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Thermal decomposition behavior and kinetics of Nitrocellulose in the presence of Cobalt Oxide Supported on Activated Carbon

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In this study, the catalytic effect of cobalt oxide (CoO) supported onto activated carbon (AC) on the thermal behavior of nitrocellulose (NC) was investigated using differential scanning calorimetry (DSC) and three isoconversional kinetic methods. The successful grafting of CoO onto AC was confirmed through Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and adsorption-desorption isotherms. The thermal properties and reactivity of the NC/AC-CoO composite were comprehensively analyzed using DSC, providing valuable insights into the composite's thermal decomposition behavior. Kinetic analysis revealed that the incorporation of AC-CoO significantly reduced the apparent activation energy of NC by up to 28%. These findings underscore the potential of AC-CoO as an effective additive for enhancing the catalytic combustion properties of NC, paving the way for future advancements in this field.

* 1. Introduction

The investigation of energetic materials, including nitrocellulose (NC), has attracted considerable interest due to their wide-ranging applications in both civilian and military domains. These materials are designed to rapidly release stored chemical energy upon exposure to thermal stimuli, mechanical shocks, or laser ignition. Recent research efforts have been directed toward analysing their decomposition and combustion behavior while seeking to enhance their energetic performance and properties ([binti Samsuri, binti Jamal, et al. 2024](#_ENREF_6), [Michalchuk, Hemingway, et al. 2021](#_ENREF_16)). To enhance the performance of nitrocellulose based energetic materials, various strategies have been explored, such as surface modification, incorporation of super-energetic molecules, and the addition of nanoscale catalysts. Among these, metal oxides like iron oxide (Fe₂O₃), zinc oxide (ZnO), and copper oxide (CuO) have demonstrated significant catalytic potential due to their favorable physicochemical properties. However, their catalytic efficiency in NC-based systems can be affected by factors such as particle size, shape, and dispersion, with aggregation often limiting their overall effectiveness. ([An and Somorjai 2012](#_ENREF_1), [Cuenya 2010](#_ENREF_8)). Activated carbon plays a vital role in improving the thermal decomposition and combustion behavior of nitrocellulose-based energetic materials. Its high surface area facilitates adsorption and catalytic activity, while also preventing the agglomeration of catalytic species like metal oxides. Beyond acting as a burning rate modifier, activated carbon stabilizes catalysts and enhances their dispersion, ensuring better reactivity. Moreover, it serves as a reaction medium, promoting controlled decomposition of gaseous intermediates such as NO and NO₂. These properties collectively contribute to lowering activation energy and accelerating NC decomposition kinetics.([Iwanow, Gärtner, et al. 2020](#_ENREF_12), [Muller and Gany 2022](#_ENREF_19), [Sinha, Banerjee, et al. 2020](#_ENREF_26)).

