Research of the laws of combustion catalysis of mixed systems based on various oxidizing agents in a wide pressure range

Gulakov M. Yu.

Relevance of the research topic

Gunpowder and solid composite propellants are the energy basis of all types of weapons, as well as many devices used for civilian purposes (in gas generators, car airbags, fire-extinguishing systems, anti-hail and geophysical rockets, etc.).

One of the most important characteristics of powders and fuels that determine the design features of various systems and their effectiveness is the burning rate and its dependence on the pressure and initial temperature of the charge.

For ballistic missile propellants (BRTT), regulation of these characteristics is mainly achieved by introducing combustion catalysts into their composition. This problem was solved at the Mendeleev Russian Technical University, FCDT Soyuz etc. organizations. Practically all BRTS contain catalysts that ensure the necessary patterns of their combustion.

The possibilities of targeted regulation of the ballistic characteristics of fuels have increased significantly as a result of the conditions established in the work of the MUCTR, ensuring high efficiency of the catalysts:

1) a carbon black frame should form on the combustion surface, on which a significant accumulation of catalyst particles occurs.
2) The coefficient of thermal conductivity of this frame should be higher (by ~ 3 times or more) than the coefficient of thermal conductivity of the gas zone above the combustion surface.

In this case, the main amount of heat required for the propagation of combustion enters the condensed phase (c-phase) from the zone of the frame, which becomes the leading one. Obviously, in order to reduce the value of v in the combustion law ($U=BP^{v}$), the effectiveness of the catalyst decreases significantly with increasing pressure.

When solving this issue, it can be concluded that there are uniform conditions for the catalysis of combustion of energy-saturated systems, during combustion of which heat release occurs as a result of redox reactions. This will make it possible to more purposefully regulate their burning rate.

The degree of development of the topic

Recent work by the MUCTR has shown that the combustion of various nitro compounds is catalyzed by the same mechanism as for double-base propellants. Therefore, the question naturally arises whether the same mechanism of combustion catalysis can be manifested for mixed systems based on various oxidizing agents.

In the works of Sinitsky V.P. and his collaborators, it is only assumed that the combustion catalysis of systems based on ammonium perchlorate (AP) can occur in the same way as for BRTT. The same results have been shown in isolated studies of the MUCTR, but experimental studies have not been conducted in this regard.

Regarding fuels used for civilian purposes, it should be noted that they should have low sensitivity to various influences and their combustion products should not contain environmentally harmful substances. It is also important that they have a low cost. Obviously, these fuels require the ability to regulate their burning rate. In this regard, fuels based on ammonium nitrate are of undoubted interest. Previously at the D.I. RSTU. It was shown by Mendeleev that this can be achieved using a combined catalyst consisting of nickel carbonate and potassium bichromate, and especially in combination with carbon black. However, when they burn, toxic products (Cr_2O_3 and Ni) are formed. The effect of combined catalysts in combination with carbon nanotubes (CNTs) and the sensitivity of fuels to mechanical stress has also not been studied.

Purpose and tasks of the work

The purpose of this work was:

1. Experimentally find out the applicability of the mechanism of catalysis of combustion of BP and nitro compounds to the catalysis of combustion of mixed systems based on AP.

To achieve this goal, the following tasks were solved in the work:

• To establish the role of carbon materials in the combustion catalysis of mixed samples with different oxidant excess coefficients (α=0.54; α=0.99).

• To study the effect of combustion catalyst and CNT (without catalyst) on the parameters of the combustion wave of mixed fuels based on ammonium perchlorate.

• Investigation of the structure and composition of the combustion surface of extinguished fuels based on ammonium perchlorate.

2. Another purpose of the work was to develop a fuel with a high content of ammonium nitrate for civilian use.

To achieve this goal, the following tasks were solved in the work:

• Study of the effect of carbon nanotubes on the effectiveness of ammonium nitrate-based fuel combustion catalysts.

To study the possibilities of reducing the sensitivity to mechanical effects (impact and friction) of fuels based on ammonium nitrate.

• To investigate the effect of additives on the combustion patterns of ammonium nitrate-based fuels containing explosives and metallic fuels.

Scientific novelty of the work

• It has been shown for the first time that for the studied model samples, as well as for BRT, the effectiveness of the catalysts depends on the energy and rate of combustion of the base composition. The higher these parameters, the less the influence of the catalysts and the smaller the pressure range in which their action is manifested.

• For the first time, it has been experimentally established that the combustion of fuels based on AP occurs by the same mechanism as for BRT, i.e., a carbonaceous frame forms on the combustion surface, on which a significant accumulation of catalyst particles occurs, which accelerate the interaction of the oxidizer and fuel decomposition products and increase its thermal conductivity. Combustion of the catalyzed sample occurs according to the gas-phase model as well as the sample without a catalyst.

• It has been shown for the first time that the addition of copper oxide can have a double effect: at low pressure, it is a combustion catalyst, and with increasing pressure, it is a heat–conducting element.

• For the first time, the patterns of catalysis of combustion of fuel based on AN in a wide pressure range (0.1-200 MPa) have been investigated.

• For the first time, it has been shown that iron salicylate is the most effective catalyst among the studied environmentally friendly additives (reduces v from 0.92 to 0.43).

• It has been shown for the first time that when 20% octogen is introduced into the fuel (T = 2559 K) by reducing the amount of AN, the fuel combustion rate increases, which leads to a decrease in v from 0.92 to 0.32. On the contrary, metallic fuel (ASD-4 or AMD-10) reduces the effectiveness of the combined catalyst.

• It has been shown that catalysts have little effect on the catalysis of high-energy fuels (T = 3298 K) with 15% metallic fuel and 20% octogen (due to a decrease in ammonium nitrate) due to a deterioration in the formation of a carbon skeleton. This is due to the high temperature and increased rate of combustion, as well as the accumulation of metal particles on surface, which make it difficult for reacting molecules to access the catalyst.

Theoretical and practical significance of the work

The theoretical significance of the work lies in the fact that, based on previously obtained data on the catalysis of combustion of ballistic powders, various individual nitro compounds, and the data from this work on the catalysis of combustion of

mixed samples based on perchlorate and ammonium nitrate, it can be assumed that the mechanism of catalysis of combustion of energy materials is unified. Based on this conclusion, it is possible to predict the possibility of catalysis of systems or individual substances. For example, catalysts do not affect the rate of combustion of nitroguanidine, since it contains only 11.5% carbon. The addition of CNT to the catalyst makes it possible to increase burning rate by ~4 times.

This conclusion is also of practical importance, since understanding the unified mechanism of combustion catalysis makes it possible to purposefully and cost-effectively address issues related to the regulation of the combustion rate of compounds and reduce its dependence on pressure for a wide variety of systems.

Based on the data obtained on the complex of various characteristics of ammonium nitrate-based fuels, a patent was obtained for formulations with a controlled combustion rate and a reduced dependence on pressure, with low sensitivity to mechanical action and with environmentally friendly combustion products for use in various gas generators and rockets for civilian use.