Thermal Behavior and Decomposition Mechanism of Ammonium Perchlorate and Ammonium Nitrate in the Presence of Nanometer Triaminoguanidine Nitrate

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ABSTRACT: Nanometer triaminoguanidine nitrate (TAGN) with mean size of 218.7 nm was fabricated, and its structures were characterized by scanning electron microscopy, X-ray diffraction, IR, and X-ray photoelectron spectroscopy analyses. As an energetic accelerator for thermal decomposition of ammonium perchlorate (AP) and ammonium nitrate (AN), 10% nano TAGN blended with AP and AN, and samples [90% AP + 10% (nano TAGN)] and [90% AN + 10% (nano TAGN)] were obtained, respectively. Differential scanning calorimetry (DSC) analyses were employed to investigate the decomposition kinetics and thermodynamics of the samples. The results indicated that [90% AP + 10% (nano TAGN)] presented a higher activation energy (152.34 kJ mol⁻¹) than pure AP (117.21 kJ mol⁻¹) and [90% AN + 10% (nano TAGN)] possessed a lower activation energy (147.51 kJ mol⁻¹) than pure AN (161.40 kJ mol⁻¹). All activation free energies (ΔG°) were positive values. This means that activation of the molecules was not a spontaneous process. The decomposition peak temperature of AP decreased from 478.5 °C (for pure AP) to 287.2 °C (for [90% AP + 10% (nano TAGN)]). The decomposition peak of AN also advanced via doping with nano TAGN. Using DSC-IR analysis, the decomposition products of nano TAGN, pure AP, [90% AP + 10% (nano TAGN)], pure AN, and [90% AN + 10% (nano TAGN)] were investigated, and their decomposition mechanisms were proposed. The key factors, i.e., the formation of hydrazine in the decomposition of nano TAGN, were speculated, which substantially promoted the consumption of HNO₃, HClO₄, and their decomposition products in kinetics. Additionally, the energy performances of AP- and AN-based propellants doping with TAGN were evaluated. It is disclosed that the introduction of TAGN would not result in improvement in the energy performance of propellants, but due to its energetic property and high hydrogen content, proper introduction of TAGN will not reduce the energy performance of propellants in a large degree compared with the introduction of inert catalysts.

1. INTRODUCTION

Ammonium perchlorate (AP) is an oxidizer that is extensively used in composite solid propellants. AP is of almost the highest effective oxygen content among the oxidizers, i.e., its oxygen balance (OB) is up to +34%, which results in the oxidation of Al and the binder in combustion of propellants. Meanwhile, another advantage of AP lies in its high content of hydrogen. Higher hydrogen content means higher energy conversion efficiency, i.e., the same heat energy, released from combustion of propellants, will do more work. Today, with the emergence of new oxidizers, such as ammonium dinitramite (ADN), the inferiority of AP is obviously exposed. For example, its formation enthalpy (−2536 kJ kg⁻¹) is considerably lower than that of ADN (−1218 kJ kg⁻¹); its gas production (0.929 m³ kg⁻¹) is somewhat lower than that of ADN (0.992 m³ kg⁻¹); and its combustion heat (4587 kJ kg⁻¹) is lower than that of ADN (5145 kJ kg⁻¹); moreover, the kinetic characteristic of its combustion is much inferior to that of ADN because of its much higher decomposition temperature (>400 °C) compared to the decomposition temperature of ADN (~160 °C). Based on these data, it seems that it is time to completely replace AP by ADN or other high-energy oxidizers just like hydrazinium nitroformate (HNF); however, for most countries, it is unrealistic because they have not addressed the issue of mass production of ADN and HNF, let alone some severe defects of ADN and HNF, which have not been solved yet. Thus, now, AP is still the most ideal oxidizer used in various propellants. For the most powerful propellant, i.e., nitrate ester plasticized polyether propellant, there is 7–15% AP in the formula, which is needed to regulate the burning rate, optimize the oxygen balance, and lower the combustion pressure exponent. Hence, now it is too early to give up AP. So, in the past two decades, there are dozens of works reporting on how to improve the decomposition property or combustion performance of AP or AP-based propellants. For metal oxides, nano Fe₂O₃, nano CuO, nano NiO, etc. were recruited to accelerate thermal decomposition of AP. In addition, metallic nanoparticles such as nano Fe₆, nano Zn₇, nano Cu₈−₁₀, nano Ni₁,₁ etc. were also prepared to promote thermolysis of AP. Besides these, there were still too many
nanomaterials fabricated to give positive effects on thermolysis of AP and AP-based propellants.\textsuperscript{13−16}