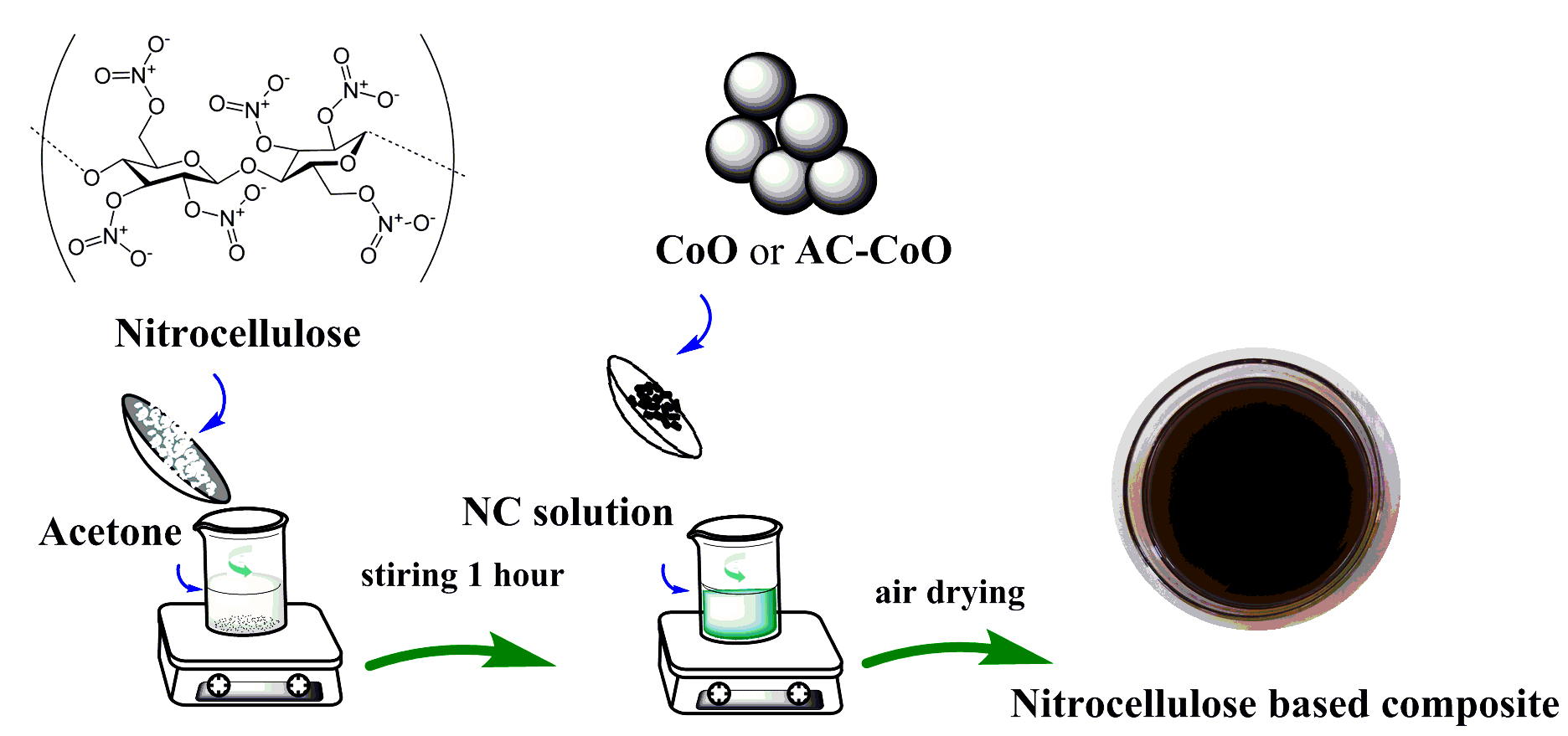
This study focuses on preparing Cobalt (II) oxide (CoO) supported on activated carbon (AC-CoO) and investigating its catalytic efficiency on the thermolysis of nitrocellulose (NC) using differential scanning calorimetry analysis at various heating rates. The research aims to uncover the synergistic interactions between CoO and activated carbon, advancing our understanding of catalytic strategies to enhance the performance of energetic materials (EMs).

* 1. Experimental section
     1. Materials

Cobalt (II) oxide (CoO) was provided by Sigma Aldrich. Activated carbon was synthesized by chemical activation from olive waste provided by local oil mills and chemically activated with phosphoric acid (H3PO4) following the procedure detailed elsewhere ([Bouriche, Tazibet, et al. 2021](#_ENREF_7)). Nitrocellulose, with a nitration content of 12.61%, was synthesized and fully characterized in our laboratory following the procedures indicated in our recent works ([Benhammada, Trache, et al. 2023](#_ENREF_5)).

* + 1. Preparation of the energetic composite

The sample preparation involved a two-step process. First, cobalt oxide (CoO) was supported on activated carbon (AC), to create AC-CoO, following the methodology of Atamanov et al. ([Atamanov, Yelemessova, et al. 2019](#_ENREF_3)). This was achieved through a solvent-free milling approach, where thoroughly dried AC and CoO were mixed at a 90:10 wt% ratio and processed in a planetary mill at 500 rpm for 15 minutes. In the second step, the synthesized AC-CoO was incorporated into nitrocellulose (NC). Specifically, 1 g of NC was dissolved in 60 mL of acetone and stirred at 20 °C for one hour, while 5 wt% of AC-CoO or (CoO) was dispersed in 40 mL of acetone. Both solutions were then combined, stirred for an additional hour, and air-dried to obtain the final energetic composite.



