nitrate was added to a beaker containing deionized water under constant stirring between 60 and 70 °C for 5 min. Praseodymium (III) nitrate hexahydrate was added and the system was homogenized for another 5 min. Gelatin was then added to the solution at a temperature of 70 °C and stirred for 40 min. Next, the temperature was increased to 90 °C for 1 h, resulting in a resin, which was pre-calcined at 350 °C for 2 h with a heating rate of 5 °C min^{-1} to eliminate part of the organic matter present in the compound. The resulting material was then calcined 700 C and 900 °C for 4 h.

The thermal analyses (TG and DTA) used for the experiments were carried out simultaneously using Shimadzu 60H equipment. Because the Flynn and Wall and "Model-free Kinetics" models require at least three dynamic curves with different heating rates, the following were used: 10, 20, and 30 °C min^{-1} between room temperature and 700 °C. The mass of the samples was approximately 1 mg, the sample support was alumina, and the carrier gas was synthetic air with a flow of 50 mL min^{-1}.

Results and discussion

The thermogravimetric curves (TG/DTG) of the $PrCoO_3$ and $PrNiO_3$ systems, represented in Figs. 1 and 2, have three stages of mass loss. The first stage of loss, between 25 and 300 °C, is associated with moisture (water of hydration) and

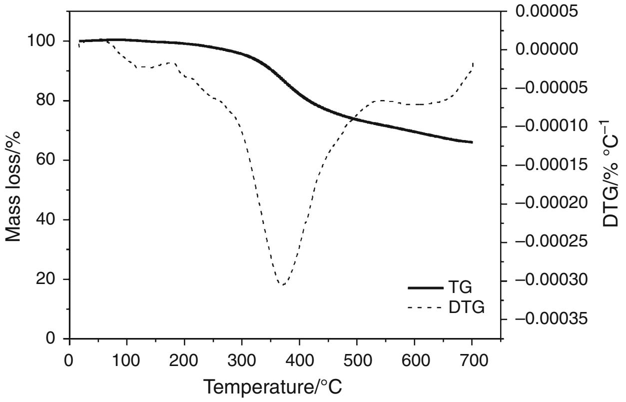

Fig. 1 TG and DTG curves for the $PrCoO_3$ system at a heating rate of 10 °C min^{-1}

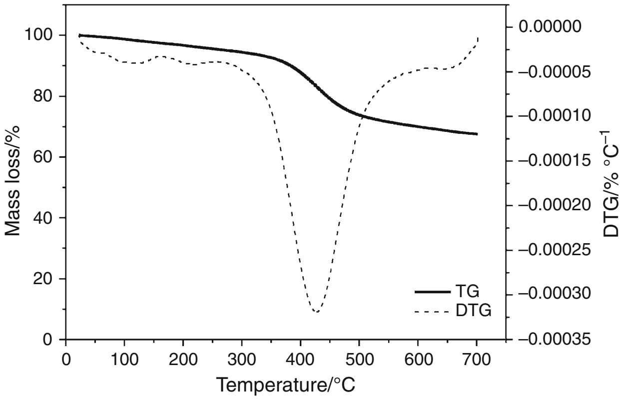

Fig. 2 TG and DTG curves for the $PrNiO_3$ system at a heating rate of a 10 °C min^{-1}

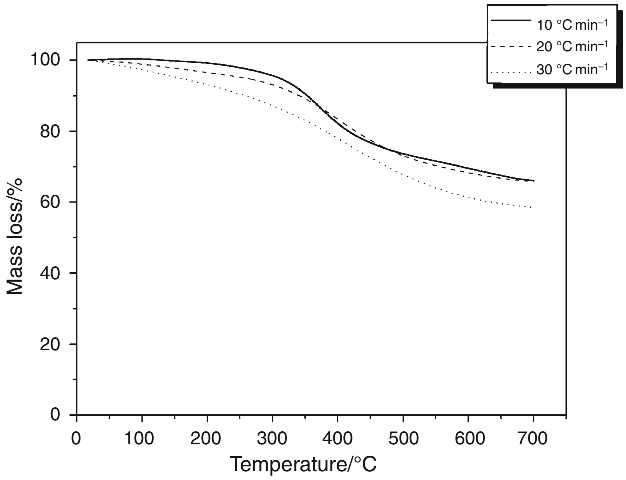

Fig. 3 Superimposition of the non-isothermal thermogravimetric curves obtained at different heating rates for the $PrCoO_3$ system

