

Article

Thermodynamics and Kinetic Modeling of the $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ Thermal Decomposition in the Presence of a $\text{Pd}/\text{Al}_2\text{O}_3$ Catalyst

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Abstract: The sulfur–iodine thermochemical water-splitting cycle is a promising route proposed for hydrogen production. The decomposition temperature remains a challenge in the process. Catalysts, such as Pd supported on Al_2O_3 , are being considered to decrease reaction temperatures. However, little is known regarding the kinetic behavior of such systems. In this work, zinc sulfate thermal decomposition was studied through non-isothermal thermogravimetric analysis to understand the effect of a catalyst within the sulfur–iodine reaction system context. The findings of this analysis were also related to a thermodynamic assessment. It was observed that the presence of $\text{Pd}/\text{Al}_2\text{O}_3$ modified the reaction mechanism, possibly with some intermediate reactions that were suppressed or remarkably accelerated. The proposed model suggests that zinc sulfate transformation occurred in two sequential stages without the Pd-based material. Activation energy values of 238 and 368 $\text{kJ} \cdot \text{mol}^{-1}$ were calculated. In the presence of $\text{Pd}/\text{Al}_2\text{O}_3$, an activation energy value of 204 $\text{kJ} \cdot \text{mol}^{-1}$ was calculated, which is lower than observed previously.

Keywords: zinc sulfate; thermal decomposition kinetics; Pd catalyst



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1. Introduction

Over the last few decades, the question regarding how energy systems must be updated to reduce carbon emissions and to lower their contribution to climate change has become increasingly urgent. This can be observed in reports issued by international agencies, such as the United Nations [1], and studies on the affordability and security of these future systems, as published by Sencar et al. [2]. In this context, hydrogen presents itself as a potential cleaner fuel compared to carbon-based fossil fuels, as only water results from H_2 combustion. Thus, research devoted to the production and storage routes of this resource is considered strategic for sustainable development [3,4].

Chemical processing routes for H_2 production are diverse [5–11]. However, not all methods are based on renewable sources, and the most relevant alternatives explored so far are based on methane decomposition [12,13] or thermochemical water-splitting cycles [14]. For the latter, the sulfur–iodine cycle has been extensively studied [15–24]. The water-splitting cycle is a three-step process, in which sulfuric acid thermal decomposition occurs in the third step. This step represents an energy challenge concerning sulfur dioxide and oxygen formation, prompting investigations of methods that can convert sulfate-bearing materials at lower temperatures [25]. Therefore, a promising alternative for H_2 production at lower temperatures is the metal oxide–metal sulfate thermochemical water-splitting cycle [26]. From this perspective, zinc sulfate turns out to be a strong candidate among the different metal sulfates, as it has a high yield, low cost, and low toxicity [27].

The use of catalysts has been studied for the H_2SO_4 decomposition process during the initial development of sulfur-based thermochemical hydrogen production cycles. General

Atomic tested a wide range of materials [16]. Pt, Fe₂O₃, V₂O₅, Cr₂O₃, CuO, MnO₂, CoO, and NiO have been used with various supports, where the most efficient were Pt, Fe₂O₃, and CuO. More recent studies [17,28–31] also show that Pt and Pd catalysts supported on metal oxides are a promising alternative due to their high potential for catalytic activity.

In this context, metal sulfate decomposition has been proposed as a feasible alternative. Some of these salts may decompose at lower temperatures than sulfuric acid or do not require manipulating a highly reactive liquid material. Prosini et al. [32] studied the use of nickel sulfate, while in the work of Tizzoni et al. [33], iron sulfate was tested as a possible sulfur precursor. The same sulfates were also investigated in the work of Bhosale et al. [26,34], who also studied the use of zinc sulfate. However, the high decomposition temperatures found in these systems seem to hinder their large-scale application. Therefore, some alternatives in the field of heterogeneous catalysis have been recently proposed, such as the one presented by Soto-Díaz et al. [27], who employed catalysts with Pd supported on a SiC or Al₂O₃ matrix.

As kinetic data can have an essential role in understanding every chemical process, several authors have performed experimental studies on the thermal decomposition of zinc sulfates [35–39], reporting activation energy values between 96 and 350 kJ·mol^{−1} for different decomposition models and apparent orders between 0 and 1.1. However, there is a paucity of information on the effects of incorporating catalytic materials on the kinetic parameters of these thermal decomposition processes. Consequently, there is a lack of information about the behavior of the reaction system through a more quantitative approach, with one reported work so far for MgSO₄·7H₂O thermal decomposition [40]. Nevertheless, this sulfate tends to decompose directly into its oxide in a manner that is novel to systems in which an intermediate is formed (e.g., ZnO·2ZnSO₄ from ZnSO₄ and FeSO₄ from Fe₂(SO₄)₃).