In fact, the most fatal defect of AP is the high chlorine content in its molecules (30.2 wt % Cl). Hydrogen chloride is the main combustion product of AP-based propellants, and it destroys the ozone layer. Due to this, the alternative oxidizer, which is halogen-free and easily available, comes to our sight, i.e., ammonium nitrate (AN). Combustion products of AN-based propellants do not contain hydrogen chloride and other chlorinated compounds. The AN-based propellants have the feature of low combustion signature because the combustion does not produce white smoke or white fog. The second advantage of AN lies in its super low sensitivity. AN cannot burn at ambient pressure and also when the pressure is up to 100 MPa.\textsuperscript{17} Moreover, AN will not explode or decompose under any external impact and friction action. Hence, AN is a kind of ideal insensitive energetic material. Notwithstanding, it is unexpected that no propellant formula uses AN as the main oxidizer and only few gas-generation agent formulas try to use AN as the main oxidizer.\textsuperscript{18−20} This is because AN and AN-based propellants show poor energy and combustion performance. The heat formation of AN is low to $-4600$ kJ kg$^{-1}$, and the value of AP is $-2536$ kJ kg$^{-1}$. Especially, the explosion heat of AN is only $1450$ kJ kg$^{-1}$ and the value of AP is $3720$ kJ kg$^{-1}$. Thus, the energy performance of AN-based propellants is obviously lower than that of AP-based propellants. For combustion performance, the burn rates of AN- and AP-based propellants are about $1$ mm s$^{-1}$ (at 7 MPa) and $10$ mm s$^{-1}$, respectively. Meanwhile, unlike AP-based propellants, AN-based propellants cannot burn at low pressure. Some researchers try to improve the combustion performance of AN-based propellants by adding some catalysts, but with little success. For example, Naya finds that thermal decomposition of AN doped with 4 wt % MnO$_2$ does not change compared to pure AN, and the propellant does not burn when the pressure is less than 1 MPa.\textsuperscript{21} Moreover, some nanometer materials, such as nano Al, nano γ-Al$_2$O$_3$, nano CuO, nano TiO$_2$, nano LiF, etc., also have no obvious effects on thermal decomposition of AN.\textsuperscript{22,23} High-nitrogen compounds like bis-(1H-tetrazolyl) amine ammonium salt (BTA-NH$_3$) are also employed to promote the combustion performance of AN-based propellants.\textsuperscript{24} The propellant doped with BTA-NH$_3$ burns at 1 MPa pressure. This is a substantial improvement for AN-based propellants. But it is regretful that the burn rate is still very low, i.e., only $1−2$ mm s$^{-1}$ at 7 MPa. The effect of high-nitrogen

![Figure 1.](image)

**Figure 1.** SEM images (a–d) and size distribution (e, f) of nano TAGN.
compound on the combustion of AN-based propellant was also studied by Miyata, and the result is similar to that of BTA·NH₃. Additionally, it is widely accepted that chloride compounds have obvious effects on the combustion of AN and AN-based propellants. In Sinditskii’s work, addition of 7 wt % NaCl makes AN/glycidyl azide polymer (GAP) propellant burn at 0.5 MPa pressure, but the burn rate is still less than 1 mm s⁻¹. Therefore, it can be seen from previous studies that increasing the burning rate of AN and AN-based propellants is a very difficult task. For this purpose, the used catalyst must be able to remarkably promote thermal decomposition of AN in mechanism.

Regardless of the studies of AP or AN, the reported catalysts are almost inert materials, which cannot decompose accompanying with the decomposition of AP or AN. This will result in a penalty on the energy performance of propellants. In addition, some metallic powders were also used as catalysts on the decomposition or combustion of propellants. These metallic particles are different from metal oxides because they can react with the oxidizer and release some heats. Especially, when the particle size of metallic particles falls into nanometer scale, they are fleetly oxidized and act as many active centers due to the extremely high exothermic rate. The high exothermic rate will greatly promote the decomposition or combustion of AP and AN. However, despite this, adding metallic powders into a formula will also obviously deteriorate the energy performance of propellants. Thus, it is desired to find a material that can not only quickly release many heats to support the decomposition of AP or AN but also does not negatively affect the energy performance of propellants. However, please note that this does not mean that traditional explosives are capable or competent of accelerating the decomposition of AP and AN. For example, introduction of explosives, such as trinitrotoluene, hexogen (hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX), octogen (1,3,5,7-tetranitro-1,3,5,7-tetrazocane, HMX), etc., could not affect the decomposition of AP and AN. When they are mixed with AP or AN, they decompose individually. Hence, we need a catalyst whose decomposition product must be able to strongly induce thermolysis of AP and AN at low temperature, so it promotes decomposition of AP and AN in kinetics. Therefore, it is very necessary to master the decomposition feature of the catalyst. To achieve this objective, nanoscale triaminoguanidine nitrate (TAGN) was fabricated, and the thermal behavior and decomposition mechanism of AP and AN doped with nano TAGN were investigated here.

2. RESULTS AND DISCUSSION

2.1. Characterization of Nano TAGN. Scanning electron microscopy (SEM) images of nano TAGN are shown in Figure 1. Figure 1a–c shows that the particle size of nano TAGN is very small. The particles are not spherical and have a certain aspect ratio. The length-to-diameter ratio is about 2–3. Via measuring the diameter of the particles, the particle size distributions of nano TAGN are given in Figure 1f. The frequency distribution shows obvious normal distribution. Volume distribution is obtained by integrating the curve of frequency distribution. Then, the median diameter of nano TAGN, i.e., \( d_{50} = 218.7 \) nm, is obtained.