**Figure 1.** Preparation process of the composites.

* + 1. Experimental techniques

**Structural, textural characterizations, and thermal measurements**

The studied compounds were analyzed using a Perkin–Elmer 1600 Fourier-transform infrared spectrometer in transmission mode. Samples were dried to remove moisture before analysis. Measurements were conducted at room temperature, covering frequencies from 4000 to 400 cm-1 with a resolution of 4 cm-1. The crystalline structures were analyzed using a PANalytical X’pert PRO X-ray diffractometer equipped with Cu Kα radiation operating at 45 kV and 40 mA. Data were collected over an angular range of 2θ = 5° to 80°, with a step size of 0.02°. Adsorption-desorption isotherms of N2 at -196 °C were determined using an Autosorb Nova surface analyzer. Before each adsorption experiment, the samples are outgassed at 120 °C under vacuum for 24 h. The surface area is determined using the BET equation, and the total volume of pores (Vt) is calculated at a relative pressure (P/P0) of 0.975. The thermal behavior of the samples was further assessed using a PerkinElmer 4000 differential scanning calorimeter. Sample masses of 1–2 mg were sealed in aluminum crucibles, placed under a nitrogen atmosphere, and heated from 50°C to 350°C at various rates (10, 15, 20, and 25 °C/min).

* 1. Theoretical background of kinetic analysis

Kinetic analysis plays a crucial role in evaluating key decomposition parameters such as the activation energy (*E*a), the pre-exponential coefficient (), and the kinetic model (g(α) or f(α)). The following kinetic equations are typically recommended by the International Committee of Thermal Analysis and Calorimetry (ICTAC) to explain the single-step thermal decomposition process ([Koga, Vyazovkin, et al. 2022](#_ENREF_14)).

(1)

(2)

Where , *Ea*, *f*(*α*) and *g*(*α*) are the preexponential factor, activation energy, differential and integral forms of the model, respectively, and is the extent of conversion (0 < < 1). The collection of these parameters is termed the kinetics triplet (*E*a, Log (*A*), *g*(*α*)). It is interesting to point out that forty-one types of common kinetic models have previously been presented based on or ([Pourmortazavi, Mirzajani, et al. 2019b](#_ENREF_21)).

DSC technique is the commonly employed tool for studying the kinetic processes, as it allows the determination of the kinetic factors by linking the heat flow to the reaction rate. The value of *α* can be determined from the temperature integral of the thermograms by using Equation (3), in which ∆*H* is the measured heat change and is the total reaction heat ([Zhang, Binienda, et al. 2011](#_ENREF_30)).

(3)

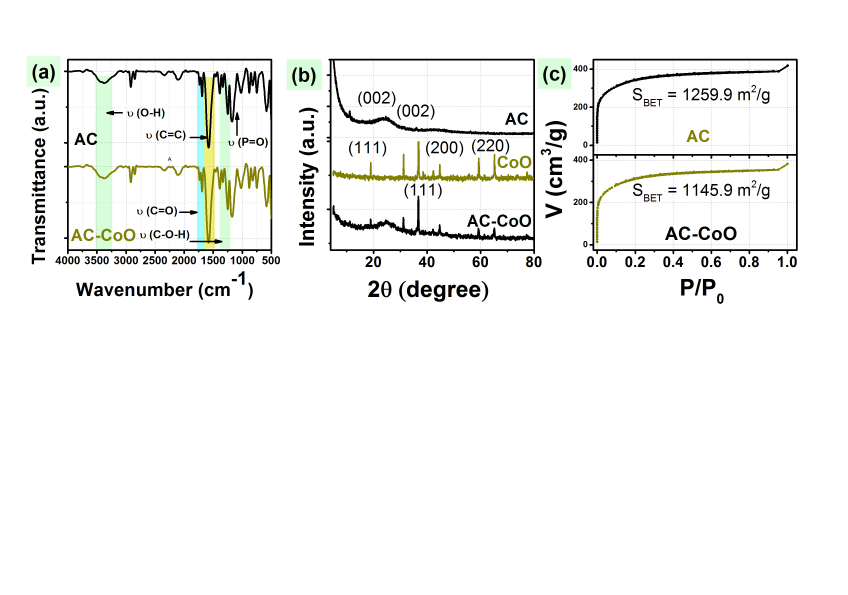
Isoconversional methods are considered the most dependable approaches for determining the kinetic triplet of thermally activated reactions ([Arshad and Maaroufi 2014](#_ENREF_2)). In this study, the kinetic parameters were computed using isoconversional methods, namely, Trache-Abdelaziz-Siwani (TAS) ([Trache, Abdelaziz, et al. 2017](#_ENREF_28)), iterative Kissinger-Akahira-Sunose (it-KAS)([Kissinger 1957](#_ENREF_13)), and Vyazovkin's method (VYA) coupled with the compensation effect approach (CE) ([Sbirrazzuoli 2020](#_ENREF_25)).