In the present work, zinc sulfate was processed both in the presence and in the absence of a Pd/Al₂O₃ catalyst. This salt was chosen for this study since it is a promising candidate for use in H₂ production processes because of its lower decomposition temperature compared with other sulfates. It is recognized that an intermediate compound is formed as the decomposition progresses. Until now, there have been no kinetic studies dedicated to understanding the effect of a catalyst on the kinetics of this thermally stimulated process. Therefore, the purposes of the present work are multifold. The first objective was to develop a detailed thermodynamic study in which intermediate formation is assessed using its weight fraction at equilibrium (wt.%). The second goal was to develop a kinetic analysis based on a graphical modeling approach to estimate the process parameters with and without the Pd/Al₂O₃ material. The third objective was to analyze and understand the catalyst effect on the reaction system behavior based on the previously detailed thermodynamic findings. A kinetic study based on thermogravimetric data (TGA) was performed to accomplish these tasks.

2. Materials and Methods

2.1. Thermodynamic Study

Thermodynamic calculations were performed to understand the equilibrium behavior of the reaction system as a function of temperature. The data are presented in diagrams of varying nature, equilibrium composition and predominance diagrams, constructed using HSC Chemistry software v.9.9.2.3 for the MS Windows environment [41].

2.2. Thermogravimetric Analysis and Kinetic Modeling

Figure 1 presents the experimental methodology, described in detail in the work of Kurban [42], which was applied in this study to perform a kinetic modeling assessment of ZnSO₄ thermal decomposition in the presence and absence of a Pd/Al₂O₃ catalyst.

