The influence of nanoxide additives on the characteristics of thermal decomposition of ammonium nitrate

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Abstract. Thermal decomposition of ammonium nitrate (NH₄NO₃) containing 5% (by weight) of catalytic additives in the form of metal oxides (NiO, CuO, Co₃O₄) has been studied. The experiment was performed by thermogravimetric analysis at a heating rate of 5°C/min to a maximum temperature of 800°C in argon atmosphere. Based on the results of DTA, physical and kinetic characteristics of thermal decomposition we analytically assessed. The addition of catalytic agents was found to lead to a decrease of onset temperature of active NH₄NO₃ decomposition, which promotes the reaction shift to the low-temperature region. The effect of the initiation additive manifested in a significant reduction of sample residence time within preheating stage (Δtᵢ = 5.2 min). In presence of catalytic additives the total time of thermal decomposition tᵣ was found to decrease. The greatest change of Δtᵣ (2.8 minutes) was recorded for the sample modified by addition of Co₃O₄. The maximum decrease of the average activation energy (for decomposition of 5%Co₃O₄/NH₄NO₃) was 14.2 kJ/mol.

Introduction

Ammonium perchlorate is used as the main oxidizer of most solid rocket fuels. Its combustion products are toxic and environmentally harmful [1]. In search of a way to solve this problem, scientific works aimed at finding alternative solutions for obtaining "green" energy systems (ES) are being conducted. Potential substitute of ammonium perchlorate, during decomposition of which HCl [1] is released, is ammonium nitrate – NH₄NO₃. Despite poor flammability, low burning rate and hygroscopicity [2] (compared to ammonium perchlorate), ammonium nitrate is an inexpensive and environmentally friendly material. With variations in composition (type) of additives, rate of thermal decomposition of ammonium nitrate can vary over a wide range [2]. According to [3] nanodispersed powders of Cu and Ni metals (and their combined use) exert an accelerating effect on thermal decomposition of NH₄NO₃. Promotion of the process manifests in displacement of initial decomposition temperature of ammonium nitrate into the region of lower temperatures. These catalytic additives also contribute to a decrease of temperature corresponding to the maximum heat release. At the same time, metal oxides, known for their ability to accelerate various solid-phase transformations, are also of interest as possible agents promoting decomposition of inorganic salts [4]. In this paper, results of experimental study of NH₄NO₃ thermal decomposition features are presented under catalytic action of a small amount of nanodispersed metal oxides - NiO, CuO and Co₃O₄.
1 Experimental part

1.1 Characteristics of researched samples
Ammonium nitrate powder (GOST 22867-77) was used as initial sample of ES. Nanooxide additives were synthesized by precipitation from an aqueous solution of the corresponding salts (nitrates). A 0.5 M solution of sodium carbonate was used as a precipitant. Obtained settlings were washed carefully, dried for 24 hours at room temperature and then calcinated at 500°C (2 hours). Figure 1 shows TEM images, according to which the average primary particle size of the samples was 10-30 nm.

![TEM images of nanooxides](image)

**Figure 1.** Nanodisperse oxides of nickel (A), copper (B) and cobalt (C) obtained by precipitation. TEM data

Table 1 summarizes x-ray diffraction analysis of synthesized catalytic additives obtained by Shimadzu XRD-7000S diffractometer (Shimadzu, Japan). It can be seen that all samples are single-phase oxides: NiO, CuO and Co$_3$O$_4$. The size of primary crystallites (coherent scattering region, CSR) lies in the range of 10-22 nm.

| Name of catalytic additive | Phases content, % | Lattice parameters, Å | Crystallites size by CSR, nm |
|---------------------------|------------------|-----------------------|-----------------------------|
| Co$_3$O$_4$               | 100              | a=8.0691              | 10                          |
|                           |                  | a=4.6779              |                             |
|                           |                  | b=3.4266              |                             |
|                           |                  | c=5.1232              |                             |
|                           |                  | $\beta=99.3637$       |                             |
| CuO                       | 100              | a=4.1734              | 22                          |
| NiO                       | 100              | a=4.1734              | 15                          |

1.2 Application of catalytic additive
The catalytic additive was applied to the sample by mechanical mixing. NH$_4$NO$_3$ powder was vigorously stirred for 5 minutes with metal oxides (CuO, NiO, Co$_3$O$_4$). Mass fraction of catalytic additive in the obtained mixture was 5%. Reference sample (without additives) was prepared for comparative analysis and subjected to exactly the same treatment procedures.