* 1. Results and discussion
     1. Structural and morphological results

The synthesized AC-CoO samples, containing cobalt oxide supported onto activated carbon, were characterized using FTIR, XRD, and nitrogen adsorption isotherm analyses. The results are presented in Figures 2(a), (b), and (c), respectively. FTIR spectra confirmed the presence of key characteristic bands of both AC and CoO. Peaks at 1700 cm⁻¹ and 1610 cm⁻¹ correspond to the stretching vibrations of carbonyl (C=O) groups and C=C bonds, respectively. The peak at approximately 1400 cm⁻¹ is attributed to the C-O-H vibration of carboxylic groups, while the broad band in the range of 3100–3650 cm⁻¹ is associated with O-H stretching from hydroxyl and carboxylic groups as well as adsorbed water ([Tazibet, Boucheffa, et al. 2016](#_ENREF_27), [Tzvetkov, Mihaylova, et al. 2016](#_ENREF_29)). Additionally, the FTIR spectra displayed characteristic metal oxide peaks within 500–1000 cm⁻¹, attributed to metal-oxygen bonds including Co-O stretching vibrations below 600 cm⁻¹ ([Razmara and Janczak 2021](#_ENREF_23)).

The XRD patterns, shown in Figure 2b, revealed that the AC-CoO samples retained the characteristic features of activated carbon, such as two broad peaks near 2θ = 25° and 44°, corresponding to the amorphous (002) and graphitic (100) carbon diffractions ([Danish, Hashim, et al. 2013](#_ENREF_9), [Mu, Shao, et al. 2011](#_ENREF_18)). Moreover, distinct diffraction peaks of CoO were observed at 2θ = 18.9°, 31.2°, 36.9°, 44.8°, and 65.2°, which correspond to the (111), (220), (111), (200), and (220) crystal planes of CoO, respectively ([Garces, Hincapie, et al. 2015](#_ENREF_10)).

Nitrogen adsorption isotherms, presented in Figure 2c, indicated that the isotherms for all samples conform to type Ib, as classified by Rouquerol et al. ([Rouquerol, Rouquerol, et al. 2013](#_ENREF_24)). This is characteristic of microporous materials with a diverse range of micropores sizes. The pore structure analysis showed a decrease in BET surface area from 1259.9 m²/g (AC) to 1145.9 m²/g (AC-CoO) after CoO grafting. Similarly, the total pore volume decreased from 0.6190 cm³/g to 0.5663 cm³/g, while the mean pore diameter increased slightly from 1.9651 nm to 1.9766 nm, suggesting partial pore filling or blockage due to the CoO deposition.



**Figure 2.** a) FTIR spectra, b) XRD patterns, and c) Nitrogen adsorption isotherm.

* + 1. Determination of the thermo-kinetic parameters

To better understand the influence of the studied additives (CoO and AC-CoO) on the thermal behavior of nitrocellulose, a thermo-kinetic analysis was carried out on the formulated energetic composites. This analysis employed isoconversional methods, including TAS, it-KAS, and VYA/CE, using non-isothermal DSC data recorded at heating rates of 10 °C/min to 25 °C/min, incremented by 5 °C/min.