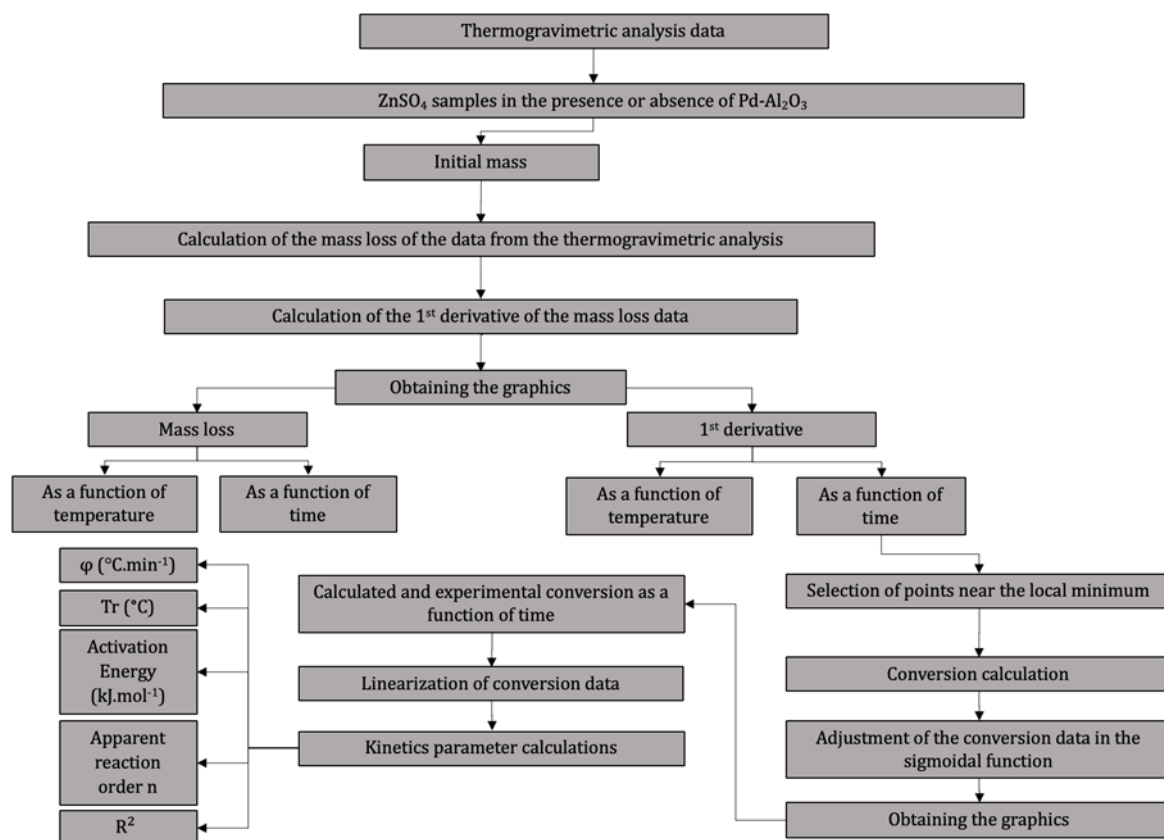


Figure 1. Flowchart describing the modeling algorithm for the calculations of the kinetic parameters.

Thermogravimetric analyses of zinc sulfate monohydrate thermal decomposition were performed to measure the conversion achieved as a function of time during dynamic runs conducted under a N_2 atmosphere ($20 \text{ mL} \cdot \text{min}^{-1}$) at a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The TGA tests were conducted in a Netzsch instrument model STA 449 F3 Jupiter and covered a temperature range from 25 to $1000 \text{ }^\circ\text{C}$. Around 5 mg of pure sulfate (P.A., Sigma-Aldrich, St. Louis, MO, USA) and mixtures with $\text{Pd}/\text{Al}_2\text{O}_3$ were used, using a 1:1 mass ratio between sulfate and catalyst in the latter case. The $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst was prepared following the methodology presented by Mello [43]. The kinetic modeling carried out in the present work was based on Equation (1) [44,45], where T_r , ϕ , and f represent the reference temperature, heating rate, and thermal decomposition conversion at a specific time (t), respectively.

$$(\phi t + T_r)^2 \frac{d^2f}{df \, dt} = -n \left[\frac{(\phi t + T_r)^2 \left(\frac{df}{dt} \right)}{1 - f} \right] + \frac{E_a \phi}{R} \quad (1)$$

Experimental conversion values were first fitted (α and β are adjustable parameters) to a sigmoidal function (Equation (2)) to analytically calculate the first- (df/dt) and second-order time derivatives (d^2f/dt^2). In Equation (2), parameters α and β were estimated based on a simplex algorithm applied to a least-squares function of the differences between experimental and calculated conversion values.

$$f = \frac{1}{1 + \exp(-\alpha \cdot (t - \beta))} \quad (2)$$

With these derivative values in hand, the global activation energy (E_a) and apparent reaction order (n) were determined after the linearization of the TGA data by employing Equation (1) and subsequently performing linear regression analysis. The n value is

determined by the slope, and E_a is calculated through the evaluation of its linear coefficient. For each analysis, the modeling quality was determined by the value of the correlation coefficient (R^2) calculated for each dataset. This methodology was recently successfully applied for the thermal decomposition modeling of MgSO_4 [40] and potassium alum [46] reaction systems.

3. Results

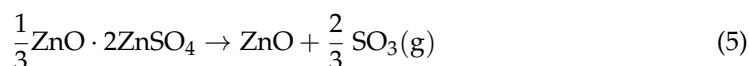
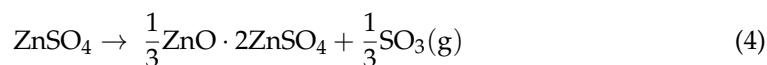
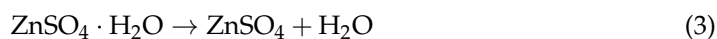
3.1. Thermodynamic Modeling

Figure 2 presents the equilibrium compositions for the gas and pure species as a function of the temperature. The initial condition used was 1 mol of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ with N_2 in the initial phase for stability improvement. It can be observed that sulfate dehydration takes place until 400 °C. Based on the gas-phase behavior, anhydrous sulfate starts to transform to $\text{ZnO} \cdot 2\text{ZnSO}_4$ at approximately 500 °C, with SO_2 and SO_3 evolution. After 600 °C, the system enters into competitive, or more likely sequential, decomposition reactions with the onset of ZnO production. The intermediate is present in the reaction system until 1000 °C. Complete sulfate conversion is achieved at 1200 °C. It can be observed that some species considered for the equilibrium composition simulations are not present in the graphical result.