The crystal phases of TAGN before and after milling were analyzed by X-ray diffraction (XRD) analysis, and the XRD patterns are shown in Figure 2a. It is obvious that nano TAGN has almost the same diffraction peaks as raw TAGN. The peak intensity of raw TAGN is 70 times higher than that of nano TAGN, which attributes to the nanometer size of nano TAGN.
IR spectra are illustrated in Figure 2b. The IR spectrum of nano TAGN is consistent with that of the raw TAGN. Specifically, peaks at 3317 and 3214 cm\(^{-1}\) relate to the stretching vibration of the N\(\equiv\)H bond; the peak at 1680 cm\(^{-1}\) corresponds to the stretching vibration of C\(\equiv\)N bond; the peak at 1607 cm\(^{-1}\) corresponds to the in-plane bending vibration of N\(\equiv\)H bond; the peak at 1381 cm\(^{-1}\) refers to the stretching vibration of N\(\equiv\)O bond in NO\(_3^\text{-}\); the peak at 1126 cm\(^{-1}\) attributes to the in-plane swaying vibration of NH\(_2\); the peak at 950 cm\(^{-1}\) ascribes to the out-plane bending vibration of N\(\equiv\)H bond; the peak at 828 cm\(^{-1}\) corresponds to the deformation vibration of N\(\equiv\)O bond in NO\(_3^\text{-}\); and the peak at 602 cm\(^{-1}\) relates to the out-plane swaying vibration of NH\(_2\). X-ray photoelectron spectroscopy (XPS) images of nano TAGN are shown in Figure 3. Figure 3a indicates that only three elements O, N, and C are detected, which is consistent with the elements in the molecule of nano TAGN. Figure 3b indicates that N 1s splits into two peaks. One relates to the N atom in NO\(_3^\text{-}\); another corresponds to N atom in N\(\equiv\)H.

### 2.2. Thermolysis of AP Doped with Nano TAGN

To probe the catalysis effect of TAGN on thermolysis of AP, 0.9 g AP is homogeneously mixed with 0.1 g of nano TAGN, and the sample named "[90% AP + 10% (nano TAGN)]" is obtained. Thermal analyses are carried out for both pure AP and [90% AP + 10% (nano TAGN)] at different heating rates, and the differential scanning calorimetry (DSC) traces are illustrated in Figure 4. Figure 4a shows the DSC traces of pure AP. In each curve, an endothermic peak appears at 244 \(^\circ\)C relating to phase transformation of AP. The exothermic peaks located at 431\(\sim\)479 \(^\circ\)C relate to thermolysis of AP. Please note that no low-temperature decomposition peak exists in the curve. Usually, there are two exothermic peaks in the DSC curve of AP: one corresponds to its low-temperature decomposition; another ascribes to its high-temperature decomposition. Herein, because the samples did not perform a tablet pressing before testing, there was only one exothermic peak in the curve. However, due to the same test condition for all samples, the experimental results are comparable and persuasive. Figure 4b shows the DSC curve of [90% AP + 10% (nano TAGN)]. A small exothermic peak appears at 190\(\sim\)208 \(^\circ\)C, which should relate to thermal decomposition of nano TAGN. At elevated temperature, an endothermic peak appears relating to phase transformation of AP. The main exothermic peak, which attributes to the decomposition of AP, locates at 267\(\sim\)287 \(^\circ\)C. By comparing Figure 4a with Figure 4b, it is obvious that decomposition temperature of AP decreases remarkably when 10% nano TAGN are doped. In fact, in most of the references that reported the catalysts (or accelerator) for thermal decomposition of AP, it is very rare that the decomposition temperature of AP can be reduced to less than 300 \(^\circ\)C. As an exceptional case, an active catalyst was reported by Guo, in which an energetic ionic salt K\(_2\)Pb[Co(NO\(_2\))\(_6\)] was prepared and employed to promote thermal decomposition of AP.\(^{27}\) Therein, the decomposition temperature of AP decreased to 295.9 \(^\circ\)C when K\(_2\)Pb[Co(NO\(_2\))\(_6\)] was doped. K\(_2\)Pb[Co(NO\(_2\))\(_6\)] decomposed first at

| samples                      | \(T_p\) (K) | \(\Delta H^\circ\) (kJ mol\(^{-1}\)) | \(\Delta G^\circ\) (kJ mol\(^{-1}\)) | \(\Delta S^\circ\) (J mol\(^{-1}\) K\(^{-1}\)) | \(E_k\) (kJ mol\(^{-1}\)) | \(\ln A_k\) | \(k\) (s\(^{-1}\)) |
|------------------------------|-------------|-------------------------------------|------------------------------------|---------------------------------------------|---------------------------|-------------|----------------|
| pure AP                      | 739.05      | 111.06                              | 192.89                             | 110.72                                      | 117.21                    | 18.05       | 0.36           |
| [90% AP + 10% (nano TAGN)]   | 557.25      | 147.70                              | 130.36                             | 31.13                                       | 152.34                    | 34.83       | 7.00           |
| low-temperature reaction     | 475.95      | 133.24                              | 118.48                             | 31.02                                       | 137.19                    | 34.66       | 0.99           |

The DSC curves are shown in Figure 4. The thermodynamic and kinetic parameters derived from DSC traces are presented in Table 1.
272.8 °C, and its decomposition products induced thermolysis of AP.

