Investigating the kinetics of the thermolysis of 3-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one (NTO) and reduced size NTO in the presence of cobalt ferrite additive

Pragnesh N. Dave¹* and Ruksana Sirach¹

¹Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Anand, Gujarat 388 120, India

ABSTRACT

The co-precipitation technique was used to successfully produce nanometer cobalt ferrite (CoF). Utilizing the solvent-antisolvent approach, the reduction in the size of sensitive HEM 3-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one (NTO) was effectively achieved. Using simultaneous thermal analysis, the effect of 5% by mass CoF on the thermolysis of NTO and nanosize NTO (r-NTO) was investigated. The kinetic parameter of NTO and r-NTO in the presence of CoF additive was assessed using three isoconversional methods: Flynn–Ozawa–Wall, Kissinger–Akahira–Sunose and Starink. It was found that lowering NTO’s size and adding CoF may both lower the material’s thermal breakdown temperature, with the former dropping it more significantly than the latter. The activation energy of both NTO and r-NTO was raised in the presence of CoF additive.

1 Introduction

High energetic materials (HEMs) are extensively utilized in propellants, explosives, and pyrotechnics due to extensive heat and gas released during their thermal decomposition. A few of the most widely known HEMs include ammonium perchlorate (AP), cyclotetramethylene tetranitramine (HMX), and cyclotrimethylene trinitramine (RDX). These HEMs are highly sensitive to external stimuli such as shock, and friction; therefore, it is a very challenging task to handle such sensitive HEMs during their handling as a small mistake can lead to an accident [1, 2]. More research is required to replacing the highly sensitive HEMs with less sensitive HEMs. The preparation of new less sensitive HEMs has certain limitations such as chemical compatibility, poor stability, and decomposition performance [3]. Hence, more research is devoted to improving the performance of the existing less sensitive HEMs. 3-nitro-2,4-dihydro-3H-1,2,4-triazol-5-one (NTO)’s highly insensitive, ease of manufacturing, safe handling, and high detonation velocity make NTO one of the most promising candidates [4, 5]. The improvement in the thermal decomposition of NTO can be achieved by (1) the use of additives [3, 4, 6], (2) reducing the size of NTO [7], and (3) formation of co-crystal with other HEMs [8, 9]. One of the most widely studied additives for HEMs is transition metals and their analogs.
The transition metal oxides can act as an effective additive due to (1) availability of a wide range of oxidation states that can participate during the thermal decomposition process, (2) availability of large surface, and (3) activeness to participate in the reactions. The transition metals of the 3d series specifically Fe, Co, Ni, Cu, and Zn are known to possess good catalytic activity for reducing the thermal decomposition temperature of HEMs. Transition metal ferrites are widely employed in catalytic applications because of their effectiveness, ease of synthesis, utilization of less expensive chemicals, and environmental friendliness as they can be easily separated using a magnet due to their magnetic nature. Prabhakaran et al. have reported that the presence of additives can affect (increase or decrease) the decomposition temperature of NTO. Cobalt ferrite (CoFe$_2$O$_4$ or CoF) is well known to influence the thermal decomposition of HEM like AP. CoF can be synthesized using various methods such as co-precipitation, sol–gel, hydrothermal, green synthesis, flash auto-combustion, etc. Although the co-precipitation process produces nanosize particles with a wide range, it has benefits over other approaches because it is simpler to use, less expensive, uses less toxic chemicals, and uses less energy-consuming. Hydrothermal, sol–gel, ultrasound, or microwave-aided methods, in situ self-assembly, thermal breakdown, and chemical co-precipitation methods can all be used to fabricate nanomaterials. For this purpose, various solvents can be utilized. However, the results may differ depending on the solvent, i.e., recrystallization of ammonium dinitramide (oxidizer in propellants) in solvents like ethanol, acetone, propanol, iso-propanol/NaF, and dimethyl sulfoxide can alter the morphology of ammonium dinitramide. Since NTO is a HEM, it explodes when heated, restricting the use of processes like hydrothermal, sol–gel, or thermal decomposition. NTO contains acidic ‘H,’ and hence, it can form metal complexes. Additionally, modifications to NTO’s morphology may modify the temperature at which it decomposes. As a result, the wet chemical techniques like chemical precipitation, ultrasound or microwave-assisted solution mixing may yield NTO with altered morphology or NTO metal complex. Additionally, the use of solvent raises the total cost of the NTO: CoF synthesis; therefore, NTO: CoF composition synthesized using wet chemical techniques and ultrasonic or microwave-aided solution mixing will not be appropriate to compare the additive impact of CoF. As a result, in the current study, the composition of NTO including nanoadditive was made utilizing straightforward mixing with a mortar and pestle.

This paper reports the effect of CoF on NTO, and NTO with reduced size ($r$-NTO). CoF was synthesized via the co-precipitation route and characterized using X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), Raman, and ultraviolet–visible (UV–Vis) analysis. The effect of 5% by mass CoF additive on both NTO and $r$-NTO was investigated using simultaneous thermogravimetry–differential scanning calorimetry–derivative thermal analysis (TG-DSC-DTA). Three isoconvervational methods namely Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), and Starink method were used to evaluate the kinetic parameter.

2 Materials and methodology

Semicarbazide hydrochloride (SC.HCl; 98%), Formic acid (HCOOH; 98%), Ferric nitrate (Fe(NO$_3$)$_3$; 98%), Cobalt nitrate (Co(NO$_3$)$_2$; 98%), Sodium hydroxide (NaOH; 99%), Tetrahydro Furan (THF; 99%), $n$-hexane (99%), ethanol (99%) were acquired from Sisco research laboratories. All the chemicals were of the reagent grade and used as received.