As depicted in Figure 3a, the DSC thermograms consistently display a single exothermic peak at all heating rates, corresponding to the thermolysis of the energetic and thermally unstable O-NO₂ groups ([Mirzajani, Farhadi, et al. 2018](#_ENREF_17)). The thermograms also reveal that the exothermic decomposition is strongly dependent on the heating rate. Specifically, as the heating rate increases, the decomposition peak shifts to higher temperatures. This phenomenon arises due to the more rapid input of thermal energy at higher rates, which shortens the time available for decomposition at lower temperatures ([Zhu, Dong, et al. 2014](#_ENREF_33)). These observations align with findings from non-isothermal DSC studies in the literature ([Pourmortazavi, Rahimi-Nasrabadi, et al. 2012](#_ENREF_22)). The incorporation of cobalt oxide (CoO) and cobalt oxide supported on activated carbon (AC-CoO) induces a notable reduction in the maximum peak decomposition temperature of nitrocellulose (NC), underscoring the pronounced catalytic influence of these additives on its thermal decomposition behavior. Specifically, at a heating rate of 15 °C/min, the peak decomposition temperature (Tpeak) of pristine NC is observed at 214.9 °C. The introduction of CoO reduces Tpeak to 213.2 °C, while AC-CoO further enhances this catalytic effect, lowering Tpeak to 212.7 °C. These shifts highlight the enhanced catalytic efficiency of AC-CoO in promoting a more facile thermal decomposition pathway for NC. These findings align with previous studies on the catalytic decomposition of nitrocellulose-based energetic composites. Benhammada et al.([Benhammada, Trache, et al. 2023](#_ENREF_5)) investigated the thermal decomposition behavior of NC/DEGDN (nitrocellulose/diethylene glycol dinitrate) composites in the presence of α-Fe₂O₃ and α-Fe₂O₃-CMS (iron oxide–carbon mesospheres). Their results demonstrated a reduction in decomposition peak temperature by 3.1°C and 4.7°C, respectively, while also decreasing the activation energy by 11.9 kJ/mol and 27.97 kJ/mol. The superior catalytic efficiency of α-Fe₂O₃-CMS was attributed to the role of carbon mesospheres (CMS) in enhancing Fe₂O₃ nanoparticle dispersion, preventing agglomeration, and improving the overall catalytic activity.

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**Figure 3.** a) DSC thermograms of NC energetic composites at various heating rates, b) Evolution of activation energy (Ea) as a function of conversion, and c) Average activation energy values for the synthesized NC energetic composites.

To calculate the kinetic parameters, particularly the activation energy (Ea), MATLAB software was employed, which enabled precise calculations by evaluating the extent of conversion at each temperature. This approach involved integrating the peak areas of DSC thermograms recorded at different heating rates. To minimize errors associated with the initial and final stages of decomposition, the conversion range was set between 0.02 and 0.98.

Figures 3b and 3c illustrates the evolution of activation energy (Ea) as a function of the conversion rate for all the prepared composites. The key observation from the data is the consistent activation energy values across all NC-based composites, which were investigated using isoconversional methods. This consistency highlights the reliability and accuracy of the applied techniques. Furthermore, the average activation energy (Ea) for all the studied NC-based composites falls within the range of 120 to 200 kJ/mol, a range typical for nitrocellulose-based materials ([Pourmortazavi, Mirzajani, et al. 2019a](#_ENREF_20)). The catalytic effect of CoO is evident, as its incorporation reduces the activation energy to 152 kJ/mol, indicating an enhanced decomposition process. When CoO is supported on activated carbon (AC-CoO), the activation energy decreases further to 136 kJ/mol, demonstrating a significant improvement in catalytic performance. To better situate these findings, Table 1 presents a comparison of activation energy values reported for various NC-based energetic composites.

***Table1.*** *Comparison of activation energy (ea) values for various nc-based energetic composites*

|  |  |  |  |
| --- | --- | --- | --- |
| **NC-based energetic composite** | **Ea (kJ/mol)** | |  | | --- | | **Reference** | |
| Nitrocellulose (NC) | 207.48 | Guo et al. ([Guo, Zhao, et al. 2019](#_ENREF_11)) |
| NC / Cr₂O₃ (chromium oxide nanoparticles) | 184.40 |
| Nitrocellulose (NC) | 180 | Benhammada et al. ([Benhammada and Trache 2022](#_ENREF_4)) |
| NC / CuO (copper oxide nanoparticles) | 170 |
| Nitrocellulose (NC) | 118.5 | Zhao et al.([Zhao, Yu, et al. 2022](#_ENREF_32)) |
| copper oxide (CuO) with zinc-based metal-organic frameworks (ZIF-8) | 108.2 |
| Nitrocellulose (NC) | 207.48 | Zhao([Zhao, Li, et al. 2016](#_ENREF_31)) |
| NC / α-Fe₂O₃ | 192.11 |
| Nitrocellulose (NC) | 170 | Benhammada et al.([Benhammada, Trache, et al. 2023](#_ENREF_5)) |
| NC / α-Fe₂O₃-CMS (hematite supported on carbon mesospheres) | 160 |

