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## A New Mechanism of Sodium Zirconate Formation

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### Abstract

The objective of this study was to synthesize sodium zirconate ( $\text{Na}_2\text{ZrO}_3$ ) from the thermal decomposition of two reactants; sodium acetate ( $\text{CH}_3\text{COONa}$ ) and Zirconium(IV) acetylacetonate ( $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ ). The  $\text{Na}_2\text{ZrO}_3$  formation mechanism has not been previously reported as it is shown in this work. Also, the reagents are soluble in ethanol; making it possible to apply the mechanism proposed in a spray pyrolysis process. The solid-state reaction was derived from the thermal decomposition of its precursors through the thermogravimetric analysis techniques (TG). The desired product formation was proven by means of an x-ray diffraction technique while the gaseous by-products of the reaction were analyzed using of the IR spectroscopy method (FTIR). Solid-state reaction has three significant weight losses and the TG technique displays these behaviors. The kinetic reaction study was completed using the determination of the activation energy, the pre-exponential factor and the reaction order of such regions. Finally, it was numerically proven that the chemical reaction behavior is well reproduced using the Arrhenius-type kinetic model.

**Keywords:** Sodium zirconate, Arrhenius equation, solid-state reaction, thermal decomposition.

### 1. Introduction

Natural gas reformation is a predominant course for large scale hydrogen ( $\text{H}_2$ ) production. In order to optimize this process,  $\text{CO}_2$  is captured in situ by means of a solid absorbent. The sodium-based ceramics ( $\text{Na}_2\text{ZrO}_3$ ,  $\text{Na}_2\text{TiO}_3$ ,  $\text{Na}_3\text{SbO}_4$ ) are good  $\text{CO}_2$  sorbents and the sodium zirconate ( $\text{Na}_2\text{ZrO}_3$ ) has better characteristics for capturing  $\text{CO}_2$  as compared to those of  $\text{Li}_2\text{ZrO}_3$  (López *et al.* 2005). Due to its good sorbent properties, designing an efficient process to produce sodium zirconate in a controlled manner was interesting. The  $\text{Na}_2\text{ZrO}_3$  may be obtained in a liquid-state reaction between  $\text{NaNO}_3$  and  $\text{ZrO}(\text{NO}_3)_2$  using citric acid and ethylene glycol as the complex agent (Näfe and Subasri 2007). Another method exists for synthesizing  $\text{Na}_2\text{ZrO}_3$  and sodium hydroxide (Lazar *et al.* 2002), an industrial process that aims to purify minerals, mainly composed of  $\text{ZrO}_2$   $\text{SiO}_2$ . This process breaks down the minerals in alkaline fusion with sodium hydroxide at temperatures above 600 °C; and it produces a mixture of sodium zirconate, sodium silicate and sodium silicate zirconium. This mixture is then subjected to various separation and purification processes. Another method to synthesize sodium zirconate is through a solid state reaction between sodium carbonate and zirconium oxide (Escobedo *et al.* 2009). It is generally agreed that the formation of  $\text{Na}_2\text{ZrO}_3$  by means of a solid-state reaction is more efficient than other techniques. The objective of this paper was to propose a new mechanism of synthesis of  $\text{Na}_2\text{ZrO}_3$  from zirconium(IV) acetylacetonate and sodium acetate in solid state. The mechanism will be coupled to a formation of sodium zirconate nanoparticles in a spray pyrolysis process as previously described by Cortés and Díaz 2006. In the literature, articles and reports dealing with the selected reactants can be found. The thermal decomposition of sodium acetate between 400 and 550 °C releases an acetone molecule, leaving a solid residue of sodium carbonate (Judd *et al.* 1974). The reactions of zirconium(IV) acetylacetonate decomposition in nitrogen demonstrated that  $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$  has a complete decomposition into  $\text{ZrO}_2$  at 800 °C through the intermediates of  $\text{Zr}(\text{CH}_3\text{COO})_2(\text{C}_5\text{H}_7\text{O}_2)_2$  at 190 °C,  $\text{ZrO}(\text{CH}_3\text{COO})_2$  at 340 °C and  $\text{ZrOCO}_3$  at 450 °C (Hamdy 1995). On