2.1 Synthesis of NTO

NTO was synthesized from previously reported methods. Equal amount of formic acid and SC. HCl was mixed with continuous stirring and refluxed at 102 $^\circ$C. After the completion of the reaction excess formic acid was removed by distillation and 2,4-dihydro-3$^H$-1,2,5-Triazol-3-one(TO) was obtained (MP = 232 $^\circ$C). Thereafter, TO was added to an excess of nitric acid maintaining the temperature below 5 $^\circ$C. The solution was refluxed in a micro-wave reactor (Uwave-1000; serial no.: UW162) at 60 $^\circ$C, 200 W for 15 min. The reaction progress was monitored using TLC employing Ethyl acetate: $n$-Hexane (8:2) as a mobile phase. After the completion of the reaction, the solution mixture was poured onto ice, NTO was filtered re-crystallized using ethanol solvent, and dried in an oven overnight at 60 $^\circ$C. (Yield of NTO = 68.5%).
2.2 Reduction in size

The size of the synthesized NTO was reduced using the solvent-antisolvent technique [24]. A saturated solution of NTO was prepared in 100 mL THF solvent and sonicated for half an hour. This saturated solution of NTO was added to the chilled n-hexane (< 0 °C, 400 mL) via a syringe under magnetic stirring to obtain small size NTO precipitates (r-NTO). The obtained precipitates were filtered and dried in an oven overnight at 60 °C (Yield = 66.17%) (Fig. 1).

2.3 Synthesis of cobalt ferrite

CoF was synthesized using the co-precipitation method. Equal quantity of salts of Co(NO₃)₂ (0.2 M, 150 mL) and Fe(NO₃)₃ (0.4 M, 150 mL) were mixed with continuous stirring (mole ratio of Fe³⁺:Co²⁺ was 2:1) at 30 °C. To this mixture, 2 M NaOH solution was added to obtain black precipitation. The precipitation was completed at ~ 11–12 pH (consumed 2 M NaOH = 125 mL). The obtained precipitates were filtered, washed with warm water, and calcined at 500 °C for 5 h. The obtained CoF powder was utilized for the characterization and as an additive.

2.4 Incorporation of nanoadditive

For the preparation of NTO + CoF, NTO and CoF were mechanically mixed using a mortar pestle in a 95:5 mass ratio. Similarly, for r-NTO + CoF, r-NTO and CoF were mixed in a 95:5 ratio. The prepared compositions were further used for simultaneous TG-DSC-DTA analysis for the evaluation of the thermal decomposition parameters.

2.5 Characterization

The UV–Vis analysis was carried out using Shimadzu UV-1800 UV/VIS Spectrophotometer. UV–Vis spectrum was recorded between 200 and 800 nm range in dilute hydrochloric acid solution. Raman analysis was performed by JobinYvon Horiba LabRam, HR800 laser sources with 532 nm wavelengths. Powder XRD patterns were analyzed by a Rigaku Ultima IV powder X-ray diffractometer instrument equipped with a Cu Kα radiation source (λ = 0.15406 nm). AFM (AFM, NT-MDT, Ntegra Aura) and SEM (ESEM XL-30 Philips; Netherlands) was employed for the topographic investigations.

2.6 Catalytic activity

The catalytic activity of the synthesized CoF particles on both NTO and r-NTO was investigated using simultaneous TG-DSC-DTA (Perkin Elmer, STA 8000) at three heating rates (5, 10, and 15 °C/min) from room temperature to 400 °C temperature under N₂ atmosphere in a platinum pan. The thermal data was further utilized to calculate the activation energy of NTO and r-NTO in the presence of CoF additive.

As per the ICTAC kinetics committee recommendations [25], three heating rates (5, 10, 15 °C/min) were used to evaluate the kinetic parameters. DSC
peak area was used to evaluate the extent of conversion ($\alpha$) at various heating rates using Eq. 1. Where $dH/dt$ represents heat flow. Three isoconversional integral methods FWO (Eq. 2) [26, 27], KAS (Eq. 3) [28, 29], and Starink (Eq. 4) [30] were used to evaluate activation energy ($E_a$), and pre-exponential factor ($A$) at the varying extent of conversion. Where, $\beta$, $R$, $T$, and $g(x)$ represent heating rate (K/min or °C/min), universal gas constant (8.314 J/K mol), Temperature (K), and integral reaction model, respectively. Among the 41 reaction models $g(x)$ reported elsewhere [31], the most suitable model for NTO, r-NTO, NTO + CoF, and r-NTO + CoF is represented in Table S1. $E_a$ was evaluated from the slope and $\ln A$ from the intercept of the Plots of $\ln \beta$, $\ln (\beta/T^2)$, and $\ln (\beta/T^{1.92})$ against 1000/$T$ (1/K)

$$\alpha = \frac{\int_0^{t_2} \left(\frac{dH}{dt}\right) dt}{\int_0^{t_2} \left(\frac{dH}{dt}\right) dt} = \frac{\Delta H}{\Delta H_{total}}$$  \hspace{1cm} (1)

$$\ln \beta = \ln \left(\frac{0.0048AE_a}{g(x)R}\right) - 1.0516 \frac{E_a}{RT}$$  \hspace{1cm} (2)

$$\ln \left(\frac{\beta}{T^2}\right) = \ln \left(\frac{AR}{g(x)E_a}\right) - \frac{E_a}{RT}$$  \hspace{1cm} (3)

$$\ln \left(\frac{\beta}{T^{1.92}}\right) = \ln \left(\frac{AR^{0.92}}{E_a^{0.92}}\right) - 0.312 - 1.0008 \frac{E_a}{RT}.$$  \hspace{1cm} (4)

3 Results and discussion

XRD patterns of CoF, and r-NTO are depicted in Fig. 2. CoF belongs to Fd3m space group and has a cubic ferrite crystal structure. The unit cell of NTO belongs to the triclinic space group P1. The XRD patterns of CoF appear at peak positions at 18.36°, 30.27°, 35.60°, 43.7°, 53.22°, 54.06°, and 62.65° at planes (111), (220), (311), (400), (422), (511), and (440), respectively [32]. The peaks of r-NTO appear at 18.01°, 19.50°, 20.84°, 24.86°, 27.24°, 28.44°, 31.41°, 32.90°, 35.14°, 36.45°, 38.41°, 40.94°, 42.43°, 44.97°, 47.80°, 51.50°, 53.75°, 55.98°, 60.60°, 65.67°. The XRD pattern confirmed the formation of r-NTO [33]. The Scherrer formula (Eq. 5) was used to calculate the crystalline size of CoF, and NTO from maximum peak intensity (i.e., CoF = 35.60° (311); r-NTO = 27.24°) of the XRD pattern. The smallest particle size is a crystallite, which usually is a single crystal in powder form.