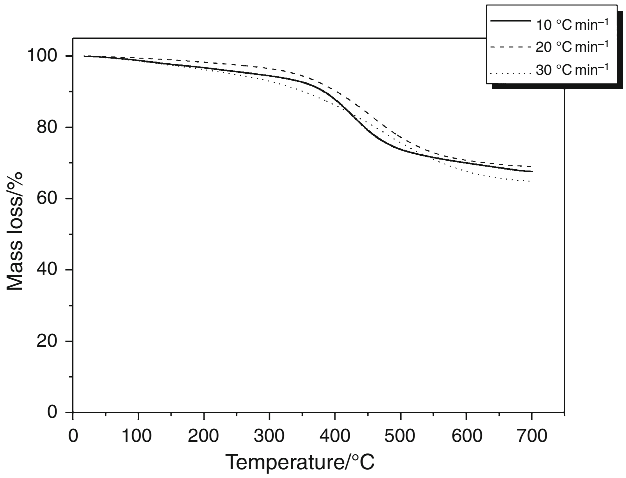

Fig. 4 Superimposition of the non-isothermal thermogravimetric curves obtained at different heating rates for the $PrNiO_3$ system

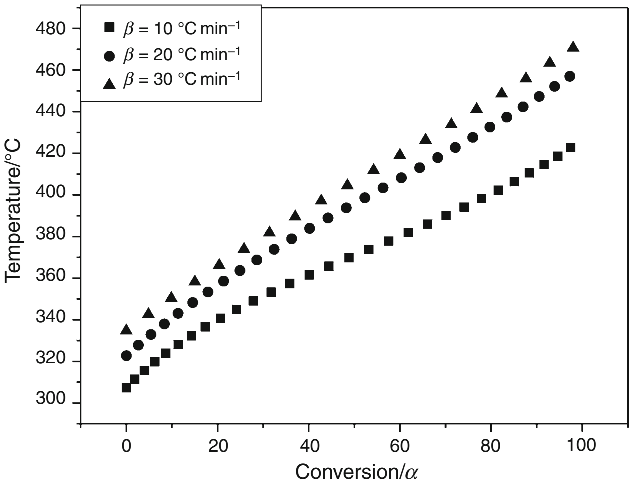

Fig. 5 Conversion curves as a function of temperature for the $PrCoO_3$ sample

can also be attributed to the removal of fragments of amino acids from gelatin [14]. The second and third stages of mass loss, above 300 °C, are generally associated with combustion of organic matter and attributed to the decomposition processes of organic groups and the breaking of bonds between the metal ions and the carboxyl groups of the polymerizing agent.

Figures 3 and 4 show the TG curves of the $PrCoO_3$ and $PrNiO_3$ samples for three heating rates.

With the integral data of the TG curves in the linear heating rates (10, 20, and 30 °C min^{-1}), the E_a values were estimated for each degree of conversion (α). Both the Flynn and Wall method and the "Model-free Kinetics" method evaluate the degrees of conversion of a specific event that will be studied based on Eq. 10:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{10}$$

where α is the conversion, m_0 the initial mass of the sample, m_∞ the mass of the sample at the end of the stage

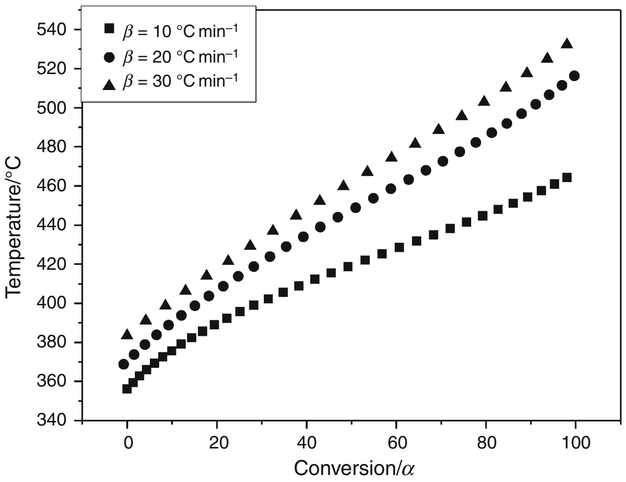

Fig. 6 Conversion curves as a function of temperature for the $PrNiO_3$ sample

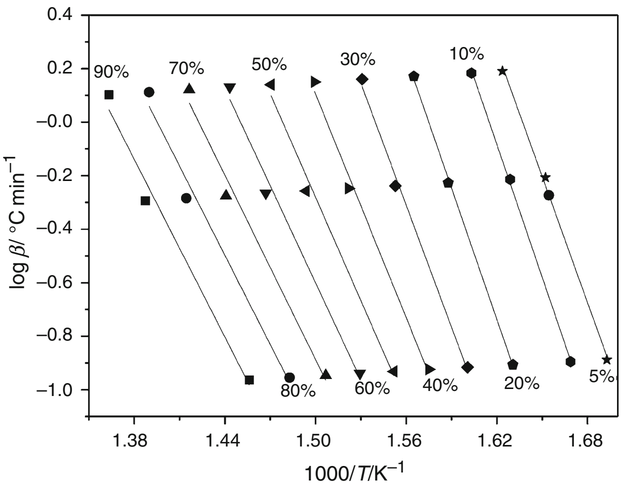

Fig. 7 Logarithm of the heating rate as a function of the inverse of the temperature for various conversion levels of the thermal decomposition stage of organic matter for $PrCoO_3$

being studied, and m_t the mass of the sample that varies with time (t) or temperature (T).