1.3 DTA and MS analyses
Thermal decomposition of ammonium nitrate samples (initial and modified samples) was studied by means of STA 449 C Jupiter synchronous thermal analyzer (Netzsch, Germany), were conducted under the same conditions, at a heating rate of 5°C/min in a corundum crucible with perforated cover (sample weight of ~5 mg) in the temperature range of 45-600°C. Inert gas, argon (60 ml/min), was used as a gas medium. Qualitative determination of NO$_x$ in the composition of gas phase products was
performed during thermal conversion of researched samples with the use of STA in the form of QMS 403 D Acelos quadrupole mass spectrometer (Netzsch, Germany). All experiments were conducted at atmospheric pressure.

1.4 Determination of physical parameters and kinetic analysis of the process

Physical parameters of thermal decomposition of researched samples were determined graphically (Figure 2) with the help of obtained TG and DTG curves. Points A and B on TG curve characterize onset temperature of ammonium nitrate thermal decomposition (T_i) and the end of sample's mass loss (T_f). Characteristic point C lying on DTG curve corresponds to the maximum value of reaction rate (w_{max}) and temperature (T_{max}) at the given moment.

![Figure 2. TG and DTG curves of thermal decomposition of an unmodified sample of ammonium nitrate in inert medium](image)

Dependence of the activation energy of oxidation process (E_a) on conversion was determined in this paper using the Friedman method [5]. This method is based on the following equation obtained by converting the Arrhenius equation:

\[
\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,i} = \ln \left[ f(\alpha) \cdot A_\alpha \right] - \frac{E_\alpha}{RT_{\alpha,i}}
\]

here \( \frac{d\alpha}{dt} \) is the sample conversion rate at the moment of conversion level \( \alpha \) with heating rate \( i \), K/min; \( f(\alpha) \) is the value of kinetic function corresponding to the value of conversion level \( \alpha \); \( A_\alpha \) is the pre-exponent corresponding to the value of conversion level \( \alpha \), 1/s; \( E_\alpha \) is the activation energy corresponding to the value of conversion level \( \alpha \), J/mol; \( R \) is the absolute gas constant, J/(mol·K); and \( T_{\alpha,i} \) is the temperature of the sample when conversion level is \( \alpha \) with heating rate \( i \), K/min. Values of kinetic constants corresponding to each level of conversion were determined using linear approximation constants of experimental dependence \( \ln \left( \frac{d\alpha}{dt} \right) \) on \( 1/T \). To determine the values of pre-exponential factor of the reaction rate constant, kinetic model of the first order reaction was used [6]: \( f(\alpha) = (1-\alpha) \). Dependences of kinetic parameters on conversion were determined with steps of 0.05 in the range of 0.05–0.95, according to recommendations presented in [6].

2 Results and discussion

2.1 Effect of initiation additive on coal oxidation and pyrolysis

Figure 3 shows experimental TG, DTG and DSC curves of NH_4NO_3 thermal decomposition in the presence of catalytic additives. It follows from the results that samples modified by additives of metal oxides have different nature of thermal decomposition in contrast to the reference sample.
Analysis of obtained results (Figure 3) allows distinguishing four endothermic stages of mass change of the initial sample: 1) loss of physically adsorbed moisture (up to 100°C); 2, 3) phase transition and melting of NH₄NO₃ (characteristic DSC curve peaks (Figure 3C) at 125°C and 166°C); and 4) thermal decomposition of NH₄NO₃ (230-320°C) [7]. It also follows from Figure 3 that promotion of NH₄NO₃ sample by metal oxides additions initiated thermal decomposition process at a lower temperature. Thus, the greatest displacement of the initial decomposition temperature $\Delta T_i$ is observed for the sample modified by addition of Co₃O₄ ($\Delta T_i^{Co_3O_4} = 26^\circ C$), while the minimum effect is established for the sample containing NiO additive ($\Delta T_i^{NiO} = 8^\circ C$).

Similar dependence of $\Delta T_i$ on the type of additive (Figure 3A) also appeared for characteristic points on DTG curves corresponding to the maximum decomposition rate of NH₄NO₃ (Figure 3B). The largest change of parameter $T_{max}$ (temperature corresponding to the highest reaction rate) was 31°C (Table 2). It should be noted that the position of endothermic maxima on DSC curves (Figure 3C) differs from the values of $T_{max}^{DTG}$ corresponding to the maximum rate of thermal decomposition (Figure 3B). Endothermic effects observed in figure 3C were associated with destruction of ammonium nitrate. With an increase of catalytic additive activity, the tendency of characteristic curve to shift into the region of lower temperatures was intensified. This effect was most pronounced in case of thermal decomposition stage, for which displacement of extremum $\Delta T_{max}^{DSC}$ was 28°C.

### 2.2 MS-analysis

Figure 4 shows mass-spectrometric curves corresponding to formation of gaseous reaction products - nitrogen oxides NOₓ.

![Figure 4. MS-curves of NOₓ formation in the composition of gas-phase products of catalytic thermal decomposition of NH₄NO₃](image-url)
Results of mass-spectrometric data analysis (temperature of the extrema characterizing maximum intensity of NOx release during decomposition of researched samples) are summarized in table 2.