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (5)

where $\lambda$ represents wavelength, $\beta$ represents the full-width half maxima (FWHM) of the peak, $\theta$ represents the peak position, and $D$ is the calculated crystalline size (nm). CoF and r-NTO have predicted crystal sizes of 22.14 and 38.39 nm, respectively. Both estimated and measured sizes support the materials’ nanoscale crystalline dimensions. The SEM image of CoF (Fig. 3a) suggest that particles were having a cubic shape having different sizes. Agglomeration was also observed, which could have been because of the cluster of smaller size particles. The agglomeration give image that suggest a micron size particle. Therefore, AFM image of CoF was used to confirm the size. The formation of nanosized CoF particles was confirmed by the AFM picture of CoF (Fig. 3d). The SEM image of NTO (Fig. 3b) and r-NTO (Fig. 3c) confirms the reduction in size of NTO. The SEM image suggests that morphology of NTO remains the same upon reducing the size (i.e., needle shape crystals). CoF particles display a diverse particle size distribution, as shown in the Figure. The bulk of the particles are found between 69 and 92 nm in size. The size of a crystal is finer than the particle size, and therefore, the crystalline size of CoF was smaller than its particle size. There are several crystals with the same alignment inside the particle, it is instead made up of two or more distinct crystallites. Using Eqs. (6–
and the XRD data, the structural characteristics of CoF were calculated.

\[ a = d\left( h^2 + k^2 + l^2 \right)^{1/2} \]  
(6)

\[ \delta = \frac{1}{D^2} \]  
(7)

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  
(8)

\[ \rho = \frac{8M}{N_\Lambda V} \]  
(9)

where \( a, \delta, \varepsilon, \rho, N_\Lambda, V, \) and \( M \) represent lattice constant, dislocation density, microstrain, X-ray density, Avogadro constant \((6.022 \times 10^{23} \text{ molecules/mol})\), cell volume \( (V = a^3) \), and molar mass \((204 \text{ g/mol})\), respectively. The \( \rho \) is the theoretical density predicted by the lattice constants and the number of atoms in the unit cell. That is the density of the material in the absence of any lattice fault/defect, which does not exist in reality but only theoretically. The values obtained for CoF are reported in Table 1 with previous reported values. The parameters’ stated values in Table 1 agreed with those that had been previously published [34]. According to the literature, increasing crystallite size is associated with a reduction in microstrain, which is consistent with the findings of the current study. The differences in the microstrain and lattice parameters show lattice distortions that can be caused by the nanocrystallites’ grain boundaries. The associated increase in crystallite size can indeed be ascribed to the lattice’s expansion as a result of defects around the atoms caused by the mismatch between ionic radius, which would increase the crystallite size [34–36].

The UV–Vis spectrum of CoF, NTO, r-NTO, NTO + CoF, and r-NTO + CoF is given in Fig. 4. Every sample demonstrates the typical absorbance in the 200–400 nm wavelength range. The nitration of TO into NTO was confirmed by the absorbance in the wavelength range of 250–400 nm since TO does not exhibit absorption in this range (Fig. S1). Because r-NTO absorbs light at a lower wavelength than NTO does, this indicates that the two compounds are different in sizes. According to the previous studies [37, 38]. The same substance exhibits increased absorbance over a wider range of wavelengths when it is larger in size. Because CoF also absorbs in this wavelength range, the absorbance of NTO and r-NTO was higher in the presence of CoF additive than it was without it. Using Eq. 10, the Tauc’s plot (Fig. 4-inset) was utilized to determine the band gap energy of CoF. Where \( h\nu \) is the photon energy (eV), \( E_g \) is the band gap energy, \( \alpha \) is the absorption coefficient, and \( B \) is constant. A Tauc’s Figure revealed an estimated band gap energy for CoF of 3.19 eV, which was higher than the previously published value of 2.89 eV.
The optical characteristics are greatly influenced by dependent structural features. In various particle size regimes, electron confinement, Coulomb interactions, and binding energy affect the band-gap energy of the material. It was reported that the optical band gap energy increases with increasing size [40]. This was most likely due to the increase in crystallite size and the decrease in defect states. Another cause for the band gap energy to fluctuate might be an alteration in the extent of hybridization between the Co, O, and the Fe. In addition to that, the impurity phases have had a significant impact on the change of the band gap energy. Co substitution can lead to the formation of certain crystal defects, resulting in confined states in the band structures, lowering the $E_g$ [35, 41, 42].

$$\alpha h \nu^2 = B (h \nu - E_g) \quad \text{(10)}$$

The change in polarizability for nuclear displacement must be non-zero for a substance to be Raman active. The Raman spectrum of CoF, NTO, $r$-NTO are given in Fig. 5. CoF gives five Raman active modes in the region of 200–800 cm$^{-1}$. The peaks at Raman shift 206, 314, 394, 479, and 687 cm$^{-1}$ correspond to $T_{2g}$, $E_g$, $T_{2g}$, $T_{2g}$, and $A_{1g}$ respectively, and correspond to vibrational modes at octahedral and tetrahedral sites [39, 43]. The presence of these peaks confirms the formation of spinel CoF. In CoF, the local site symmetry of the cubic lattice was lowered by microstrain. Due to the lack of long-range order, the line broadening is a typical nanoscale characteristic (i.e., particles having less size). The Raman spectrum confirms the formation of NTO as the peaks match that of the reported values [44]. The details regarding the peak position of NTO can be found in Table S2. Upon reducing the size of NTO, (1) the corresponding Raman peaks of NTO are broadened, (2) Shifting of Raman peak position to higher wavenumbers, and (3) increased Raman intensity of the peaks (Fig. 6). It was reported that particles with smaller sizes (e.g.,

![Fig. 4 UV–VIS spectrum of NTO, $r$-NTO, CoF, NTO + CoF, and $r$-NTO + CoF (inset Tauc’s plot of CoF)](image)