For a further investigation in catalysis effect of nano TAGN on thermolysis of AP, the thermodynamic kinetic parameters are calculated with eqs 1−5.38 and the results are listed in Table 1. $E_k$ of pure AP is 117.2 kJ mol$^{-1}$ and $E_k$ of [90% AP + 10% (nano TAGN)] is 152.34 kJ mol$^{-1}$. This is an abnormal result because decomposition of [90% AP + 10% (nano TAGN)] should be

Figure 5. DSC-IR analysis: (a, e, h) total absorbance of gas products; (b, f, i) DSC traces; and (c, d, g, j, k) IR spectra of gas products.
easier to initiate than the decomposition of pure AP. Thus, I do not think these data are correct. But the date of rate constant (k) is representative. The k value of [90% AP + 10% (nano TAGN)] is 20 times larger than the value of pure AP. This means that nano TAGN considerably promoted thermal decomposition of AP. AP will not decompose spontaneously. Its initiation needs some heats (i.e., ΔH°). According to the ΔH° values in Table 1, [90% AP + 10% (nano TAGN)] needs more heats to be activated. As similar as the case of E°p, this result also fails to elucidate the acceleration effect of nano TAGN on the decomposition of AP, in comparison with the substantial advance of decomposition peak showed in DSC traces. All ΔG° are positive values, which confirms that the decomposition of AP will not be initiated spontaneously. The values of activation entropy (ΔS°) are calculated using eq 5. We could find that all ΔS° are positive values. This makes the −TΔS° term in eq 5 a negative value. Meanwhile, a positive value for ΔS° corresponds to an increase in the randomness or disorder of the system when the activation of the molecules occurs

\[
\frac{\ln \beta}{T_p} = \ln \left( \frac{RA_k}{E_k} - K \right) - \frac{E_k}{T_p}
\]

(1)

\[k = A_k \exp \left( - \frac{E_k}{T_p} \right)
\]

(2)

\[
A \exp \left( - \frac{E_k}{RT_p} \right) = \frac{K}{h} \exp \left( - \frac{\Delta G°}{RT_p} \right)
\]

(3)

\[
\Delta H° = E_k - RT_p
\]

(4)

\[
\Delta G° = \Delta H° - T_p \Delta S°
\]

(5)

where \(T_p\) is the peak temperature, \(K; K_b\) and \(h\) are the Boltzmann \((K_b = 1.381 \times 10^{-23} \text{ J K}^{-1})\) and Plank constants \((h = 6.626 \times 10^{-34} \text{ J s}^{-1})\), respectively; \(\beta\) is the heating rate; \(E_k\) and \(A_k\) are the activation energy and preexponential factor, respectively; \(\Delta H°\) is the activation enthalpy, J mol\(^{-1}\); \(\Delta G°\) is the activation free energy, J mol\(^{-1}\); and \(\Delta S°\) is the activation entropy, J mol\(^{-1}\) K\(^{-1}\).

To probe the decomposition mechanism of AP doped with nano TAGN, DSC-IR analyses were conducted, and results are shown in Figure 5. In Guo’s work, he had confirmed that decomposition products of \(K_2\text{Pb}[\text{Co(NO}_3\text{)]_6}\) react with decomposition products of AP, which resulted in a substantial promotion in thermal decomposition of AP. Thus, herein, we first study the decomposition mechanism of nano TAGN. Figure 5a, b illustrates the DSC trace of nano TAGN, synchronously displaying the curve of total absorbance of gas products. At different temperatures (or time lapses), the IR spectra are extracted and illustrated in Figure 5c. The main products for thermal decomposition of nano TAGN are NH\(_3\), N\(_2\), CO\(_2\); few C−N−H and N−H fragments are also detected. We know that there is no NH\(_3\) existing in TAGN molecules. Hence, the formation of NH\(_3\) would not ascribe to the movement of proton from NH\(_4\)• cation to anion just like the dissociation of AP or AN. Via carefully observing Figure 5c, we find that the appearances of NH\(_3\), C−N−H, and N−H do not coincide with the appearances of N\(_2\)O and CO\(_2\). Well, I mean NH\(_3\), C−N−H, and N−H fragments form first, corresponding to the low-temperature decomposition in Figure 5b; the N\(_2\)O and CO\(_2\) produce at elevated temperature, relating to the high-temperature decomposition in Figure 5b. This result agrees with Kubota’s work.\(^{29}\) Therein, he also found that there are two exothermic stages in the thermal decomposition of TAGN: one stage corresponds to splitting of NH3 radicals from TAGN molecules, which is a very quick process accompanying with 27% weight loss (accessing to the theoretical value of 30%); another stage relates to the decomposition of the remainder. I consider that Kubota’s proposal is correct; otherwise, we cannot explain where the massive NH3 comes from. Two *NH\(_3\) radicals combine with hydrazine (H\(_2\)N−NH\(_2\)). The hydrazine is oxidized by HNO\(_3\) to generate N\(_2\) and few N\(_2\)O. Meanwhile, many H\(_2\)N−NH\(_2\) also decompose to NH\(_3\), and the NH\(_3\) is oxidized by HNO\(_3\) at elevated temperature to form substantial N\(_2\)O. Thus, the decomposition mechanism of nano TAGN is suggested as eqs 6–12. In Figure 5c, it is obvious that, at a time lapse of 1416.3 s (233.1 °C in Figure 5b), there are no CO\(_2\) and N\(_2\)O formed, i.e., the first exothermic stage is independent of eqs 7–12. The split of *NH\(_3\) radicals from TAGN (i.e., eq 6) molecules solely accounts for the first exothermic stage. Now, based on the decomposition mechanism of nano TAGN, let us come into subject to discuss the decomposition of AP doped with nano TAGN

\[\text{TAGN} \rightarrow \text{NH}_3 + \text{GN}\]

(6)

\[\text{GN} \rightarrow \text{HN} + \text{HNO}_3\]

(7)

\[*\text{NH}_3 + *\text{NH}_3 \rightarrow \text{H}_2\text{N} − \text{NH}_2\]