the other hand, the zirconium acetylacetonate decomposition in air (Wang *et al.* 2000), using thermogravimetry and infrared spectrometry (IR) show significant losses occur in three temperature regions; 110–187 °C, 187–245 °C and 245–440 °C. The IR spectrum of zirconium(IV) acetylacetonate heated at different temperatures up to 450 °C indicated that every acetyl acetone structure was completely decomposed at 310 °C. The decomposition of precursors ends at 440 °C. The thermal decomposition of zirconium(IV) acetylacetonate produces a final solid residue of zirconium oxide (zirconia). Additionally, a kinetic study is proposed to describe the chemical reaction progress since the precursors, zirconium(IV) acetylacetonate and sodium acetate.

## 2. Materials and Methods

The materials used for studying the solid-state reaction were the Aldrich sodium acetate and the Sigma-Aldrich zirconium acetylacetonate with 99% and 98% purity, respectively. These two reactants were mixed in a pestle with a stoichiometric ratio of 1:2 (Escobedo *et al.* 2009).

In order to accomplish the kinetic study of the sodium zirconate synthesis from the thermal decomposition, we used the Arrhenius parameter determination methodology (Gill *et al.* 1992), through the thermogravimetric analyses (TG). TG is a thermal analysis technique which measures the weight change degree and rate of a material as a function of temperature or time in a controlled environment. The analyses were conducted in a heating ramp at 15 °C min<sup>-1</sup> at room temperature up to 950° C, in a flow of air and argon in the same proportion, at 20 ml min<sup>-1</sup> in an SDT Q600, TA. A TG analysis was performed separately for each reactant and the stoichiometric mixture of both reactants. The mixture was then subjected to other TG analyses with six different heating rates (2, 5, 8, 10, 15 and 20° C min<sup>-1</sup>) to estimate the parameters of the following model.

The kinetic constant of the solid-state reaction (*k*) was determined by Arrhenius law (Levenspiel 1998):

$$k = Z \exp\left(-\frac{E}{RT}\right) \quad (1)$$

Where:

*k* = The kinetic coefficient

*Z* = The frequency factor

*E* = The reaction activation energy

*R* = The gases constant

*T* = The temperature

The equation (1) interfaces with the experimental data in wide temperature intervals and is considered as the first adequate estimation to study the temperature impact on the kinetic equation. For example, this equation may be applied to the kinetic study of polymers and composites (Yuzay *et al.* 2010), as well as solid-state formation of oxides (Roduit *et al.* 1996). The thermal decomposition often follows the Arrhenius kinetic model (Tanaka 1995):

$$\frac{d\alpha}{dt} = f(\alpha) \left[ Z \exp\left(-\frac{E}{RT}\right) \right] \quad (2)$$

Where:

$\alpha$  = The weight loss fraction

$f(\alpha)$  = The function of  $\alpha$  not depending on *T*, in this case is:  $(1 - \alpha)^n$

*n* = The reaction order

*t* = The time

At a constant heating rate of:  $\frac{d\alpha}{dt} = \frac{d\alpha}{dT}\beta$ , where  $\beta$  is the heating rate.

The activation energy has a slight deviation from the Arrhenius standard kinetic (Flynn and Wall 1996) so that:

$$E = -\frac{R d(\ln \beta)}{b d\left(\frac{1}{T}\right)} \quad (3)$$

Where:

$b$  is a parameter which depends on the value of  $E/RT$ .  $b$  could be deduced from tables and by means of an iterative method (Flynn and Wall 1996).

Using this technique for a given temperature, a preliminary estimation of  $E$  is selected and yields a first estimation of  $b$ . This value of  $b$  then provides a new approximation of  $E$ ; the iterations are repeated until  $b$  and  $E$  converge. In this report, parameters  $b$  and  $E$  were determined for each significant weight loss during the global reaction; in other words, each weight loss corresponded to an intermediate reaction.

