

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). 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). 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. (Muller and Gany 2022).

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).

2. Experimental section

2.1 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). 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).

2.2 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). 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.

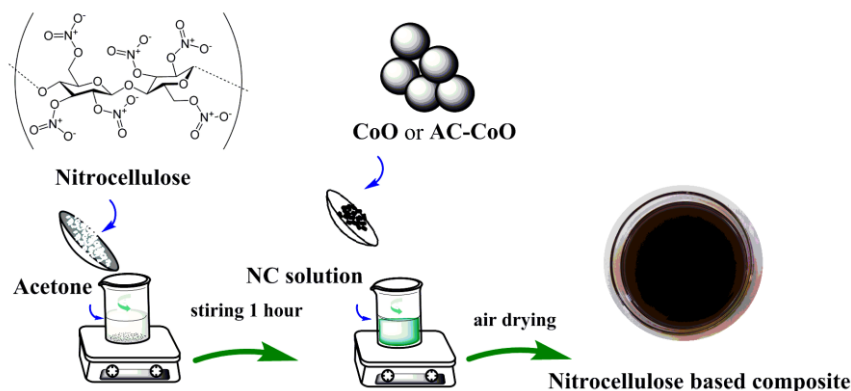


Figure 1. Preparation process of the composites.

2.3 Experimental techniques

Structural, textural characterizations, and thermal measurements

The compounds were characterized by FTIR (4000–400 cm⁻¹, 4 cm⁻¹ resolution) using a Perkin-Elmer 1600 spectrometer. XRD was performed on a PANalytical X'pert PRO (Cu K α , 45 kV, 40 mA) over 2 θ = 5–80°. Nitrogen adsorption-desorption at -196 °C was done with an Autosorb Nova; samples were degassed at 120 °C for 24 h. Surface area and pore volume were determined via BET and P/P₀ = 0.975, respectively. Thermal behavior was analyzed by DSC (PerkinElmer 4000) under N₂, heating from 50–350 °C at various rates (10, 15, 20, and 25 °C/min).

3. 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 (A_α), and the kinetic model ($g(\alpha)$ or $f(\alpha)$). 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).

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (1)$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad (2)$$

Where A , E_a , $f(\alpha)$ and $g(\alpha)$ are the preexponential factor, activation energy, differential and integral forms of the model, respectively, and α is the extent of conversion ($0 < \alpha < 1$) derived from DSC thermograms using the heat ratio (Equation 3), in which ΔH is the measured heat change and ΔH_{total} is the total reaction heat (Zhang, Binienda, et al. 2011).

$$\alpha = \frac{\int_{t_0}^t (dH/dt) dt}{\int_{t_0}^t (dH/dt) dt} = \frac{\Delta H}{\Delta H_{total}} \quad (3)$$

In this study, the activation energy (E_a) was computed using isoconversional methods, namely, Trache-Abdelaziz-Siwani (TAS) (Trache, Abdelaziz, et al. 2017), iterative Kissinger-Akahira-Sunose (it-KAS) (Kissinger 1957), and Vyazovkin's method (VYA) coupled with the compensation effect approach (CE) (Sbirrazzuoli 2020).

4. Results and discussion

4.1 Structural and morphological results

The synthesized AC-CoO samples, containing cobalt oxide supported onto activated carbon, were characterized using XRD, FTIR, and nitrogen adsorption isotherm analyses. The results are presented in Figures 2(a), (b), and (c), respectively. The XRD patterns, revealed that the AC-CoO samples retained the characteristic features of activated carbon, such as two broad peaks near $2\theta = 25^\circ$ and 44° , corresponding to the amorphous (002) and graphitic (100) carbon diffractions (Danish, Hashim, et al. 2013). Moreover, distinct diffraction peaks of CoO were observed at $2\theta = 18.9^\circ$, 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). 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 $3100\text{--}3650 \text{ cm}^{-1}$ is associated with O-H stretching from hydroxyl and carboxylic groups as well as adsorbed water (Tazibet, Boucheffa, et al. 2016). Additionally, the FTIR spectra displayed characteristic metal oxide peaks within $500\text{--}1000 \text{ cm}^{-1}$, attributed to metal-oxygen bonds including Co-O stretching vibrations below 600 cm^{-1} (Razmara and Janczak 2021). 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). 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 $1259.9 \text{ m}^2/\text{g}$ (AC) to $1145.9 \text{ m}^2/\text{g}$ (AC-CoO) after CoO grafting. Similarly, the total pore volume decreased from $0.6190 \text{ cm}^3/\text{g}$ to $0.5663 \text{ cm}^3/\text{g}$, 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.

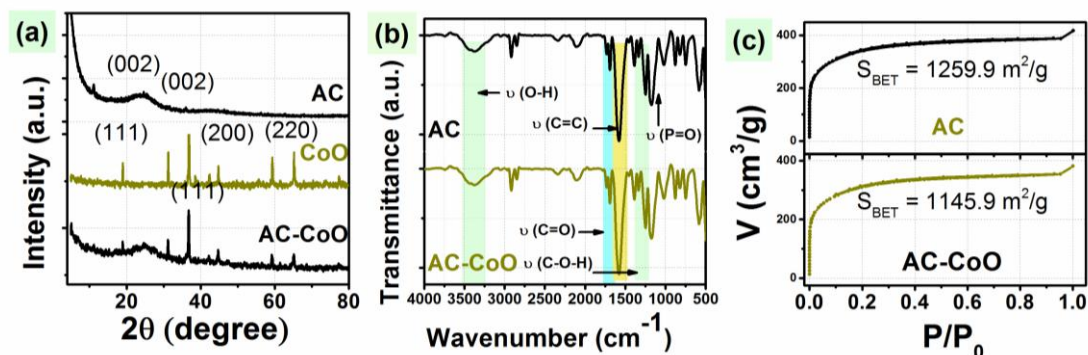


Figure 2. a) XRD patterns, b) FTIR spectra, and c) Nitrogen adsorption isotherm.