To further understand the behavior of the ZnSO_4 thermal decomposition process, Figure 3 shows the predominance diagrams of the Zn-S-O reaction system as a function of temperature. For that purpose, p_{O_2} was fixed at negligible levels (1×10^{-20} bar). Thermodynamically, the system must go through the formation of $\text{ZnO} \cdot 2\text{ZnSO}_4$ to decompose ZnSO_4 into ZnO . It seems that there is no direct reaction from this sulfate into its oxide for the presented temperature range. Moreover, considering that the process would be typically conducted in furnaces with continuous gas flow, with simultaneous removal of reaction products, it is expected that the equilibrium is shifted. Consequently, there is a possibility that the transformations (ZnSO_4 into $\text{ZnO} \cdot 2\text{ZnSO}_4$ and then into ZnO) occur at lower temperatures than those indicated by the equilibrium lines for the reaction between these phases.

3.2. Thermogravimetric Analysis and Kinetic Modeling

Following the described methodology, Figure 4 presents the samples' thermal behavior through weight loss (wt.%) and DTG. It is important to mention that the presented results were calculated by subtracting the thermal behavior of the $\text{Pd}/\text{Al}_2\text{O}_3$ sample from the signal. Regarding the pure sulfate sample, it can be observed that around 250 °C, there is a mass loss close to 10 wt.%, which can be explained by the elimination of hydration water (one mole per mole of sulfate—Equation (3)). These temperatures agree with thermodynamic predictions (Figures 1 and 2) and the previous literature [47,48], suggesting that above 250 °C, anhydrous sulfate should be the most stable zinc-bearing species. For higher temperatures, it is observed that the system behaves as a sequential process with two well-defined steps. The first step (Equation (4)—700 to 800 °C) accounts for a mass loss of around 25 wt.%, as has already been observed in earlier studies [47,49], representing the formation of an intermediate phase (such as $\text{ZnO} \cdot 2\text{ZnSO}_4$), which further decomposes in the range between 800 and 950 °C (Equation (5)), resulting in a relative weight loss of 55%.



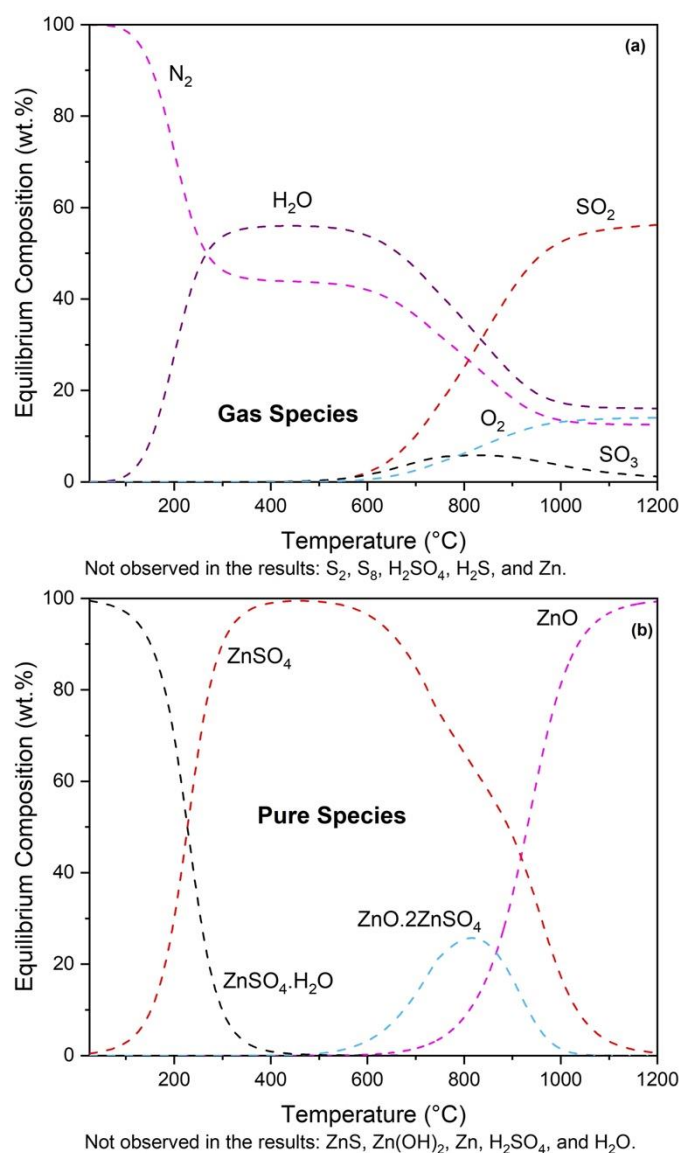
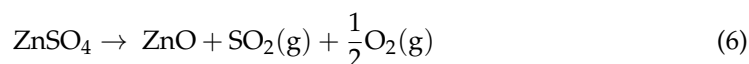


Figure 2. Equilibrium compositions for ZnSO₄·H₂O thermal decomposition: (a) gas-phase behavior; (b) pure species behavior.