A TG analysis at a constant temperature or with minor temperature variations, was performed for each one of the significant weight losses in the global reaction to determine the reaction order  $n$ . The curve of  $\ln(d\alpha/dt)$  vs  $\ln(1-\alpha)$  was plotted and the slope of a linear regression fit provided the value of  $n$  as described previously (Gill *et al.* 1992). Equation 3 then yields the frequency factor:

$$\ln Z = \ln\left[\frac{d\alpha}{dt}\right] + \frac{E}{RT} - \ln(1-\alpha)^n \quad (4)$$

In this compartment, the values of  $E$ ,  $Z$  and  $n$  were obtained for each significant weight loss in the global reaction.

The gas compounds, which were produced as byproducts of the thermal degradation in the TG device, were transported to a cell with NaCl windows by means of airflow at a  $20 \text{ ml min}^{-1}$  rate. These gases were then analyzed with IR spectroscopy, using a Nicolet System Magna-IR 750 Spectrometer Series II. A Fourier transform infrared spectroscopy (FTIR) was then used to obtain a spectrum over a  $500\text{--}4,000 \text{ cm}^{-1}$  range for each  $20^\circ \text{ C}$  temperature increment in the TG device.

The crystalline structure of the final solid product of the thermal decomposition was analyzed by making use of the X-ray diffraction technique (XRD) in a PANalytical X'pert PRO MPD device with a (Cu K $\alpha$ ) X'Celerator detector in a range of 10 to 80 degrees.

### 3. Results and Discussion

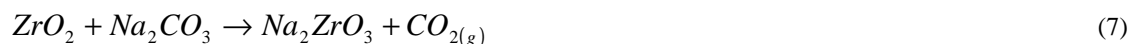
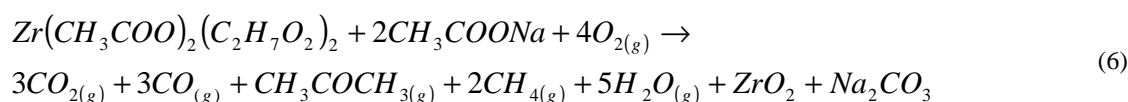
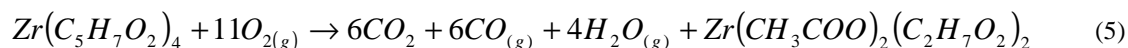
Three thermogravimetric analyses were obtained; the first in zirconium acetylacetonate, the second in sodium acetate and the third in a mixture of both in a ratio of 1:2 (Figure 1). Figure 1 demonstrates three significant weight losses. Figure 2 also shows the TG analyses of the reactant mixture at six different heating rates; 2, 5, 8, 10, 15 and  $20^\circ \text{ C min}^{-1}$ . Due to these analyses, the determination of the Arrhenius parameters was performed. We get to trace the gas compounds released during the solid-state reaction. So, the gases obtained from the thermogravimetric analysis (in the conditions previously described), were analyzed with FTIR spectroscopy. The FTIR spectroscopy analyses of the output gases were performed every  $20^\circ \text{ C}$  (from  $40$  to  $940^\circ \text{ C}$  in the TG device). Figure 3 notes the more representative FTIR spectra, corresponding to the three significant weight losses;  $220$ ,  $500$  and  $700^\circ \text{ C}$ . One can also observe the characteristic stripes of the following gases; carbon dioxide (A), methane (B), acetone (C) and carbon

The composition of the final product from the zirconium acetyl acetate and sodium acetate reaction was sodium zirconate; this may be appreciated in results of the X-ray diffraction analysis of the solid residue. Figure 4 examines the characteristic peaks of the monoclinic and hexagonal phases of  $\text{Na}_2\text{ZrO}_3$  (Ampian 1968).