![Fig. 5 Raman spectrum of CoF, $r$-NTO, and NTO](image)

| $D$ (nm) | $A$ (Å) | $V$ (Å$^3$) | $\rho$ (g/cm$^3$) | $\varepsilon \times 10^{-3}$ | $\delta \times 10^{15}$ (dislocation line/m$^2$) | Reference |
|---------|--------|------------|-----------------|-----------------|------------------------|-----------|
| 21.64   | 8.35   | 582.18     | 5.34            | 2.51            | 1.00                   | [34]      |
| 22.14   | 8.32   | 575.93     | 5.40            | 1.63            | 2.04                   | Present work |
nanosize) broaden the peak compared to the corresponding bulk material [45]. The Raman peak’s widening indicates that the size of the NTO has successfully been reduced. By calculating the bulk densities of NTO and r-NTO, the same was confirmed. NTO and r-NTO powder had bulk densities of 0.51 and 0.29 g/mL, respectively. The fact that the bulk density of r-NTO powder has decreased indicates that the synthesized r-NTO was indeed smaller in size than NTO since the same amount of r-NTO has greater volume than NTO. It has also been confirmed that r-NTO was smaller in size than NTO by the shifting of the Raman peaks in the case of r-NTO to a higher Raman shift. Raman shift is size-dependent, therefore as particle size increased, the peak shifted to lower Raman shift values, which was often accompanied by a drop in dislocation density and strain [46–48].

3.1 Thermal decomposition

TG and DTG curves of NTO and r-NTO in the present as well as the absence of CoF are depicted in Fig. 7. Molecular dynamics simulations suggest that more than 10,000 chemical reactions are found taking place during the breakdown of NTO, and the number of reactions rises as the temperature rises. The majority of these chemical reactions are discovered once the quantity of NTO starts to go toward zero, demonstrating that the majority of reactions involve unstable intermediate products [49]. Thermal decomposition of NTO starts at onset temperature ($T_o$) 257.45 °C, with a maximum peak temperature ($T_m$) 259.45 °C, and ends at ($T_e$) 263.45 °C. The total decomposition occurs in only 6 °C range (corresponding time = 36 s) with a mass loss of 78.18% leaving polymeric residue after decomposition [50]. In the presence of a 5% CoF additive, the decomposition of NTO occurs at a higher temperature between the temperature range 258.28–264.28 °C with a $T_m$ of 261.28 °C. The decomposition time remains the same (i.e., 36 s) with a total mass loss of 75.40%. The mass loss in the case of NTO + CoF was 2.78% less as compared to pure NTO. Decomposition of r-NTO in the presence of additive was shifted from 254.32 to 258.32 °C (24 s) to 252.25–256.25 (24 s) °C. The DTG peak temperature was also lowered 256.32–254.32 °C. The mass loss in case of r-NTO was 77.50%, which was higher (1.06%) than in the presence of CoF additive (76.44%). The mass loss indicated that product produced during decomposition of NTO, and r-NTO may interact with CoF and yield different mass loss value. The % mass loss of CoF was 3.87% (up to 400 °C, Fig. S2). 5% CoF was added to NTO, and r-NTO this means that 0.1935% mass loss in r-NTO + CoF, and NTO + CoF could be accounted to CoF. The TG-DTG results indicated that the decomposition time of NTO and r-NTO were not affected in the presence of CoF additive, but the decomposition

Fig. 6 Enlarged view of Raman peaks of NTO, and r-NTO
temperature varies in the presence of CoF. TG-DTG curves suggested that although CoF does not exhibit the same effect on NTO, and r-NTO, CoF increases the decomposition temperature of NTO but decreases the decomposition temperature of r-NTO. This could be because in r-NTO more surfaces may be available for the interaction between CoF and r-NTO compared to micron size NTO. Further, r-NTO decomposes within a short time (i.e., 24 s) than NTO (36 s) at a lower temperature value ($\Delta T_m = 3.13 ^\circ C; DTG$).

DSC and DTA curves (10 $^\circ C$/min) of NTO, NTO + CoF, r-NTO, and r-NTO + CoF are depicted in Fig. 8. The effect of various heating rates on DSC curve is given in Fig. 9 and the corresponding DSC data is reported in Table 2. The DSC, and DTA curves are similar. In NTO, no endothermic melting peak was obtained before the decomposition indicating the decomposition of NTO occurs before melting [50]. This fact was in agreement with previous report [7]. The single exothermic peak confirms that the decomposition of NTO occurs in a single step. Both the initial decomposition temperature and peak decomposition temperature of NTO are important. The peak temperature ($T_m$) along with onset ($T_o$) and ending temperature ($T_e$) of NTO decomposition are decreased in the case of r-NTO, and NTO + CoF. This indicates that both incorporation of CoF, as well a reduction in size of NTO, are effective for decreasing the decomposition temperature of NTO. Initial decomposition of NTO involves $C_2H_4O_3N_4$ and $C_2H_3O_3N_4$ as major intermediate products. Hence, It is plausible that CoF can lower the decomposition of NTO by facilitating the formation of these two intermediates. The peak temperature plays an important role as it indicates at that temperature maximum gaseous are released with large heat released [49]. The $T_m$ of NTO was decreased by 4.71 and 14.97 $^\circ C$ using additive and reduction size approaches, respectively. The total time required for the decomposition was also reduced by 30.78 s for NTO + CoF, and 39.6 s for r-NTO compared to NTO. The DSC-DTA results indicated that reducing the size of NTO was a better approach for reducing the thermal decomposition temperature of NTO than the use of CoF additive. Further, CoF reduces the onset and ending temperature of r-NTO, but the decomposition time along with $T_m$ of DSC peak was increased by 20.58 s, and 0.75 $^\circ C$, respectively. The effect of heating rate shows that DSC curves are shifted to higher temperature values as the heating rate was increased (Fig. 9). This could be because, at a lower heating rate, the sample was heated slowly and spend a long time in the contact with the sample pans leading to decomposition at a lower temperature compared to higher heating rates.