This enhancement arises from a synergistic effect between CoO, which acts as an active site for decomposition, and activated carbon, which optimizes reaction kinetics through improved dispersion and adsorption properties. CoO facilitates the cleavage of nitrate ester bonds, thereby accelerating the thermal decomposition of nitrocellulose-based materials. Activated carbon plays a crucial role in this catalytic system due to its highly porous structure and large surface area, which promote uniform dispersion of CoO particles and enhance contact with NC molecules. Additionally, AC facilitates the adsorption of NOx gases, key intermediates in the decomposition reaction, preventing their premature release and maintaining catalytic activity. This controlled reaction environment results in a more efficient and sustained decomposition process.These findings align with the research conducted by Li et a.([Li, Li, et al. 2023](#_ENREF_15)), which examined the catalytic efficiency of defective activated carbon-encapsulated cobalt (DAC-Co) on the decomposition of ammonium perchlorate (AP). Their research demonstrated that the synergistic effect between Co nanoparticles and DAC significantly enhanced catalytic activity, reducing the activation energy of AP from 271.8 kJ/mol to 137.7 kJ/mol and 130.7 kJ/mol with DAC and DAC-Co catalysts, respectively. This parallel reinforces the importance of carbon-based supports in optimizing the catalytic efficiency of metal oxides in energetic materials.

* 1. Conclusion

This study investigated the catalytic effects of cobalt oxide (CoO) supported onto activated carbon (AC) on the thermal decomposition of nitrocellulose (NC). Through FTIR, XRD, and Adsorption desorption isotherms analyses, we confirmed the successful grafting of CoO onto AC. DSC analysis revealed that the presence of CoO and AC-CoO significantly affected the thermal decomposition of NC, and reducing the peak decomposition temperature. Kinetic studies showed that the activation energy (*E*a) of the NC composites decreased with the addition of CoO, and further reduction was observed when CoO was supported onto AC, indicating the catalytic enhancement provided by the support material. The results highlight the potential of AC-CoO composites in improving the thermal decomposition behavior of NC, offering a promising approach for enhancing the performance of nitrocellulose-based energetic materials. These findings open avenues for future research aimed at optimizing catalytic strategies to improve the combustion properties of energetic materials.

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**Revision for the Manuscript ref: 159**

**Title**: Thermal decomposition behavior and kinetics of Nitrocellulose in the presence of a Metal Oxide supported on Activated Carbon.

**Authors**: *Mohammed Dourari, Ahmed Fouzi Tarchoun, Djalal Trache, Tessnim Barkat*

Dear icheap17 ISC Chairmen,

Thank you very much for your comments and valuable suggestions concerning our manuscript entitled “Thermal decomposition behavior and kinetics of Nitrocellulose in the presence of a Metal Oxide supported on Activated Carbon”. Based on the comments and suggestions from the reviewers, we have addressed all issues to improve the quality and the readability of the manuscript in this revised version. The changes introduced are given below, where for each question an answer is given, and all the changes are highlighted in yellow in the revised manuscript. We really thank the reviewer’s efforts, as they definitely improved the overall quality of the manuscript, which is now clearer and more consistent. We appreciate your time and consideration, and we will be happy to give any further information or clarifications.

Yours sincerely,

*Mohammed Dourari*.