The thermal decomposition of each reagent was stoichiometrically summed, obtaining a theoretical prediction of the decomposition if there was not an interaction between these reagents (see Figure 5). This theoretical curve was compared to the TGA in the mixture with a stoichiometric ratio. Byproducts of the first decompositions of zirconium acetylacetate in air between 150 and 220 °C, exhibited the following bonding types (Wang *et al.* 2000);  $\gamma(\text{C}-\text{CH}_3)+\gamma(\text{C}=\text{C})$ ,  $\delta(\text{CH})+\gamma(\text{C}-\text{CH}_3)$  and  $\gamma(\text{C}=\text{C})+\gamma(\text{C}=\text{O})$ . Such decompositions are consistent with the theoretical stoichiometric calculations and correspond to the first weight loss (Figure 1). The preponderant released gases that were detected by FTIR at 220° C were  $\text{CO}_2$  and CO (Figure 3). Therefore, the first weight loss was due to the decomposition of zirconium acetylacetate since the sodium acetate did not exhibit any thermal degradation (Figure 1).

In Figure 5, after 350° C, an important difference between the curves of the theoretical sum and the experimental result, with the stoichiometric mixture, can be observed. This is due to the interaction between the two reactants. The FTIR analysis of the released gases helps to propose a possible reaction mechanism for each weight loss. In Figure 3, the FTIR analysis results are shown for each of the three weight losses. Based on the FTIR results and on previous information<sup>5,8</sup>, we propose three global reactions enclosing the three significant weight losses.

Equation 5 corresponds to the first weight loss and as previously mentioned, to the decomposition of zirconium acetylacetate; the product of this first reaction was  $\text{Zr}(\text{CH}_3\text{COO})_2(\text{C}_2\text{H}_7\text{O}_2)_2$ . In the second weight loss, sodium acetate tends to decompose and a reaction with  $\text{Zr}(\text{CH}_3\text{COO})_2(\text{C}_2\text{H}_7\text{O}_2)_2$  was proposed as shown in Equation 6. The solid byproducts were  $\text{ZrO}_2$  and  $\text{Na}_2\text{CO}_3$ . Finally, in the third weight loss, these two byproducts react to form  $\text{Na}_2\text{ZrO}_3$  (Nafe and Subasri 2007) with a  $\text{CO}_2$  release as shown in Equation 7. These three reactions comprise the transformations undergone by zirconium acetylacetate and sodium acetate.



In order to understand the reactions of the kinetic study, the first step was necessary to determine the kinetic parameters utilizing the Arrhenius equation. This was achieved through the TG data of the stoichiometric mixture with different heating rates (Figure 2). The Arrhenius parameters shown in Table 1 were obtained in this manner.

Such parameters were introduced in the kinetic equation of thermal decomposition (Equation 2) which was solved numerically. With the aim of validating the calculations, these numerical theoretical values were compared to the experimental values. Figures 6, 7 and 8, display these comparisons for the three significant weight losses. These same figures show an axis horizontal to time and in the vertical axis, the weight loss fraction (in the TG analyses: % Weight equals  $(1 - \alpha) \cdot 100$ ). The differences between the theoretical values and the real values were represented with vertical bars. These differences stem from the simplification of taking the constant temperature and the fact that in the reaction, a number of coupled changes occur in every weight loss.

#### 4. Conclusions

In this study, we synthesized sodium zirconate from thermal decomposition of the initial reagents (sodium acetate and zirconium acetylacetonate). Sodium Zirconate and gaseous sub-products were estimated. This information has proposed a formation mechanism. The Arrhenius parameters were estimated using the TG information. The kinetic model of thermal decomposition fed with the determined Arrhenius parameters, follows the chemical reaction behavior of zirconium acetylacetonate and sodium acetate in solid state. The final product of the solid-state reaction of the stoichiometric mixture of reactants is sodium zirconate (see Figure 4 and Equation 7).

The reagents thermal decomposition rates are higher than sodium zirconate formation velocity. However, at higher temperatures, both rates are increased, reducing the sodium zirconate formation time.

The results of this research will be applied to a model published in a previous work (Cortés and Díaz 2006) studying the formation of nanoparticles in a spray pyrolysis process. This model describes the influence of the solvent evaporation and the temperature drop (Lenggoro et al. 2000). The ultimate objective is optimizing the production of sodium zirconate nanoparticles in a controlled spray pyrolysis process. This product may be used as a carbon dioxide absorbent and it may be applied to obtain hydrogen in the methane gas reformation process (Escobedo *et al.* 2008).