(8)

\[\text{NH}_3 − \text{NH}_2 \rightarrow 0.5\text{N}_2 + \text{NH}_4 + 0.5\text{H}_2\]

(9)

\[2\text{NH}_2 − \text{NH}_2 + 2\text{HNO}_3 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O} + 2\text{N}_2\]

(10)

\[\text{HNO}_3 + \text{NH}_4 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}\]

(11)

\[\text{HN} + \text{HNO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}\]

(12)

Figure 5c,f shows the DSC trace of pure AP, synchronously illustrating the curve of total absorbance of gas products. In the DSC trace, it is clear that there are two exothermic processes. At 303–330 °C, the exothermic process is very broad, which relates to low-temperature decomposition of AP; at 378–421 °C, the main exothermic peak appears, which attributes to high-temperature decomposition of AP. In Figure 5e, it is clear that both processes have gaseous products formed. We extract the IR spectra of these gaseous products and illustrate them in Figure 5g. The main decomposition products of pure AP are N\(_2\), N\(_2\)O, HCl, H\(_2\)O, and NOCl, and few NO and HClO\(_4\) were also detected. The signal of CO\(_2\) in Figure 5g results from an unexpected introduction of organics contamination in DSC analysis, but this does not affect the experimental results. Please note that no NH\(_3\) gas was detected in low- or high-temperature decomposition of pure AP. This result is in accordance with the common decomposition mechanism of AP,\(^{30}\) i.e., NH\(_4\)ClO\(_4\) first dissociates to NH\(_3\) and HClO\(_4\) by a proton transfer, and HClO\(_4\) rapidly decomposed to *ClO\(_4\) and *H\(_2\)O radicals; then, the NH\(_3\) is quickly oxidized by HClO\(_4\) to produce NH\(_4\)•.\(^{31}\) At low temperature, NH\(_3\) reacts with decomposition products of HClO\(_4\). At low temperature, NH\(_3\) reacts with decomposition products of HClO\(_4\) slowly. The excessive ammonia coated on the surface of AP particles result in the cease of the decomposition. However, at low temperature (303–330 °C), we still did not find any signal of NH\(_3\). There are two possibilities accounted for this phenomenon: (i) much ammonia is adsorptively captured by...
particle surface of AP and (ii) oxidation of ammonia is very easy to occur at low temperature, which results in complete oxidation of ammonia. Just like most authors, I prefer the first speculation because the redox reaction between NH$_3$ and the oxidizing gases continues at elevated temperature.$^{31}$ I suggest that just because the reaction rate and the heat release are too low to sustain the redox reaction at low temperature, the decomposition of AP ceases. Therefore, an acceleration of HClO$_4$ consumption and its decomposition products at low temperature is very important because a violent redox reaction will produce more heats to break the "NH$_3$ prison." Obviously, it is hard to change the decomposition and the products of perchloric acid. However, we can introduce some materials whose decomposition products can be more easily oxidized than NH$_3$ by the oxidizing gases at low temperature. Decomposition of nano TAGN makes the idea satisfied. Figure 5a−d indicates that nano TAGN decomposes earlier than AP to produce many $^*$NH$_2$ radicals and $^*$NH−C− (or $^*$N−C−) fragments. These amine radicals would combine to produce hydrazine, which would instantaneously react with perchloric acid and its decomposition products at low temperature to produce many heats (see Figure 5h,i). The sample [90% AP + 10% (nano TAGN)] decomposed at very low temperature, which is consistent with the result of DSC analysis in Figure 4b. Figure 5j,k indicates that in the temperature range of 200−209 °C, only a less amount of NH$_3$ gas is generated, which is derived from the decomposition of hydrazine as the intermediate. In Figure 5j, we can find that the main decomposition products of [90% AP + 10% (nano TAGN)] are very different from those of pure AP. At a temperature of 284−304 °C, the main products are just N$_2$O and HCl, and very little CO$_2$ is detected. The intermediate products (such as NO$_2$, NOCl, and HClO$_4$), which are produced by the decomposition of pure AP, do not appear in the decomposition of [90% AP + 10% (nano TAGN)]. These oxidizing gases have reacted with hydrazine, amine radicals, and NH$_3$ with considerable heat release at low temperature, which strongly induces the decomposition of AP.

2.3. Thermolysis of AN Doped with Nano TAGN. The catalysis effects of nano TAGN on thermal decomposition of AN are also investigated here. AN (0.9 g) is homogeneously mixed with 0.1 g of nano TAGN, and the sample is named [90% AN + 10% (nano TAGN)]. DSC analyses are performed, and
the results are shown in Figure 6. In Figure 6a, each DSC curve contains four small endothermic peaks and a large endothermic peak. The peaks located at 48.8, 85.8, and 128.9 °C correspond to the phase transformation of AN. The peak located at 169 °C represents the melting point of AN. The large peak at elevated temperature relates to thermal decomposition of AN. In the case of [90% AN + 10% (nano TAGN)] (in Figure 6b), the phase transitions, which are located at 58.6 and 129.2 °C, still exist; phase transition at 85.8 °C disappeared; the melting point advanced to 155.3 °C compared to 169 °C of pure AN; and the peak temperature of decomposition also advanced about 5 °C compared to pure AN. Meanwhile, the DSC analyses of raw and nano TAGN are also performed, and the results are shown in Figure 6c,d. The decomposition process of nano TAGN is similar to the process of raw TAGN. Regardless of whether raw or nano TAGN, there are two or three exothermic peaks in the DSC curves. This is consistent with the result in Figure 5a. Thermal decomposition of TAGN releases many heats. This may not be important because the initiation of the decomposition of AN is substantially endothermic.