Therefore, compared to decomposition in the absence of the Pd/Al₂O₃ catalyst, incorporating this material should substantially affect the observed reaction mechanism (Equation (6)).



Moreover, it can be observed that complete conversion is achieved at lower temperatures (decreasing by almost 100 °C for the pure sulfate sample) and agrees with the decrease of 85 °C reported by Soto-Diaz et al. [27]. This finding could reflect improved kinetics, which is also suggested by comparing each DTG signal.

Figures 5 and 6 present the kinetic modeling results for the thermal decomposition of pure ZnSO₄ and ZnSO₄ with the Pd/Al₂O₃ catalyst. For the former, the sample mass variation is segmented in two steps to describe the reaction system behavior better.

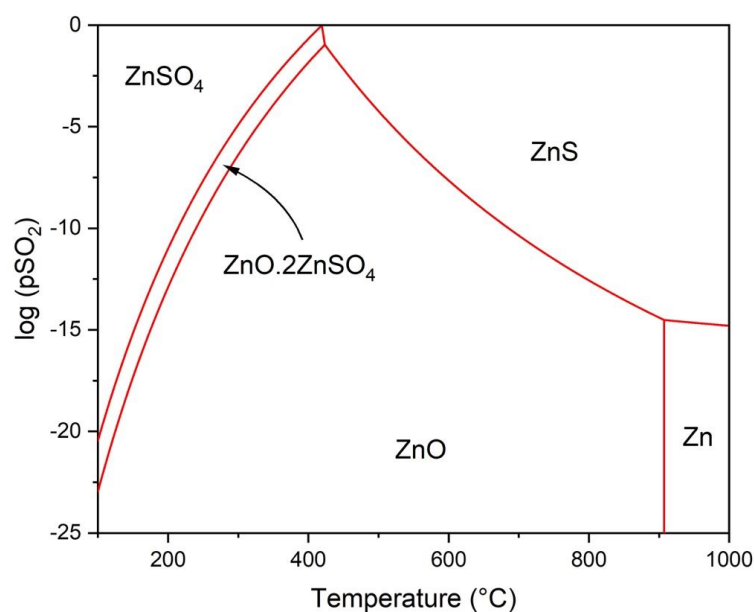


Figure 3. Predominance diagram for Zn-S-O system as a function of temperature and $\log p\text{SO}_2$.

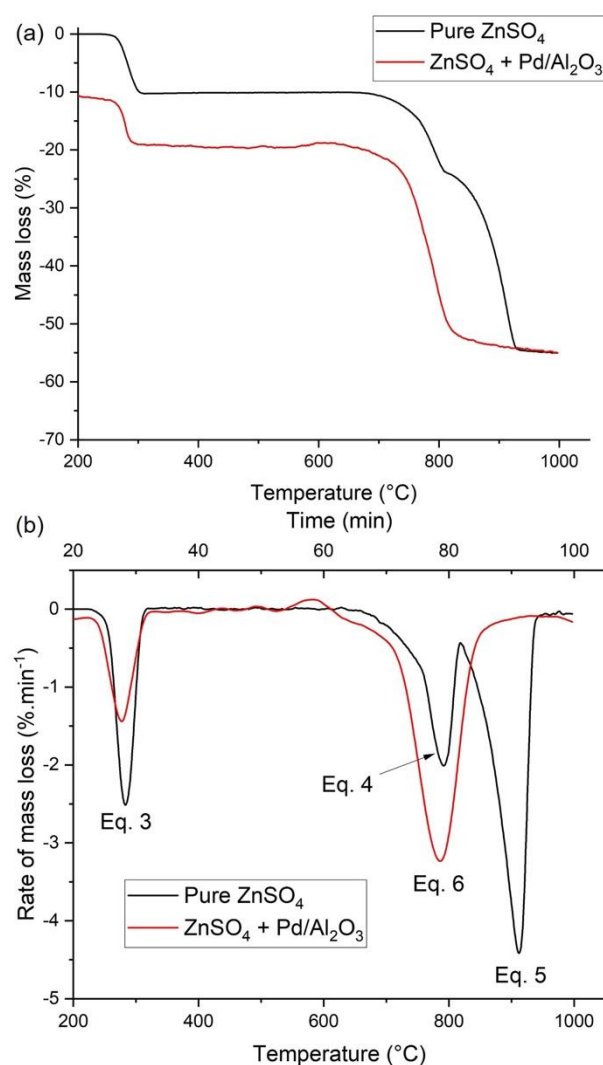


Figure 4. Thermogravimetric analyses of the thermal decomposition of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ in the presence and absence of $\text{Pd}/\text{Al}_2\text{O}_3$: (a) weight loss as a function of temperature; (b) DTG signal.