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#### Note

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Table 1. The Arrhenius parameter of the stoichiometric mixture.

Temperature (°C)	Z	E (kJ/mol)	n
1) 195	4.9E22	200	2
2) 327	5.39E17	225	1.2
3) 704	1.47E15	364	0.9

The Arrhenius parameters obtained for each significant weight loss.

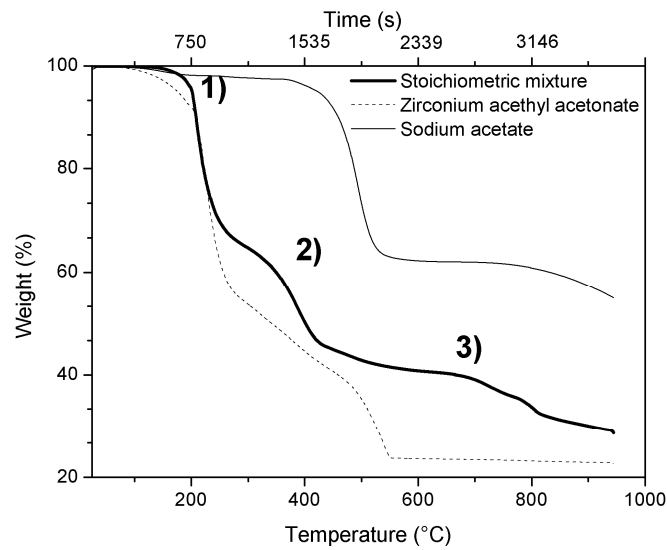


Figure 1. Thermal gravimetric analysis of Zirconium acetylacetonate, Sodium acetate and their stoichiometric mixture.

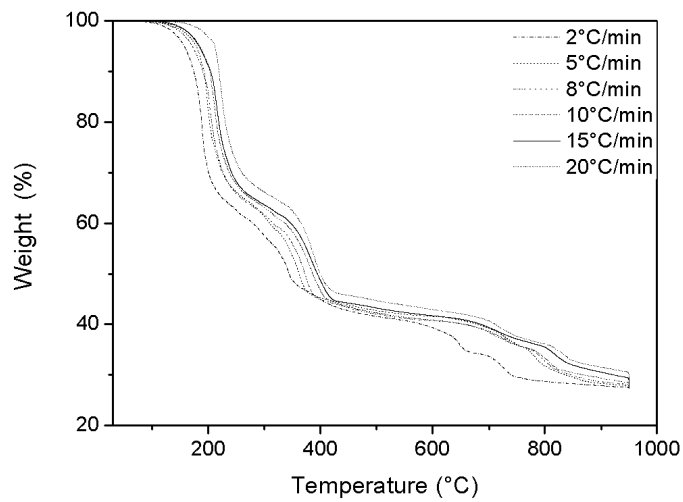


Figure 2. Thermogravimetric analyses of stoichiometric mixture with different heating rates.

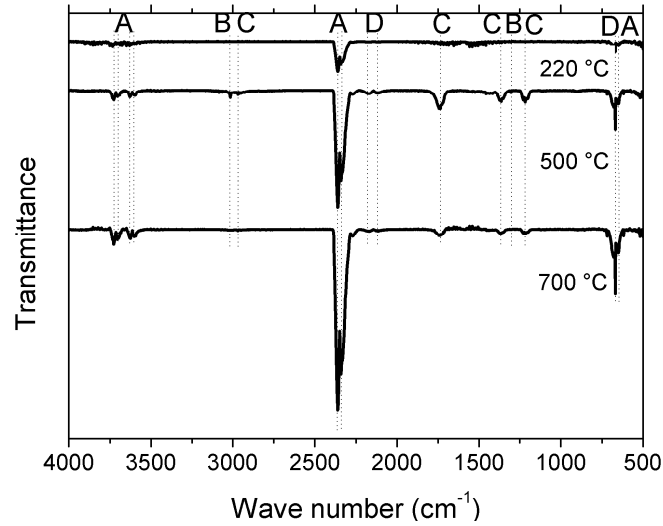


Figure 3. FTIR analyses of the gases produced during the TGA of the mixture of reactants at 220° C, 500° C and 700° C.