The heat released during the decomposition process is another important factor in deciding HEMs efficiency. The order of heat of decomposition released was (r-NTO > NTO + CoF > NTO > r-NTO + CoF), (NTO > NTO + CoF > r-NTO + CoF > r-NTO), and (NTO > r-NTO + CoF > r-NTO > NTO + CoF) at a heating rate 5, 10, and 15 $^\circ C$, respectively. No certain trend was observed in the case of the heat of decomposition. Therefore,
judging the value at only a single heating rate will not be accurate. The effect of heating rate on the peak temperature (°C), and heat of decomposition (J/g) is presented in Fig. 10 for a better understanding. As represented in Fig. 10a that in the presence of CoF, DSC peak temperature was reduced as compared to pure NTO, and r-NTO at two heating rate values. Further, the DSC peak temperature of r-NTO was less compared to NTO at all heating rates, indicating reliable results. In the case of the heat of decomposition (Fig. 10b), it was evident that although CoF, and reducing the size of NTO are efficient ways to reduce the decomposition temperature of NTO, the decreased heat of decomposition was a downside of using CoF as an additive and reducing the size of NTO. To overcome the drawback of heat released during the decomposition process, CoF can be added to NTO, as r-NTO + CoF decomposes at lower temperature with slightly increased heat of decomposition compared to r-NTO. To further evaluate the effect of the additive and r-NTO, kinetics parameters such as activation energy and the pre-exponential factors were evaluated at three heating rates.

3.2 Comparison with previous studies

The effect of various additives reported for NTO is presented in Table 3. It was reported that the addition of 1% by mass nanosize ZnO, and NiO can reduce the
DTG peak decomposition temperature of NTO from 270 to 234 and 246 °C, respectively. The results were good compared to other additives reported in Table 3, but no data regarding onset temperature was reported. In the present work, the system nNTO + CoF decreases both the initial decomposition temperature and peak temperature of the DTG curve. Despite the lower content of the additive, the nNTO + CoF shows a better performance for reducing the decomposition temperature of NTO, than the corresponding system containing other energetic catalysts of Co (i.e., GO-T-Co-T and T-Co; where T = Triaminoguanidine and GO = Graphene oxide). However, the effect of 5% by mass CoF on pure NTO was lower than the GO-T-Co-T and T-Co, this is plausible as the latter catalysts contain high energetic additive (Triaminoguanidine) in addition to large additive content. The utilization of Triaminoguanidine pose safety risks and hence, it should be better to use less hazardous additives such as Cobalt ferrite.

To Conclude, the system rNTO + CoF, can be utilized as a substitution for NTO as its’ decomposition will take place at a lower temperature compared to pure NTO. The additive CoF can also be retrieved

### Table 2: DSC curve data for exothermic thermal decomposition of NTO, and r-NTO with and without CoF additives at various heating rates

| Sample      | Heating rate (°C/min) | Exothermic peak temperature (°C) | Heat of decomposition (J/g) |
|-------------|-----------------------|----------------------------------|-----------------------------|
|             |                       | Onset (T_o)                      | Maximum (T_m)               | Ending (T_e)                 | TGA % loss |
| NTO         | 5                     | 261.02                           | 266.27                      | 267.37                      | 80.99      | 176.05 |
|             | 10                    | 254.65                           | 276.35                      | 277.60                      | 78.18      | 748.24 |
|             | 15                    | 259.14                           | 275.20                      | 281.59                      | 79.48      | 667.04 |
| NTO + CoF   | 5                     | 256.33                           | 267.26                      | 268.28                      | 77.76      | 206.15 |
|             | 10                    | 255.58                           | 271.64                      | 273.40                      | 75.40      | 370.72 |
|             | 15                    | 260.51                           | 269.92                      | 283.05                      | 71.32      | 326.55 |
| r-NTO       | 5                     | 246.94                           | 261.42                      | 262.47                      | 79.20      | 277.22 |
|             | 10                    | 253.60                           | 261.38                      | 269.95                      | 77.50      | 197.00 |
|             | 15                    | 251.93                           | 264.28                      | 277.16                      | 78.08      | 360.58 |
| r-NTO + CoF | 5                     | 251.39                           | 258.30                      | 261.40                      | 71.91      | 111.89 |
|             | 10                    | 248.60                           | 262.13                      | 268.38                      | 76.44      | 283.16 |
|             | 15                    | 249.30                           | 264.01                      | 274.91                      | 73.45      | 376.25 |

### Fig. 10: Effect of heating rates on DSC peak temperature (a) and heat of decomposition (b)
**Table 3** Effect of additives on TG-DTG parameters of NTO

| System          | $T_o$ (°C) | DTG peak temperature; $T_m$ (°C) | References       |
|-----------------|------------|----------------------------------|------------------|
| NTO + 1% ZnO   | *          | 234.0                            | [6]              |
| NTO + 1% NiO   | *          | 246.0                            | [6]              |
| rNTO + 5% CoF  | 254.2      | 261.3                            | Present work     |
| NTO + 20% GO-T-Co-T | 252.4      | 263.3                            | [3]              |
| NTO + 20% T-Co  | 255.9      | 266.3                            | [3]              |
| NTO + 5% CoF   | 261.3      | 271.6                            | Present work     |
| NTO + 1% Cu    | *          | 273.0                            | [51]             |

*aDSC peak temperature

Table 4 Thermokinetics parameters calculated using FWO, KAS, and Starink method along with the time of completion of exothermic event for NTO, r-NTO, NTO + CoF, and r-NTO + CoF

| Kinetic parameters | Isoconversional method | Composition          | NTO | NTO + CoF | r-NTO | r-NTO + CoF |
|--------------------|------------------------|----------------------|-----|----------|-------|-------------|
| $E_a$ (kJ/mol)     | FWO                    | 369.30               | 513.75 | 449.39 | 542.51 |
|                    | KAS                    | 379.50               | 531.47 | 471.08 | 561.87 |
|                    | Starink                | 379.55               | 531.41 | 463.86 | 561.77 |
| ln A               | FWO                    | 89.93                | 123.50 | 110.01 | 131.27 |
|                    | KAS                    | 82.27                | 111.80 | 97.83  | 119.64 |
|                    | Starink                | 70.86                | 104.46 | 90.72  | 112.26 |
| Completion of exothermic curve (s) | –                      | 137.70               | 106.92 | 98.10  | 118.68 |

**Fig. 11** Conversion plots of NTO, and r-NTO with and without CoF additive
from the NTO using a magnet owing to its ferromagnetic nature.