**Table 2.** Effect of nanooxide additives on the nature of NOx formation during catalytic thermal decomposition of NH4NO3

| Parameter | AN | AN+NiO | AN+CuO | AN+Co3O4 |
|-----------|----|--------|--------|-----------|
| T_{max1} (°C) | 250 | 238 | 234 | 224 |
| ΔT_{max1} (°C) | - | 12 | 16 | 26 |
| T_{max2} (°C) | 306 | 298 | 287 | 265 |
| ΔT_{max2} (°C) | - | 8 | 19 | 41 |

It can be seen from Figure 4 that the release of NOx, the main decomposition product of ammonium nitrate, is characterized by a bimodal curve. Application of catalytic additives helps to reduce temperature of decomposition beginning of NH2NO3, which, consequently, leads to proportional displacement of extrema, characterizing NOx release in the low-temperature area. The greatest shift of NOx release is observed for a sample modified by addition of Co3O4 (Δ\text{NOx}^{max1} = 26°C and Δ\text{NOx}^{max2} = 41°C), which correlates with DTA results (Figure 3). Nature of NOx release indicates that thermal decomposition of NH4NO3 in the presence of metal oxides begins already at ~145°C, which is explained by catalytic action of nanodispersed oxide materials.

2.3. Analysis of changes in characteristics of thermal decomposition of NH4NO3

Characteristics thermal decomposition of NH4NO3 with catalytic impact of nanodispersed metal oxides are presented in table 3.

**Table 3.** Physical characteristics of the process

| Sample     | T_{ν}, °C | T_{ν}, °C | W_{max}, °C/min | T_{max}, °C | t_{ν}, min | t_{ρ}, min | ΔT_{ν}, °C | ΔT_{ρ}, °C | Δt_{ν}, min | Δt_{ρ}, min |
|------------|-----------|-----------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| AN         | 256       | 330       | 14              | 300         | 42,2        | 14,8        | -           | -           | -           | -           |
| AN+NiO     | 248       | 320       | 17              | 288         | 40,6        | 14,4        | 8           | 10          | 1.6         | 0.4         |
| AN+CuO     | 237       | 302       | 24              | 274         | 38,4        | 13,0        | 19          | 28          | 3.8         | 1.8         |
| AN+Co3O4   | 230       | 290       | 27              | 269         | 37,0        | 12,0        | 26          | 40          | 5.2         | 2.8         |

Analysis of the obtained results (Table 3) leads to a conclusion that application of small amount of metal nano-oxides contributes to noticeable activation of thermal decomposition of ammonium nitrate, which is expressed in a decrease of its decomposition temperature. This in turn leads to the corresponding decrease of sample residence time in preheating region t_{ν}. It should also be noted that application of additives contributes to a decrease of sample total residence time, from the beginning of decomposition to appearance of mineral residue t_{ρ}, which allows concluding that the average rate of the process is increasing. Figure 5 shows results of changes in the activation energy of initial and modified by cobalt oxide samples of ammonium nitrate determined by the Friedman method. Coefficient of determination for all obtained approximations was higher than 0.99.

Three characteristic stages can be distinguished for the initial sample of NH4NO3 corresponding to three maxima in the range of conversion levels 3 – 0.15-0.25, 0.30-0.60 and 0.70-0.95. It can be seen that application of 5% Co3O4 leads to a decrease of activation energy at all three stages (Figure 5). An average decrease of activation barrier due to catalytic action of Co3O4 was 14.2 kJ/mol. Maximum difference between the values of activation energy for initial and modified samples was ~35 kJ/mol at conversion level of 0.80.
Figure 5. Effect of catalytic additive (Co₃O₄) on the dependence of activation energy on conversion for thermal decomposition of NH₄NO₃ catalytic additive (Co₃O₄)

Conclusion
As a result of the research it has been shown that application of catalytic additives in the form of metal oxides (5% by weight) to ammonium nitrate helps to lower the temperature corresponding to the onset of active decomposition of NH₄NO₃. The greatest change of onset temperature refers to the sample modified by addition of Co₃O₄. In general, results of studying the thermal decomposition of samples by DTA method served to determine the following order of "activity" of catalytic additives: NiO<CuO<Co₃O₄. According to mass spectrometric and thermogravimetric analysis, the decrease of onset decomposition temperature of ammonium nitrate is accompanied by a shift to lower temperatures of NOₓ release extreme points having bimodal distribution. Results of activation energy calculations allow concluding that application of metal oxides as catalytic additives contributes to reduction of kinetic barrier of NH₄NO₃ thermal destruction, which ultimately leads to a significant acceleration of decomposition process as a whole and its shift to the low-temperature region.

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