In fact, in Sinditski’s work, he considered that there were two major factors that determined whether the catalyst particles could become active centers in the combustion of propellants.32 First, the best situation is the catalyst can decompose and release many heats to support the condense-phase decomposition of the propellant; second, the decomposition rate of the catalyst must be significantly higher than the decomposition rate of propellants. Just like ammonium dichromate, it easily decomposes at low temperature and quickly releases many heats. Thus, the AN-based propellant doped with 8 wt % ammonium dichromate burns sustainedly at 0.5 MPa.33 The exothermic decomposition of nano TAGN is confirmed in Figure 6c,d. In addition to this, the maximum heat flow ($Q_{\text{max}}$) of nano TAGN is also obviously larger than the $Q_{\text{max}}$ of pure AN. The value of heat flow characterizes the rate of heat release of the measured sample in DSC analysis. Moreover, in Table 2, the kinetic calculation indicates that the activation energy ($E_k$) for thermal decomposition of [90% AN + 10% (nano TAGN)] is lower than the $E_k$ of pure AN, and the rate constant (k) of [90% AN + 10% (nano TAGN)] is somewhat higher than k of pure AN. This means that [90% AN + 10% (nano TAGN)] decomposed easier and faster than pure AN. However, in Table 2, please note that the $E_k$ for nano TAGN almost equals $E_k$ for pure AN. But the k-

| samples                  | $T_p$ (K) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$) | $E_k$ (kJ mol$^{-1}$) | $\ln A_k$ | $k$ (s$^{-1}$) |
|--------------------------|----------|----------------------------------|----------------------------------|------------------------------------------|----------------------|---------|-------------|
| pure AN                  | 553.3    | 156.80                           | 138.66                           | 32.79                                    | 161.40               | 35.02   | 0.934       |
| [90% AN + 10% (nano TAGN)] | 550.3    | 147.51                           | 137.75                           | 9.41                                     | 147.51               | 32.2    | 0.963       |
| nano TAGN                | 511.4    | 158.69                           | 127.23                           | 61.52                                    | 162.94               | 38.4    | 1.082       |
| raw TAGN                 | 504.7    | 166.01                           | 124.80                           | 41.21                                    | 170.20               | 40.81   | 1.270       |

Figure 7. DSC-IR analysis: (a, d) DSC traces; (b, e) total absorbance of gas products; and (c, f) IR spectra of gas products.
values for nano and raw TAGN are higher than those of pure AN. These results reluctantly confirm the superiority of the decomposition of [90% AN + 10% (nano TAGN)] beyond the decomposition of pure AN in kinetics. Figure 6f shows the plot of \( \ln A_0 \) vs \( E_p \), i.e., the kinetic compensation effect. Except the point of pure AN, other points present good linear relationships. This implies that the decompositions of raw TAGN, nano TAGN, and [90% AN + 10% (nano TAGN)] have similar kinetic mechanisms. At least, in mathematics, thermolysis of [90% AN + 10% (nano TAGN)] is similar to that of TAGN. Although kinetic mechanism cannot be equated with chemical mechanism, we could also conclude that there is a great similarity between thermolysis of [90% AN + 10% (nano TAGN)] and TAGN. To disclose the relationship, DSC-IR analyses are conducted, and the results are shown in Figure 7. Other thermodynamic parameters, such as \( \Delta H^o, \Delta G^o \), and \( \Delta S^o \), show the same meaning and change rules as the parameter in Table 1, and I will not repeat it here.

In Figure 7a–c, the spectra indicate that a large amount of gas evolves in the temperature range of 238.7–322.1 °C, attributing to thermal decomposition of pure AN. The main decomposition products are \( \text{N}_2, \text{H}_2 \text{O} \), and \( \text{H}_2 \text{O} \). According to the radical mechanism for thermal decomposition of AN (eqs 13–15), ammonium nitrate first dissociates to \( \text{NH}_3 \) and \( \text{HNO}_3 \) with 2.18 kJ g\(^{-1}\) heat absorption; at elevated temperature, \( \text{HNO}_3 \) decomposes to \( \text{OH} \) and \( \text{NO}_2 \) with a molecular homolysis; \( \text{OH} \) reacts with \( \text{NH}_3 \) to produce \( \text{NH}_2 \) and \( \text{H}_2 \text{O} \), and \( \text{NH}_3 \) is oxidized by \( \text{NO}_2 \) to form \( \text{N}_2 \) and \( \text{H}_2 \text{O} \). In Figure 7c, there is no signal of \( \text{NH}_3 \) which means that all \( \text{NH}_3 \) is oxidized by decomposition products of nitric acid. This also implies that \( \text{NH}_3 \) reacts with decomposition products of \( \text{HNO}_3 \) instantaneously, which is not the rate-limiting step. The controlling step for thermolysis of AN is the homolysis of nitric acid.\(^{54} \) Because of the positive oxygen balance of AN (+20%), the remaining nitric acid does not decompose and is detected as a product of thermolysis of pure AN.