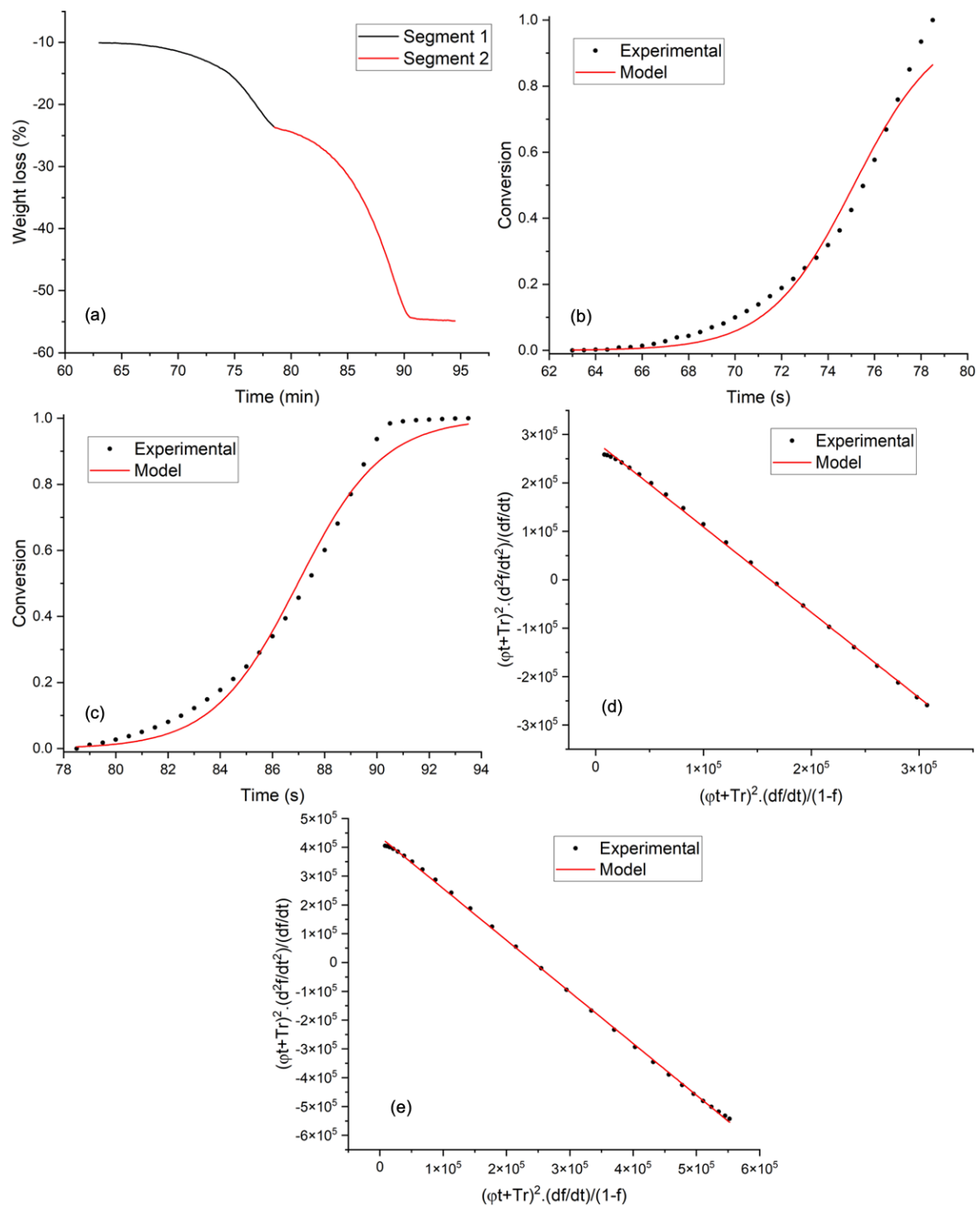


Figure 5. Graphical adjustments for thermal decomposition of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$: (a) segmentation of the sample mass variation; (b) conversion fraction of Step 1 as a function of temperature; (c) conversion fraction of Step 2 as a function of temperature; (d) linearization of conversion data associated with Step 1 segment; (e) linearization of conversion data associated with Step 2 segment.