### 3.3 Kinetic study

The conversion plots (extent of conversion vs. temperature) of NTO, NTO + CoF, \( r \)-NTO, and \( r \)-NTO + CoF at 5, 10, and 15 °C/min are presented in Fig. 11. At a lower heating rate, the decomposition process begins and ends at a lower temperature than at higher heating rates. The trend was the same for all samples, i.e., for high heating rates, the conversion process was completed at higher temperature values and vice versa. Further, from the conversion plots, it was evident that in the presence of CoF additive, the conversion begins was completed within a short temperature range as compared to pure NTO, or \( r \)-NTO. The temperature at the various extent of conversion at an interval of 0.025 was evaluated at three heating rates for calculation of activation energy (\( E_a \)) and the pre-exponential factor (A). The plots of three methods (FWO, KAS, and Starink) for NTO, NTO +
CoF, r-NTO, and r-NTO + CoF are presented in Figs. S3 and S4, in the supplementary file. The average value of the $E_a$ and $\ln A$ are reported in Table 4. The variation in the $E_a$ and $\ln A$ with the extent of conversion ($x$) is depicted in Fig. 12. As visible, the pattern of the changes in the $E_a$ and $\ln A$ concerning $x$ was not altered in the presence of CoF additive (i.e., NTO, and NTO + CoF exhibit similar patterns as well as r-NTO and r-NTO + CoF also exhibit similar pattern). Further, the patterns in the case of NTO, and r-NTO are different. The possible cause for this could be a change in the mechanism pathways. The presence of CoF increases the activation energy along with the pre-exponential factor for the decomposition of both NTO, and r-NTO (Fig. 12). Further, the value of $E_a$ and $\ln A$ was lower in the case of r-NTO compared to NTO up to halfway through the reaction, ($x = 0.5$), After that the value of $E_a$ and $\ln A$ drops drastically. From the activation energy calculations, it was clear that the decomposition of NTO requires high activation energy barrier to surpass ($-369.30$ kJ/mol) which matches with the reported value of ($322-368$ kJ/mol) \cite{52}, efforts are devoted to decreasing this large activation energy barrier \cite{3}.

4 Conclusions

CoF was synthesized using the co-precipitation method. XRD confirms the crystalline size of CoF falls in the nanoscale region. The CoF show wide particle size distribution with cubic shape. In the presence of CoF, the exothermic curve of NTO was shifted to a lower temperature than pure NTO. NTO + CoF has 4.71 °C lower peak temperature than NTO. r-NTO and r-NTO + CoF also decomposes at lower temperature than NTO. The lowered decomposition temperature can provide better burning rate performance of corresponding energetic formulations than NTO. However, the activation energy of NTO was increased and heat released was decreased for all three compositions (i.e., r-NTO, NTO + CoF, and r-NTO + CoF). These limits the NTO + CoF’s use as an energetic formulation.

Acknowledgements

Author RS is thankful to DST (SR/NM/NT-1014/2016 (G)) for providing Junior Research Fellowship.

The authors are grateful to the Department of Chemistry for the research facility, the Department of Physics, Sardar Patel University, India, for providing the XRD and Raman Facility, and Indukaka Ipcowala Center for Interdisciplinary Studies in Science and Technology (IICISST) for Simultaneous thermal analysis.

Author contributions

Both authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by RS. The first draft of the manuscript was written by RS and PD and both authors commented on previous versions of the manuscript. Both authors read and approved the final manuscript.

Funding

The present work was funded by the Department of Science and Technology (DST), Nanomission, New Delhi, India (SR/NM/NT-1014/2016 (G)).

Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

Informed consent Not applicable.

Research involving human participants and/or animals Not applicable.

Supplementary Information: The online version contains supplementary material available at http://doi.org/10.1007/s10854-022-09643-2.
References

1. R.R. Sirach, P.N. Dave, 3-Nitro-1,2,4-triazol-5-one (NTO): high explosive insensitive energetic material. Chem. Heterocycl. Comput. 57, 720–730 (2021). https://doi.org/10.1007/s10593-021-02973-9

2. S. Hanafi, D. Trache, S. Abdous, Z. Bensalem, A. Mezroua, 5-Nitro-1,2,4-triazole-3-one: a review of recent advance. Chin. J. Energy Mater. 27, 326–347 (2019). https://doi.org/10.11943/CJEM2018371

3. S. Hanafi, D. Trache, W. He, W.-X. Xie, A. Mezroua, Q.-L. Yan, Catalytic effect of 2D-layered energetic hybrid crystals on the thermal decomposition of 3-nitro-2,4-dihydro-3H-1,2,4-triazole-5-one (NTO). Thermochim. Acta 692, 178747 (2020). https://doi.org/10.1016/j.tca.2020.178747

4. K.V. Prabhakaran, S.R. Naidu, E.M. Kurian, XRD, spectroscopic and thermal analysis studies on 3-nitro-1,2,4-triazole-5-one (NTO). Thermochim. Acta 241, 199–212 (1994). http://dx.doi.org/10.1016/0040-6031(94)87018-7

5. M. Zhang, C. Li, H. Gao, W. Fu, Y. Li, L. Tang, Z. Zhou, Promising hydrazinium 3-nitro-1,2,4-triazol-5-one and its analogs. J. Mater. Sci. 51, 10849–10862 (2016). https://doi.org/10.1007/s10853-016-0296-7

6. D. Kumar, I.P.S. Kapoor, G. Singh, P.F. Siril, A.M. Tripathi, Preparation, characterization, and catalytic activity of nanosized NiO and ZnO: part 74. Propellants Explos. Pyrotech. 36, 268–272 (2011). https://doi.org/10.1002/prep.201000013

7. G. Yang, F. Nie, J. Li, Q. Guo, Z. Qiao, Preparation and characterization of nano-NTO explosive. J. Energ. Mater. 25, 35–47 (2007). https://doi.org/10.1080/07370650601107104

8. J.C. Li, Q.J. Jiao, Y.G. Gong, Y.Y. Wang, T. Liang, J. Sun, Explosive performance of HMX/NTO co-crystal. IOP Conf. Ser. Mater. Sci. Eng. 292, 012032 (2018). https://doi.org/10.1088/1757-899X/292/1/012032

9. C. Guo, H. Zhang, X. Wang, X. Liu, J. Sun, Study on a novel energetic cocystal of TNT/TNB. J. Mater. Sci. 48, 1351–1357 (2013). https://doi.org/10.1007/s10853-012-6881-5

10. S. Elbasuney, G.S. El-Sayyad, The potentials of TiO2 nanocatalyst on HMX thermolysis. J. Mater. Sci. Mater. Electron. 31, 14930–14940 (2020). https://doi.org/10.1007/s10854-020-04054-7