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3 + 2.18 \text{kJ g}^{-1} \tag{13}
\]

\[
\text{HNO}_3 \rightarrow \cdot \text{OH} + \text{NO}_2 \tag{14}
\]

\[
\text{NH}_3 + \cdot \text{OH} \rightarrow \cdot \text{NH}_2 + \text{H}_2\text{O} \tag{15}
\]

\[
\text{NH}_2 + \text{NO}_2 \rightarrow \left[ \text{NH}_2\text{NO}_2 \right] \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \tag{16}
\]

Decomposition of [90% AN + 10% (nano TAGN)] is very different from the decomposition of pure AN. Its main products are \( \text{N}_2\text{O}, \text{CO}_2 \), and \( \text{H}_2\text{O} \), and few \( \text{NH}_3 \) are detected. Please note that as mentioned above, herein, the key factor is the formation of \( \text{NH}_3 \). These \( \text{NH}_3 \) are derived from the decomposition of TAGN rather than from the decomposition of AN because no \( \text{NH}_3 \) is detected in the decomposition of pure AN. Just like eqs 6–9, \( \text{NH}_2 \) radicals splitting from \( \text{TAGN} \) combine with \( \text{H}_2\text{N}–\text{NH}_2 \). Hydrazine has quite high reactivity as a fuel. In fact, hydrazine ignites instantaneously when it comes in contact with an oxidizer like nitric acid.\(^{55} \) Thus, in Figure 7f, no \( \text{HNO}_3 \) is detected, and all \( \text{HNO}_3 \) directly reacts with hydrazine and ammonia, i.e., \( \text{HNO}_3 \) can be consumed directly without having to be decomposed. This changes the rate-limiting step of the decomposition of AN. The remaining hydrazine decomposes to \( \text{NH}_3\text{N}_2 \) and \( \text{H}_2 \) as eq 9. \( \text{NH}_3 \) and \( \text{H}_2 \) are nonpolar molecules, which cannot be detected by infrared spectrometer, but \( \text{NH}_3 \) is detected. This is the proposed mechanism of how thermolysis of TAGN affects thermolysis of AN.

2.4. Energy Performance. In this work, to clearly study the catalysis mechanism of nano TAGN more clearly, the introduction of nano TAGN is up to 10 wt %. Thus, the evaluation of energy performance is very important. Herein, using AP or AN as the oxidizer and glycidyl azide polymer (GAP) as the binder, we calculate the energy performance of
propellants doped with different catalysts, and the results are listed in Table 3; meanwhile, the combustion products and their molar ratio for some propellants are also calculated, and the results are shown in Figure 8. For formula of AP0.8/GAP0.2, its standard specific impulse ($I_{sp}$) is 2438.3 N s kg$^{-1}$. When 10% AP is replaced by TAGN, the $I_{sp}$ value increases to 2498.0 N s kg$^{-1}$. This is not because TAGN is a high-energy material, but rather due to the change of the oxygen balance from positive value to negative value. Figure 8a discloses that AP0.8/GAP0.2 is a formula with positive oxygen balance because 2.7 mol % O$_2$ exists in its combustion products. The propellants with positive oxygen balance and zero oxygen balance usually are of low energy performance. Other than AP0.8/GAP0.2, the combustion of AP0.7/TAGN0.1/GAP0.2 produces some CO and H$_2$, which confirms that it is a negative oxygen balance formula. The oxygen balance, formation heat, and explosion heat of TAGN are $-33.4$ ($\text{OB}_{\text{CO}_2}$), $-280.6$, and 3472 kJ kg$^{-1}$, respectively. Thus, it is not counted as a high-energy material just like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). Formulas of AP0.7/RDX0.1/GAP0.2 and AP0.7/HMX0.1/GAP0.2 show somewhat higher energy performance than AP0.8/TAGN0.1/GAP0.2. But TAGN should not be devoid of any merit for energy performance. The contribution of TAGN to energy performance results from its higher hydrogen content (5.4 wt % of TAGN to 3.4 wt % of AP). Increasing hydrogen content is very effective for enhancing the specific impulse of propellants due to the increase of energy conversion efficiency in combustion process of propellants. The higher energy conversion efficiency means that the same heat energy, released from combustion of propellants, does more works. Roughly, an increase of 1.0 wt % hydrogen is equivalent to an increase of 2000 kJ kg$^{-1}$ formation enthalpy when the oxygen balance is similar. However, increase of hydrogen content also means decrease of combustion heat of propellants. Hence, despite lower hydrogen content (2.7 wt % of RDX and 2.7 wt % of HMX), RDX and HMX have a greater contribution to energy performance when the oxygen balance is similar because they are of very high explosion heats. Additionally, introduction of catalysts such as Fe$_2$O$_3$, CuO, NiO, Fe, Cu, and Ni, which could promote the decomposition or combustion performance of AP or AP-based propellants, results in a remarkable penalty on the energy performance of propellants.