Figures 5 and 6 show the conversion curves as a function of temperature. To calculate the activation energy by the method, decomposition levels of 5 to 90% were chosen.

To calculate the activation energy using the Flynn and Wall method, the logarithm of the heating rate (log β) versus the inverse of the conversion temperature ($1/T_\alpha$) was plotted for the three curves. Straight lines were obtained, Figs. 7 and 8, in the slope of each line correspond to $-E_a/R$ ($R = 8.314$ J mol^{-1} K^{-1}). For the "Model-free Kinetics" method for each conversion, $\ln\beta/T_\alpha^2$ was graphed as a function of $1/T_\alpha$, also resulting in a series of straight lines with the slope $-E_a/R$.

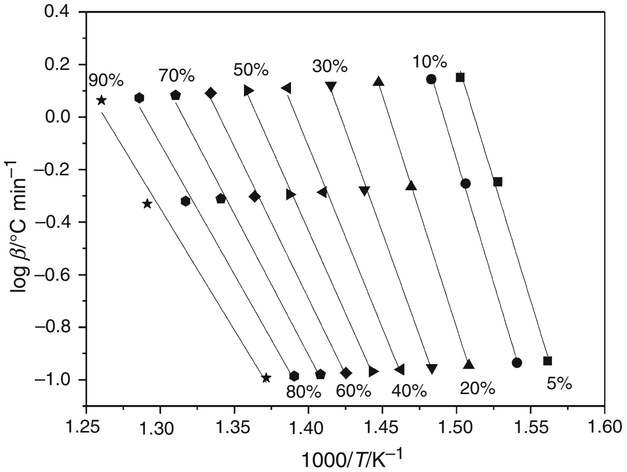

Fig. 8 Logarithm of the heating rate as a function of the inverse of the temperature for various conversion levels of the thermal decomposition stage of organic matter for $PrNiO_3$

Table 1 Activation energies for the 5.0 to 90.0% conversions for the $PrCoO_3$ samples obtained by the Flynn and Wall and "Model-free kinetics" methods

Conversion %	Model-free kinetics E_a/kJ mol^{-1}	Flynn and Wall E_a/kJ mol^{-1}
5	107.0	124.5
10	115.7	131.3
20	126.3	130.0
30	136.0	121.0
40	137.5	111.1
50	130.4	103.0
60	92.1	96.9
70	92.4	92.2
80	95.4	89.4
90	100.4	89.2

The activation energy values obtained by both methods (Tables 1 and 2) are proximate, suggesting that both the Flynn and Wall and "Model-free kinetics" methods are suitable for the determination of activation energy.

It can be noted from the results shown in Table 1 that the activation energy values from the Flynn and Wall and "Model-free Kinetics" methods for the $PrCoO_3$ sample display constants between the 0.05 to 0.9 conversion ranges. Thus, the $PrCoO_3$ sample has a higher interaction of the organic matter ligand groups with the metallic ions of the system; so that the energy needed to overcome the "barrier" is constant.

The $PrNiO_3$ sample already had a greater variation between these conversion ranges for the Flynn and Wall and "Model-free Kinetics" methods, as shown in Table 2.

Table 2 Activation energies for the 5.0 to 90.0% conversions for the $PrNiO_3$ samples obtained by the Flynn and Wall and "Model-free kinetics" methods

Conversion %	Model-free kinetics E_a/kJ mol^{-1}	Flynn and Wall E_a/kJ mol^{-1}
5	152.9	146.0
10	156.0	149.0
20	147.0	140.5
30	130.2	125.0
40	115.2	111.0
50	104.7	101.1
60	96.0	93.0
70	89.1	86.4
80	83	80.5
90	77	75.1

At first, the activation energy is relatively high; however, their values gradually decrease with each conversion. It can be said that there was a lower interaction of the desired structure with the organic matter. However, for the $PrNiO_3$ sample there was greater agreement for both kinetic models.

Conclusions

For the two samples studied, the activation energy values obtained for the second degradation region with both methods showed a similar behavioral trend, suggesting that the studied methods are adequate for determining this kinetic parameter related to decomposition energy, i.e., the interaction of organic matter ligand groups with metallic ions of the system.

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