11. S. Elbasuney, A. Hamed, M. Yahia, M. Gobara, M. Mokhtar, The significant impact colloidal nanomteric particles (Fe2O3/Al) on HMX kinetic decomposition. J. Energ. Mater. (2021). https://doi.org/10.1080/07370652.2021.1905107

12. M. Amir, K. Eskandari, M. Salavati-Niasari, Magnetically retrievable ferrite nanoparticles in the catalysis application. Adv. Coll. Interface Sci. 271, 101982 (2019). https://doi.org/10.1016/j.cis.2019.07.003

13. S. Chaturvedi, P.N. Dave, A review on the use of nanometsals as catalysts for the thermal decomposition of ammonium perchlorate. J. Saudi Chem. Soc. 17, 135–149 (2013). http://dx.doi.org/10.1016/j.jscs.2011.05.009

14. S. Chaturvedi, P.N. Dave, N.K. Shah, Applications of nanocatalyst in new era. J. Saudi Chem. Soc. 16, 307–325 (2012). https://doi.org/10.1016/j.jscs.2011.01.015

15. P.N. Dave, P.N. Ram, S. Chaturvedi, Nanoferrites: catalyst for thermal decomposition of ammonium perchlorate. Part. Sci. Technol. 33, 677–681 (2015). https://doi.org/10.1080/0272351.2015.1023479

16. A. Miri, M. Sarani, A. Najafidoust, M. Mehrabani, F.A. Zadeh, R.S. Varma, Photocatalytic performance and cytotoxic activity of green-synthesized cobalt ferrite nanoparticles. Mater. Res. Bull. 149, 111706 (2022). https://doi.org/10.1016/j.materresbull.2021.111706

17. V.R. Bhagwat, A.V. Humde, S.D. More, K.M. Jadhav, Sol-gel auto combustion synthesis and characterizations of cobalt ferrite nanoparticles: different fuels approach. Mater. Sci. Eng. B 248, 114388 (2019). https://doi.org/10.1016/j.msea.2019.114388

18. A.A.H. El-Bassuony, W.M. Gamal, H.K. Abdelsalam, Fascinating study of adding nanocomposite cobalt nano ferrite to silver nanoparticles accompanied magnetite impurity. J. Mater. Sci. Mater. Electron. (2022). https://doi.org/10.1007/s10854-022-08516-y

19. S. Goktas, A. Goktas, A comparative study on recent progress in efficient ZnO based nanocomposite and heterojunction photocatalysts: a review. J. Alloys Compd. 863, 158734 (2021). https://doi.org/10.1016/j.jallcom.2021.158734

20. Y. Lan, J. Zhai, D. Li, R. Yang, The influence of solution chemistry on the morphology of ammonium dinitramide crystals. J. Mater. Sci. 50, 4933–4939 (2015). https://doi.org/10.1007/s10853-015-9040-y

21. T. Mukundan, G.N. Pur, J.K. Nair, S.M. Pansare, R.K. Sinha, H. Singh, Explosive nitrotriazolone formulates. Def. Sci. J. 52, 127–133 (2002)

22. A. Saikia, R. Sivabalan, G.M. Gore, A.K. Sikder, Microwave-assisted quick synthesis of some potential high explosives. Propellants Explos. Pyrotech. 37, 540–543 (2012). https://doi.org/10.1002/prep.201100107

23. Journal of Chemistry: Education Research and Practice | OPAST Online Publishing Group. https://opastonline.com/journal-of-chemistry-education-research-and-practice/current-issue. Accessed 21 Oct 2021

24. K.Y. Lee, B.W. Asay, J.E. Kennedy, Method for forming energetic nanopowders, U.S. Patent No. 8,557,066. (U.S. Patent and Trademark Office, Washington, DC, 2013)

25. S. Vyazovkin, A.K. Burnham, J.M. Criado, L.A. Pe z-Maqueda, C. Popescu, N. Sbirrazzuoli, ICTAC kinetics
committee recommendations for performing kinetic computations on thermal analysis data. Thermochim. Acta 520, 1–19 (2011). https://doi.org/10.1016/j.tca.2011.03.034

26. J.H. Flynn, L.A. Wall, A quick, direct method for the determination of activation energy from thermogravimetric data. J. Polym. Sci. Part C Polym. Lett. 4, 323–326 (1966)

27. T. Ozawa, A new method of analyzing thermogravimetric data. Bull. Chem. Soc. Jpn. 38, 1881–1886 (1965)

28. H.E. Kissinger, Variation of peak temperature with heating rate in differential thermal analysis. J. Res. Natl. Bur. Stand. 57, 217–221 (1956)

29. T. Akahira, T. Sunose, Method of determining activation deterioration constant of electrical insulating materials. Res. Rep. Chiba Inst. Technol. (Sci. Technol.) 16, 22–31 (1971)

30. M.J. Starink, The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods. Thermochim. Acta 404, 163–176 (2003). https://doi.org/10.1016/S0040-6031(03)00144-8

31. D. Trache, A. Abdelaziz, B. Siouani, A simple and linear isoconversional method to determine the pre-exponential factors and the mathematical reaction mechanism functions. J. Therm. Anal. Calorim. 128, 335–348 (2017). https://doi.org/10.1007/s10973-016-5962-0

32. S. Jesus Mercy, D. Parajuli, N. Murali, A. Ramakrishna, Y. Ramakrishna, V. Veeraiah, K. Samatha, Microstructural, thermal, electrical and magnetic analysis of Mg$^{2+}$ substituted cobalt ferrite. Appl. Phys. A 126, 873 (2020). https://doi.org/10.1007/s00339-020-04048-6

33. J.-T. Wu, J.-G. Zhang, T. Li, Z.-M. Li, T.-L. Zhang, A novel cocryystal explosive NTO/TZTN with good comprehensive properties. RSC Adv. 5, 28354–28359 (2015). https://doi.org/10.1039/C5RA01124H

34. S. Das, M. Bououdina, C. Manoharan, The influence of cationic surfactant CTAB on optical, dielectric and magnetic properties of cobalt ferrite nanoparticles. Ceram. Int. 46, 11705–11716 (2020). https://doi.org/10.1016/j.ceramint.2020.01.202