The case of AN-based propellants shows a similar situation to AP-based propellants. First, note that other than AP-based propellants, the formula AN0.7/TAGN0.1/GAP0.2 is of lower energy performance than AN0.8/GAP0.2. Because the oxygen balance of AN (+20%) is lower than the OB of AP (+34%), AN0.8/GAP0.2 is a negative oxygen balance formula in comparison with the positive oxygen balance formula AP0.8/GAP0.2. The chemical energy and the energy conversion efficiency reach a balance, at which the propellant shows high combustion temperature ($T_c$) and low average molecular weight of products ($M_c$). When replacing 10 wt % AN with TAGN, oxygen balance is more negative, which does not benefit from the release of chemical energy. Meanwhile, due to the low explosion heat of TAGN (3472 kJ kg$^{-1}$), the $T_c$ and $Q_p$ of AN0.7/TAGN0.1/GAP0.2 are obviously lower than those of AN0.8/GAP0.2. However, because the hydrogen content of TAGN (5.4 wt %) is slightly higher than that of AN (5.0 wt %), $M_c$ of AN0.7/TAGN0.1/GAP0.2 is lower than that of AN0.8/GAP0.2. Figure 8c,d illustrates that the combustion of AN0.7/TAGN0.1/GAP0.2 produces more H$_2$, CO, and N$_2$ and less CO$_2$ and H$_2$O, which is beneficial to the increase of energy conversion efficiency of propellants. But the improvement of energy conversion efficiency still cannot offset the reduction of chemical energy. Thus, $I_{sp}$ of AN0.7/TAGN0.1/GAP0.2 is still lower than $I_{sp}$ of AN0.8/GAP0.2. For formulas of AN0.7/RDX0.1/GAP0.2 and AN0.7/HMX0.1/GAP0.2, despite the lower hydrogen content, they have higher specific impulse because of their very higher explosion heat of RDX (6192 kJ kg$^{-1}$) and HMX (6317 kJ kg$^{-1}$).
Hence, it almost concludes that the introduction of TAGN would not render some improvement to the energy performance of propellants, but due to its energetic property and high hydrogen content, proper introduction of TAGN will not reduce the energy performance of propellants too much. Moreover, similarly to AP-based propellants, doping with inertia catalysts such as Fe₂O₃, CuO, NiO, Fe, Cu, and Ni greatly reduces the energy performance of AN-based propellants.

3. Conclusions

Herein, as an accelerator for thermal decomposition of AP and AN, nano TAGN with high reactivity and energetic property was fabricated by mechanical milling method. Samples [90% AP + 10% (nano TAGN)] and [90% AN + 10% (nano TAGN)] were prepared via doping nano TAGN with AP and AN, respectively. The decomposition temperatures of [90% AP + 10% (nano TAGN)] and [90% AN + 10% (nano TAGN)] advance obviously compared to pure AP and AN, i.e., nano TAGN promoted thermolysis of AP and AN.

Another investigation lies in the disclosing of decomposition mechanisms of nano TAGN, pure AP, [90% AP + 10% (nano TAGN)], pure AN, and [90% AN + 10% (nano TAGN)]. It is found that there are many NH₂ formed in the decomposition of nano TAGN. TAGN does not contain the group such as NH₄⁺, which could dissociate to NH₂ at decomposition temperature. Thus, we suggested that radicals *NH₂ splitting from TAGN molecules combine with each other to form hydrazine (H₂N—NH₂). Hydrazine was oxidized by HNO₃ and HClO₄ spontaneously and quickly. The process releases many heats and accelerates thermolysis of AP and AN in kinetics. Meanwhile, some hydrazine decomposed to NH₂, N₂, and H₂ at high temperature simultaneously, which was detected by an infrared spectrometer. This is the key mechanism of how nano TAGN promotes thermolysis of AP and AN, and the speculation was also confirmed by the IR spectra for other decomposition products of samples.

Third, using AP or AN as the oxidizer, GAP as the binder, and TAGN as the catalyst, the energy performances of the propellants were calculated. It almost concludes that the introduction of TAGN would not render some improvement to the energy performance of propellants, but due to its energetic property and high hydrogen content, proper introduction of TAGN will not reduce the energy performance of propellants too much. Moreover, the combustion temperature of the propellants doped with TAGN is much lower. Therefore, nano TAGN is expected to be used as a coolant in propellants, which should not only improve combustion performance but also ensure a relatively high energy performance.

4. Experimental Section

4.1. Materials. Ammonium perchlorate (AP), ammonium nitrate (AN), ethanol (EtOH), and hydrazine hydrate (80%) are bought from Tianjin Guangfu Chemical Co., Ltd. Guanidine nitrate is bought from Zibo Nano Industry and Trade Co., Ltd., China (http://www.xiaoosuangua.com/).

4.2. Fabrication of Nano TAGN. Materials of 60 g of guanidine nitrate, 50 g of AN, 125 mL of hydrazine hydrate, and some deionized water are added into a 200 mL round-bottom flask. The flask is heated to 90–100 °C, and the temperature is maintained for 15 min. A lot of bubbles (ammonia gas) generated at this time. When there are no bubbles generating, heating is stopped, and the reaction is complete. After the temperature of the flask decreases to ambient temperature, the flask is put into an ice—water bath (0–5 °C). Gradually, a lot of white crystals precipitate out. After filtering, washing (by EtOH), and freeze drying, raw TAGN is obtained. The raw TAGN is pulverized to nano TAGN upon a high-energy ball mill (YXQM-1L) manufactured by Changsha MISTR Instrument and Equipment Corporation, China.

4.3. Characterization. Surface morphology of nano TAGN particles is investigated with a scanning electron microscope (JEOL JSM-7500). Crystal phase of nano TAGN is studied using an X-ray diffractometer (Bruker Advance D8). The molecular structure of nano TAGN is probed with an infrared spectrometer (Nicolet 6700). Surface elements of nano TAGN are studied with an X-ray photoelectron spectroscope (ULVAC-PHI). DSC analysis (TA Q600) is employed to investigate thermal decomposition of samples. DSC-IR analysis (Mettel Toledo) is recruited to investigate the decomposition products of samples.

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Notes
The authors declare no competing financial interest.

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