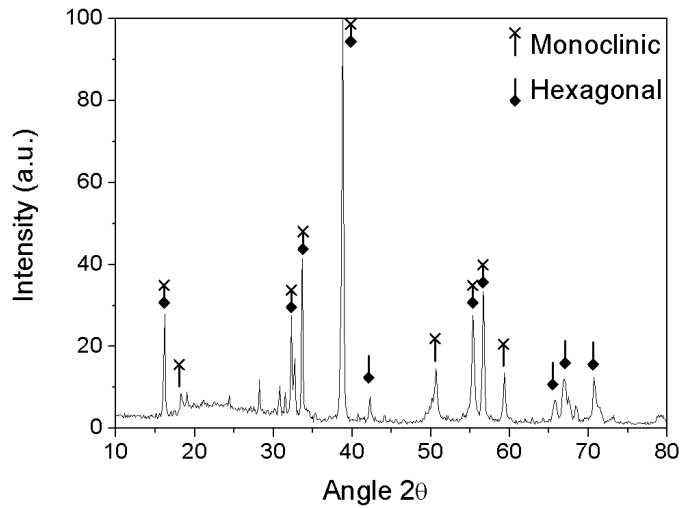


Figure 4. X-ray diffraction pattern of the solid residue and the characteristic peaks of sodium zirconate (Na<sub>2</sub>ZrO<sub>4</sub>).



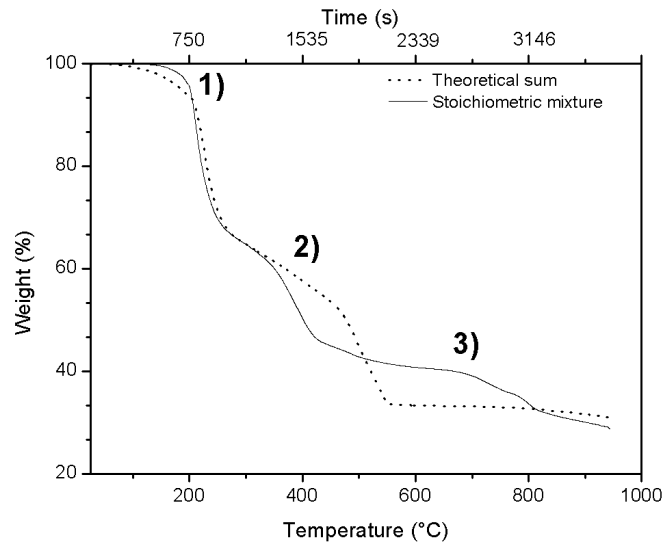


Figure 5. Thermal gravimetric analysis of stoichiometric mixture and the theoretical sum (the addition of reagents with stoichiometric calculations).