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| **Reviewer #1** | decision: accept after major revisions  The article discusses on the synthesis of Cobalt oxide supported on activated carbon (AC-CoO) as energetic materials. Below are some suggestions to improve the overall quality of the manuscript |
| **Answer** | We sincerely thank the reviewer for their kind, patient, and professional comments on our manuscript. We greatly appreciate the reviewer’s positive assessment of our investigation.  We have carefully considered the reviewer’s suggestions and have made the necessary revisions. We are confident that these revisions will improve the clarity and accuracy of the manuscript, and we hope that the revised version meets your expectations. |
| **Changes made** | **/** |
| **Reviewer #1**  **Comment 1** | The discussion content of the manuscript clearly focuses on cobalt oxide supported on AC.  As such the manuscript title should be revised for better clarity where the term ‘Metal Oxide  Supported on Activated Carbon’ in the title should be replaced as ‘Cobalt Oxide Supported on Activated Carbon |
| **Answer** | We sincerely thank the reviewer for their valuable suggestion. To enhance clarity and accurately reflect the study’s focus, we have revised the manuscript title to explicitly mention "Cobalt Oxide Supported on Activated Carbon |
| **Changes made** | **The manuscript title has been updated accordingly.** |
| **Reviewer #1**  **Comment 2** | The content in introduction section is rather general. The use of activated carbon should  be discussed to explain why activated carbon is chosen as support for this study. |
| **Answer** | We sincerely appreciate the reviewer’s insightful comment. To provide a clearer rationale for selecting activated carbon as a support material, we have expanded the introduction. Activated carbon was chosen due to its high surface area, ability to prevent particle aggregation, and favorable thermal properties, which collectively enhance the catalytic activity of cobalt oxide. |
| **Changes made** | **A discussion on the advantages of activated carbon has been added to the introduction.** |
| **Reviewer #1**  **Comment 3** | More detail experiment procedure on the solvent-free milling process is required. For instance, the milling conditions were not included in the methodology section, such as the milling temperature, speed, use of any additional bonding agent, etc. |
| **Answer** | We sincerely thank the reviewer for highlighting this point. We have now provided additional details on the solvent-free milling process, including the milling temperature, rotation speed, and duration. No additional bonding agents were used in this process. |
| **Changes made** | **Milling conditions have been detailed in the experimental section.** |
| **Reviewer #1**  **Comment 4** | From the DSC results, it is noted that introducing the AC-CoO only reduces the peak decomposition temperature of 2.2°C (from 214.9 to 212.7°C). Could this reduction contributed by the decomposition of activated carbon which has decomposition temperature point lower than nitrocellulose and cobalt oxide? The reduction in temperature is not very significant, it would be good to include brief analysis comparing this data with results reported in existing literature? |
| Answer | We are grateful to the reviewer for this thoughtful observation. While the reduction in peak decomposition temperature (2.2°C) is moderate, it aligns with findings from previous studies on catalytic decomposition of nitrocellulose. We have now a comparison with relevant literature. |
| **Changes made** | **A comparative analysis with literature data has been included** |
|  | |
| **Reviewer #2**  **Comment 1** | 1) Scientific quality and significance of the work  The study presents a thorough investigation of the catalytic effect of cobalt oxide (CoO) supported on activated carbon (AC) in the thermal decomposition of nitrocellulose (NC). The use of differential scanning calorimetry (DSC) and isoconversion kinetic methods provides a solid basis for analyzing the decomposition behavior. The results indicate a significant reduction in activation energy, demonstrating the catalytic efficiency of AC-CoO. However, a more detailed discussion comparing these results with previous studies on similar catalytic systems would strengthen the manuscript.  The authors should provide a deeper discussion on the catalytic mechanism, including:  - How does CoO interact with NC at the molecular level?  - What is the role of activated carbon in improving catalytic performance?  - Is the effect due to electron transfer, increased surface area, or thermal conductivity?  A comparison with other metal oxides (e.g., Fe2O3;, ZnO, CuO) should be included to clarify whether CoO-AC truly offers superior catalytic properties. Expand the discussion on the catalytic mechanism and compare the efficiency of CoO-AC with other metal oxide catalysts. |
| **Answer** | We sincerely appreciate the reviewer’s insightful comment. To provide a clearer understanding of the catalytic mechanism, we have expanded the discussion on the interaction between CoO and NC at the molecular level and the role of activated carbon (AC) in enhancing catalytic performance. |
| **Changes made** | **A more detailed explanation of the catalytic role of CoO and AC has been provided.** |