35. F. Mikailzade, H. Türk, F. Önol, Ö. Karataş, S. Kazan, M. Zarbali, A. Göktaş, A. Tumbul, Structural, optical and magnetic characterization of nanorod-shaped polycrystalline Zn$_{1-x}$Mn$_x$O films synthesized using sol-gel technique. Appl. Phys. A 126, 768 (2020). https://doi.org/10.1007/s00339-020-03953-0

36. A. Goktas, S. Modanli, A. Tumbul, A. Kilic, Facile synthesis and characterization of ZnO, ZnO:Co, and ZnO:ZnO: Co nanorod-like homojunction thin films: role of crystallite/grain size and microstrain in photocatalytic performance. J. Alloys Compd. 893, 162334 (2022). https://doi.org/10.1016/j.jallcom.2021.162334

37. M.A. Rios-Corripi, B.E. Garcia-Pérez, M.E. Jaramillo-Flores, V.L. Gayou, M. Rojas-López, UV–visible intensity ratio (aggregates/single particles) as a measure to obtain stability of gold nanoparticles conjugated with protein A. J. Nanopart. Res. 15, 1624 (2013). https://doi.org/10.1007/s11051-013-1624-3

38. H. Kato, A. Nakamura, K. Takahashi, S. Kinugasa, Size effect on UV–Vis absorption properties of colloidal C60 particles in water. Phys. Chem. Chem. Phys. 11, 4946–4948 (2009). https://doi.org/10.1039/B904593G

39. S. Swathi, R. Yuvakkumar, P.S. Kumar, G. Ravi, D. Velauthapillai, Annealing temperature effect on cobalt ferrite nanoparticles for photocatalytic degradation. Chemosphere 281, 130903 (2021). https://doi.org/10.1016/j.chemosphere.2021.130903

40. D. Li, H. Song, X. Meng, T. Shen, J. Sun, W. Han, X. Wang, Effects of particle size on the structure and photocatalytic performance by alkali-treated TiO$_2$. Nanomaterials 10, 546 (2020). https://doi.org/10.3390/nano10030546

41. A. Tumbul, F. Aslan, A. Goktas, M.Z. Zarbali, A. Kilic, Highly stable ethanol-based Cu$_2$ZnSnS$_4$ (CZTS) low-cost thin film absorber: effect of solution aging. Mater. Chem. Phys. 258, 123997 (2021). https://doi.org/10.1016/j.matchemphys.2020.123997

42. A. Goktas, F. Aslan, I.H. Mutlu, Effect of preparation technique on the selected characteristics of Zn$_{1-x}$Co$_x$O nanocrystalline thin films deposited by sol–gel and magnetron sputtering. J. Alloys Compd. 615, 765–778 (2014). https://doi.org/10.1016/j.jallcom.2014.06.160

43. F.R. Mariosi, J. Venturini, V.A. da Cas, C.P. Bergmann, Lanthanum-doped spinel cobalt ferrite (CoFe$_2$O$_4$) nanoparticles for environmental applications. Ceram. Int. 46, 2772–2779 (2020). https://doi.org/10.1016/j.ceramint.2019.09.266

44. R.I. Hiyoshi, Y. Kohno, J. Nakamura, Vibrational assignment of energetic material 5-nitro-2,4-dihydro-1,2,4-triazole-3-one (NTO) with labeled isomers. J. Phys. Chem. A 108, 5915–5920 (2004). https://doi.org/10.1021/jp049118i

45. M. Nazim, A.A.P. Khan, A.M. Asiri, J.H. Kim, Exploring rapid photocatalytic degradation of organic pollutants with porous CuO nanosheets: synthesis, dye removal, and kinetic studies at room temperature. ACS Omega 6, 2601–2612 (2021). https://doi.org/10.1021/acsomega.0c04747

46. P.M. Kibasomba, S. Dhlamini, M. Maaza, C.-P. Liu, M.M. Rashad, D.A. Rayan, B.W. Mwakikunga, Strain and grain size of TiO$_2$ nanoparticles from TEM, Raman spectroscopy and XRD: the revisiting of the Williamson–Hall plot method. Results Phys. 9, 628–635 (2018). https://doi.org/10.1016/j.rinp.2018.03.008
47. V. Swamy, B.C. Muddle, Q. Dai, Size-dependent modifications of the Raman spectrum of rutile TiO₂. Appl. Phys. Lett. 89, 163118 (2006). https://doi.org/10.1063/1.2364123

48. Y. Lin, Y.-J. Zhang, W.-M. Yang, J.-C. Dong, F.-R. Fan, Y. Zhao, H. Zhang, N. Bodappa, X.-D. Tian, Z.-L. Yang, G.D. Stucky, Z.-Q. Tian, J.-F. Li, Size and dimension dependent surface-enhanced Raman scattering properties of well-defined Ag nanocubes. Appl. Mater. Today 14, 224–232 (2019). https://doi.org/10.1016/j.apmt.2018.12.012

49. G. Lan, J. Li, G. Zhang, J. Ruan, Z. Lu, S. Jin, D. Cao, J. Wang, Thermal decomposition mechanism study of 3-nitro-1,2,4-triazol-5-one (NTO): combined TG-FTIR-MS techniques and ReaxFF reactive molecular dynamics simulations. Fuel 295, 120655 (2021). https://doi.org/10.1016/j.fuel.2021.120655

50. E.F. Rothgery, D.E. Audette, R.C. Wedlich, D.A. Csejka, The study of the thermal decomposition of 3-nitro-1,2,4-triazol-5-one (NTO) by DSC, TGA-MS, and ARC. Thermochim. Acta 185, 235–243 (1991). https://doi.org/10.1016/0040-6031(91)80045-K

51. R. Dubey, P. Srivastava, I. Kapoor, G. Singh, Synthesis, characterization and catalytic behavior of Cu nanoparticles on the thermal decomposition of AP, HMX, NTO and composite solid propellants, part 83. Thermochim. Acta 549, 102–109 (2012)

52. V.P. Sinditskii, S.P. Smirnov, VYu. Egorshev, Thermal decomposition of NTO: an explanation of the high activation energy. Propellants Explos. Pyrotech. 32, 277–287 (2007). https://doi.org/10.1002/prep.200700029

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.