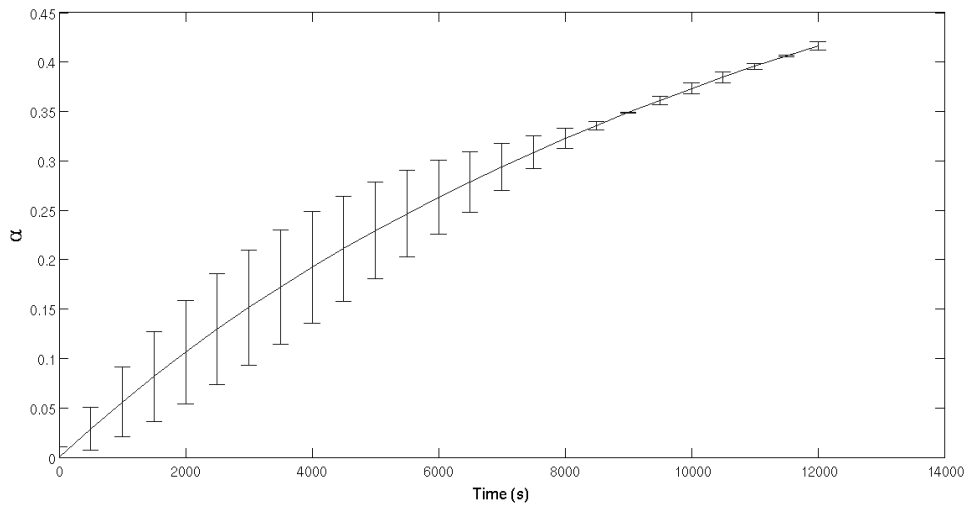


Figure 6. Comparison of the theoretical and experimental results for the first weight loss (195 °C) of the Zirconium acetyl acetonate/Sodium acetate reaction.

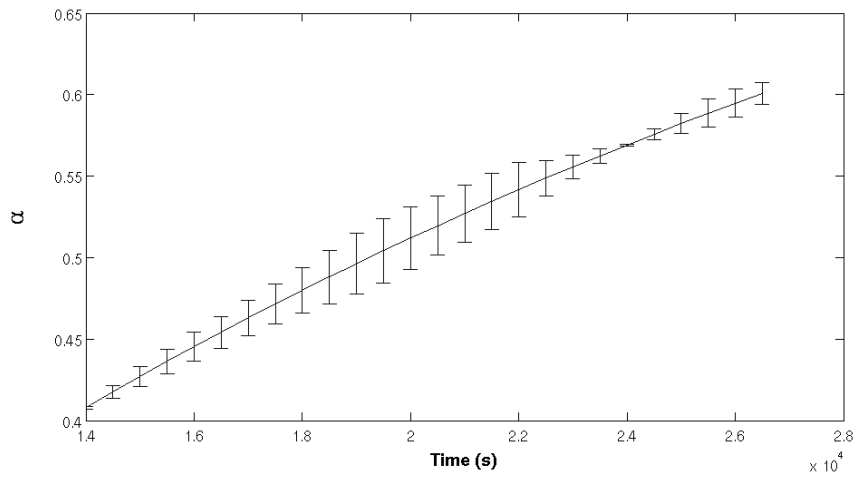


Figure 7. Comparison of the theoretical and experimental results for the second weight loss (327 °C) of the Zirconium acetyl-acetate/Sodium acetate.

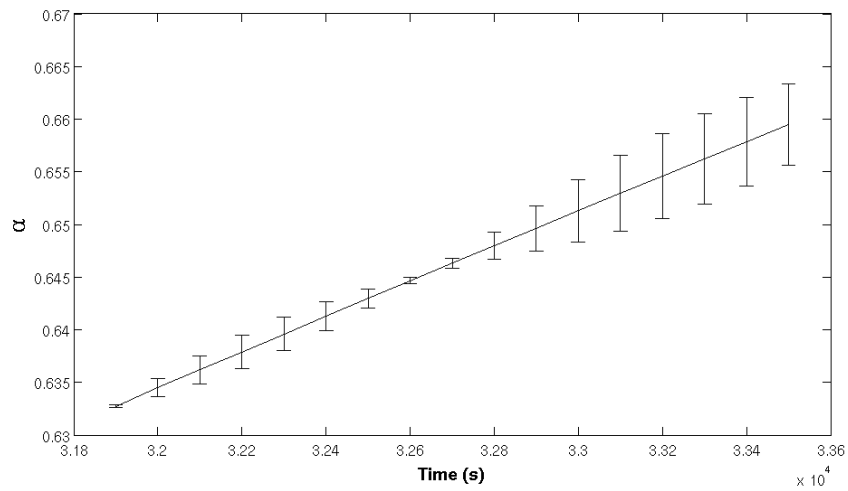


Figure 8. Comparison of the theoretical and experimental results for the third weight loss (704 °C) of the Zirconium acetylacetate/Sodium acetate.

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