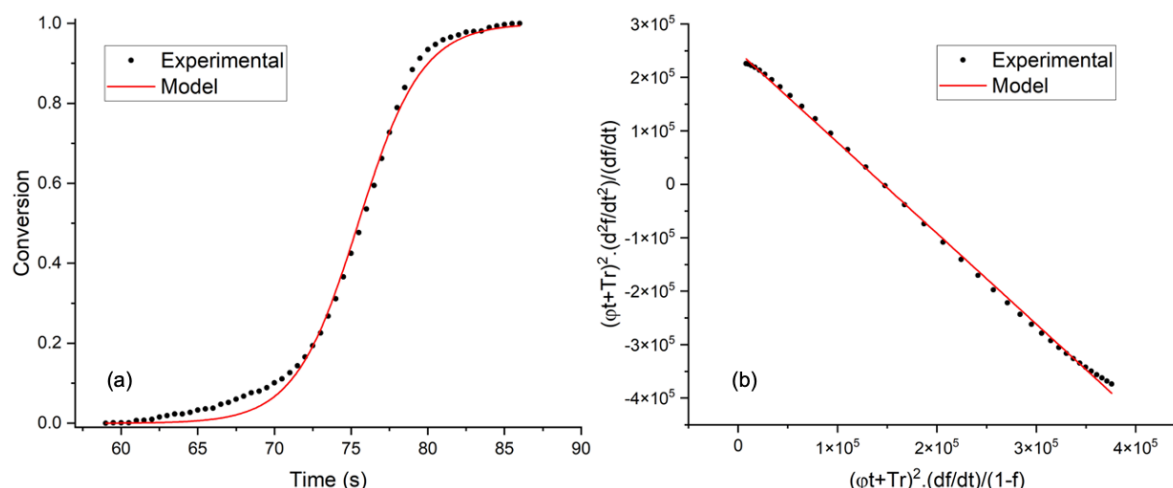


Figure 6. Graphical adjustments for thermal decomposition of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ in the presence of $\text{Pd}/\text{Al}_2\text{O}_3$: (a) conversion fraction as a function of temperature; (b) linearization of conversion data.

In both cases, the model seems to be well fitted, as the R^2 values between experimental (scatter) and model (continuous line) datasets are close to unity. These results support and are consistent with the determined kinetic parameters of the thermal decomposition of pure zinc sulfate and the mixture of ZnSO_4 and $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. The results are displayed in Table 1.

Table 1. Estimated kinetic parameters and corresponding correlation coefficient (R^2).

Sample	Step	n	E_a ($\text{kJ} \cdot \text{mol}^{-1}$)	R^2
ZnSO_4	1	1.76	238	0.979
	2	1.79	368	0.989
$\text{ZnSO}_4 + \text{Pd}/\text{Al}_2\text{O}_3$	1	1.69	204	0.997

The energy value associated with the single step observed in the catalyst presence (direct decomposition to ZnO) indeed has a much lower magnitude than the one determined for the first (intermediate formation) and second (intermediate thermal decomposition) when the catalyst is absent. Therefore, the results strongly suggest that the action of $\text{Pd}/\text{Al}_2\text{O}_3$ during zinc sulfate thermal decomposition is as expected for a catalyst, providing a new molecular path (possibly without $\text{ZnO} \cdot 2\text{ZnSO}_4$ formation through its rapid transformation) for the direct chemical transformation from sulfate to oxide with more favorable kinetics (lower E_a). Moreover, it is interesting to note that the apparent reaction order was almost constant and close to a value of 1.7 for both samples. In regard to the pure sulfate thermal decomposition, it is interesting to observe that the global activation energies calculated for the first ($238 \text{ kJ} \cdot \text{mol}^{-1}$) and second ($368 \text{ kJ} \cdot \text{mol}^{-1}$) stages lie in the range of prior literature values ($209\text{--}385 \text{ kJ} \cdot \text{mol}^{-1}$), as reported by Straszko et al. [47], Ingraham and Marier [49], and Tagawa and Saijo [50].