4.2 Determination of the thermo-kinetic parameters

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). 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). These observations align with findings from non-isothermal DSC studies in the literature (Pourmortazavi, Rahimi-Nasrabadi, et al. 2012). 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 $15 \text{ }^\circ\text{C}/\text{min}$, the peak decomposition temperature (T_{peak}) of pristine NC is observed at $214.9 \text{ }^\circ\text{C}$. The introduction of CoO reduces T_{peak} to $213.2 \text{ }^\circ\text{C}$, while AC-CoO further enhances this catalytic effect, lowering T_{peak} to $212.7 \text{ }^\circ\text{C}$. 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) 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.

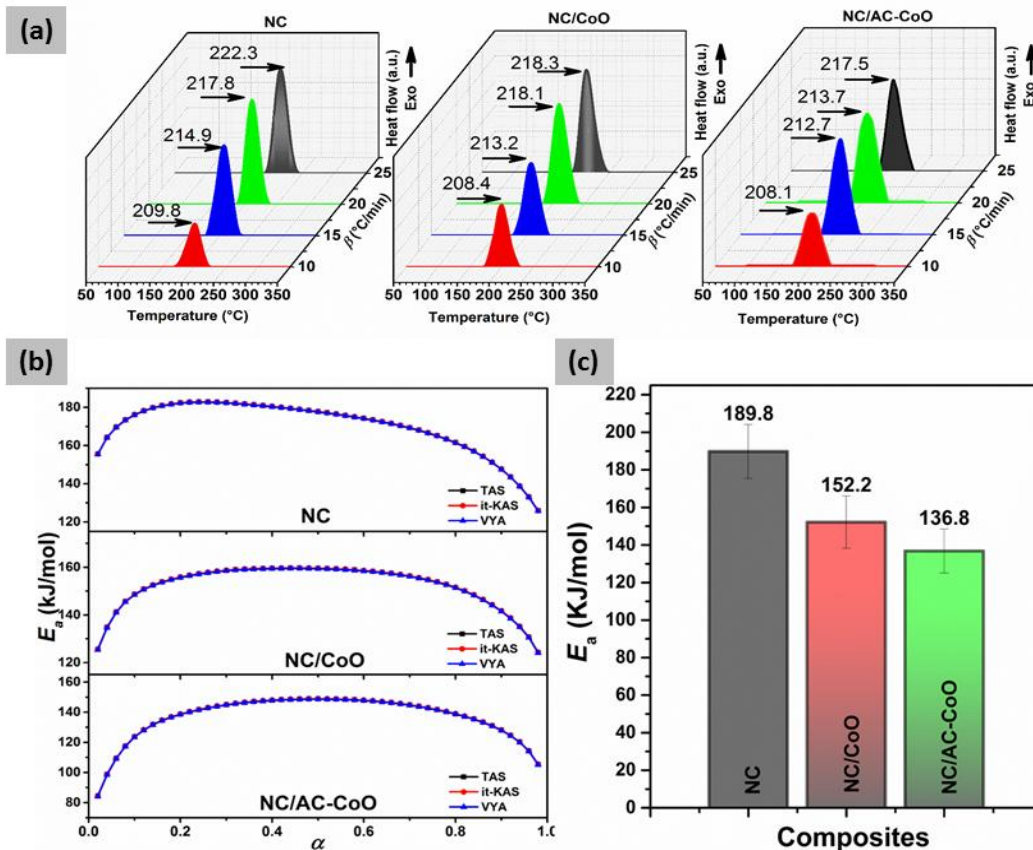


Figure 3. a) DSC thermograms of NC energetic composites at various heating rates, b) Evolution of activation energy (E_a) as a function of conversion, and c) Average activation energy values for the synthesized NC energetic composites.

To calculate the kinetic parameters, particularly the activation energy (E_a), 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 illustrate the evolution of activation energy (E_a) 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 (E_a) 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. 2019). 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.

Table 1. Comparison of activation energy (E_a) values for various NC-based energetic composites

NC-based energetic composite	E_a (kJ/mol)	Reference
Nitrocellulose (NC)	207.48	Guo et al. (Guo, Zhao, et al. 2019)
NC / Cr_2O_3 (chromium oxide nanoparticles)	184.40	
Nitrocellulose (NC)	180	Benhammada et al. (Benhammada and Trache 2022)
NC / CuO (copper oxide nanoparticles)	170	
Nitrocellulose (NC)	118.5	Zhao et al. (Zhao, Yu, et al. 2022)
copper oxide (CuO) with zinc-based metal-organic frameworks (ZIF-8)	108.2	
Nitrocellulose (NC)	207.48	Zhao (Zhao, Li, et al. 2016)
NC / $\alpha\text{-Fe}_2\text{O}_3$	192.11	
Nitrocellulose (NC)	170	Benhammada et al. (Benhammada, Trache, et al. 2023)
NC / $\alpha\text{-Fe}_2\text{O}_3$ -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 NO_x 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 al. (Li, Li, et al. 2023), 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.

5. 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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