| **Reviewer #2**  **Comment 2** | 2) Novelty & new insights into the problem  The integration of CoO with AC to enhance the thermal decomposition of NC is a novel approach with potential applications in energetic materials. The work builds on previous research but provides new insights into catalytic decomposition mechanisms. A comparative table summarizing key findings from previous studies on similar catalysts could further highlight the novelty of this work. |
| **Answer** | We appreciate the reviewer’s suggestion. To emphasize the novelty of our work, we have added a comparative table summarizing activation energy values from previous studies on similar catalysts. This table highlights the effectiveness of CoO and AC-CoO in reducing the activation energy of NC decomposition, demonstrating the enhanced catalytic performance of our approach. Additionally, we have revised the manuscript to explicitly discuss how our findings build upon and extend previous research by providing new insights into catalytic decomposition mechanisms. |
| **Changes made** | **Added Table : Comparison of Activation Energy (Ea) Values for Various NC-Based Energetic Composites to illustrate the catalytic efficiency of CoO and AC-CoO relative to existing catalysts.**  **Updated the text to integrate the table and elaborate on the significance of our findings in the context of prior studies.** |
| **Reviewer #2**  **Comment 3** | 3) Clarity and readability  The manuscript is well structured and written with sufficient clarity to make the results accessible to a broad audience. Some sections, especially the discussion of kinetic models, could benefit from additional clarification. Figures and tables are relevant and well prepared, but improving figure captions with more explanatory details would enhance readability. However, Figure 2 needs to be changed as the quality is very poor.  The authors use three different isoconversional methods (TAS, it-KAS, VYA/CE) to analyze the kinetics, but no clear explanation is given as to why these specific methods were chosen.  The selection of heating rates (10, 15, 20, 25°C/min) is not justified. Different heating rates  can affect the accuracy of activation energy calculations, so a rationale is needed.  The authors should discuss:  - Why were TAS, it-KAS, and VYA/CE selected over other kinetic models?  - How do different heating rates influence the accuracy of kinetic parameters?  - Have the authors tested the sensitivity of their results to heating rate variations?  Justify the choice of kinetic models and heating rates to strengthen the methodological foundation of the study. |
| **Answer** | We sincerely appreciate the reviewer’s insightful comment.  In the study of energetic materials, analyzing thermal decomposition behavior is fundamental to ensuring safe handling, storage, and processing while minimizing accident risks. To accurately assess the thermal stability and decomposition kinetics of the synthesized energetic composites, we employed DSC analysis alongside a rigorous thermo-kinetic investigation using the advanced isoconversional methods TAS, it-KAS, and VYA/CE.  The selection of four heating rates (10, 15, 20, and 25 °C/min) was carefully made to balance two critical factors: low heating rates slow down the reaction, making complete conversion challenging within a practical timeframe, while high heating rates may induce self-heating effects, leading to deviations from controlled thermal conditions. By opting for intermediate heating rates, we ensured reliable kinetic parameter determination while minimizing potential experimental artifacts.  The use of TAS, it-KAS, and VYA/CE was guided by their strong theoretical foundation and established reliability, as recommended by the ICTAC Kinetics Committee. These advanced isoconversional approaches allow for accurate activation energy determination under non-isothermal conditions, effectively accounting for reaction complexity and variations in decomposition mechanisms.  Moreover, the comparison of these three advanced models plays a crucial role in validating the accuracy of the kinetic results. As shown in Figures 3b and 3c, the activation energy (Eₐ) remains consistent across all NC-based composites, reinforcing the reliability of the applied isoconversional techniques and confirming the robustness of our kinetic analysis. |
| **Changes made** | **/** |
| **Reviewer #2**  **Comment 4** | Minor comment:1) sec 2.1 "Cobalt (II) oxide (CoO), " without comma.  2) sec 2.2 "...by Atamanov et al. (Atamanov, Yelemessova, et al. 2019). samples ... " there  is a . between the citation and samples  3) sec 2.3 and 5 Adsorption desorption while in the abstract is written adsorption-desorption.  4) sec 3 "Where,..." without comma.  5) sec 4.2 "..thermokinetic..." in the title is define as thermo-kinetic.  6) sec 4.2 "Tpeak", peak can be set as subscript  7) Bibliography:  for example [1] ChemCatChem ? Check that they are in accordance with the CET format. Some references are outdated (older than 15-20 years) and should be replaced with more recent studies (post-2020) on catalytic decomposition of energetic materials. |
| **Answer** | We sincerely thank the reviewer for their meticulous attention to detail. All suggested corrections related to grammar, formatting, and consistency have been carefully implemented. Furthermore, we have reviewed the reference list and replaced outdated citations with more recent studies on catalytic decomposition of energetic materials. |
| **Changes made** | **The required modifications have been done.** |