The decomposition of zinc sulfate results in ZnO production, involving the intermediate product $\text{ZnO} \cdot 2\text{ZnSO}_4$, compatible with the results obtained in the works of many authors [36–38,47,50–53]. Moreover, the intermediate step is not observed in the presence of the catalyst, as also evidenced in the work of Soto-Diaz et al. [27].

In the work of Mello et al. [40], who also used the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst, it was observed that palladium tended to oxidize and initiate the formation of PdO up to approximately 900°C in the reaction system and then dissociate, returning to the metallic form at higher temperatures. According to O’Keefe et al. [54] and Barbarossa et al. [17], the oxide’s catalytic activity forms in the decomposition of sulfur trioxide. Through the decomposition temperature observed in the TGA/DTG experiments and the similarity to MgSO_4 decomposition gas products, it can be inferred that in the ZnSO_4 system, the formation of PdO

occurs and interacts with its gaseous products, thus changing the reaction mechanism that was previously described in two stages.

An apparent change in the mechanism was also observed by Mu and Perlmutter [38] when adding carbon material to the decomposition mixture. The authors performed a series of decomposition studies involving different sulfates, observing a reduction in the decomposition temperature in all cases. Furthermore, in a more detailed study of ZnSO_4 , the decomposition temperature decreased as the carbon/sulfate molar ratio increased. In addition, the TGA results of these experiments do not show the apparent presence of an intermediate compound in the decomposition process.

The results of the kinetic analysis indicate a reduction in the activation energy when using the $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. Not only did the material reduce the energy required for the decomposition of ZnSO_4 (about $30 \text{ kJ}\cdot\text{mol}^{-1}$), but it also eliminated the energy needed for a second step in the decomposition process, which accounted for a massive reduction in the global activation energy. In their study, Narayan et al. [35] observed that the decomposition of zinc sulfate heptahydrate presented a decrease in the activation energy when using a platinum crucible ($227 \text{ kJ}\cdot\text{mol}^{-1}$) instead of a ceramic one ($298 \text{ kJ}\cdot\text{mol}^{-1}$). The authors concluded that platinum affected the equilibrium between SO_2 , SO_3 , and O_2 , which involved the decomposition of zinc sulfate. Moreover, the authors reported that other effects, such as particle size, hydration, and carrier gas, can impact the kinetic data of the thermogravimetric study.

4. Conclusions

The achieved results suggest that the thermal decomposition of monohydrate zinc sulfate under an inert atmosphere (N_2) first proceeds through hydration water removal ($250\text{--}300^\circ\text{C}$), followed by the thermal decomposition of anhydrous zinc sulfate (ZnSO_4) ($700\text{--}930^\circ\text{C}$), which develops in two steps. The first one is associated with the formation of an intermediate phase ($\text{ZnO}\cdot 2\text{ZnSO}_4$) ($700\text{--}800^\circ\text{C}$), and the second one is related to the thermal decomposition of this species generated previously ($800\text{--}850^\circ\text{C}$). These findings agree with earlier literature works and are corroborated by TGA mass balances and thermodynamic calculations. Both steps' apparent reaction order and activation energy were determined from the dynamic TGA data analysis, with the former being close to 1.7 in both cases, and the latter equal to $238 \text{ kJ}\cdot\text{mol}^{-1}$ and $368 \text{ kJ}\cdot\text{mol}^{-1}$ for steps 1 and 2, respectively. These last values proved to be consistent with earlier evaluations from the literature. In the presence of $\text{Pd}/\text{Al}_2\text{O}_3$, it can be said that the reaction mechanism changed appreciably, and a sole step was identified in the TGA signal, which could be associated with the direct conversion of the sulfate (ZnSO_4) to the oxide (ZnO). As expected for the action of a catalyst, $\text{Pd}/\text{Al}_2\text{O}_3$ enabled a different molecular path for the decomposition reaction with improved kinetics (degradation starts almost 100°C earlier), with a global activation energy of $204 \text{ kJ}\cdot\text{mol}^{-1}$, which is much lower than the values determined for pure ZnSO_4 . For the other thermal events studied in the present paper, the apparent reaction order for the catalytic decomposition was also close to 1.7. The catalytic activity of $\text{Pd}/\text{Al}_2\text{O}_3$ evidenced in this paper regarding the thermal decomposition of ZnSO_4 could also be present for other sulfates, motivating further studies. Processes can be improved by lowering the decomposition temperatures, such as those reported in thermochemical water-splitting cycles.

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Conflicts of Interest: The authors declare no conflict of interest.

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