ABSTRACT

of dissertation for the degree of Doctor of Philosophy (PhD)
6D073400 – Chemical technology of explosives and pyrotechnics
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New nano metal-organic framework energy materials for pyrotechnics

General characteristics of the work. This dissertation work is devoted to the development of highly effective catalytically active energy additives for enhancement of the basic characteristics of the combustion process of pyrotechnic compositions. The goal was solved by the development of metal-organic framework structures (MOF) based on renewable raw materials such as rice husk with addition of transitional metal oxides and the study of the MOF effect on the kinetics of the thermal decomposition process and combustion of a pyrotechnic composition based on ammonium nitrate.

Relevance of the research topic. Energy materials are materials with a high content of accumulated internal energy which can be released during a chemical reaction. The list of energy materials includes hydrocarbon fuel, rocket fuel, explosives, pyrotechnic compositions, etc. Energy materials consist of chemical compounds which are combustible and oxidizing substances while entering into a chemical reaction, intensively release energy. These materials differ in energy intensity - the amount of energy released during complete combustion relative to their specific volume. An intensive search for new compositions to increase the energy intensity of energy materials is carried out without compromising their important characteristics, such as decomposition initiation temperature, burning rate and temperature, as well as environmental protection. One of the ways to increase the efficiency and optimize the properties of energy materials is to use nanosized transitional metal oxides as catalytic additives as well as various carbon-containing materials.

Currently, pyrotechnic compositions are widely used in many industries as pyro automatics, pyrotechnic heaters, airbags, igniters in rocket engines, fireworks, compositions causing rainfall to extinguish fires, etc. In this regard, the development of environmentally friendly pyrotechnic compositions with predetermined performance characteristics is an urgent task. To solve this problem, one of the promising areas is the development of special additives for pyrotechnic compositions that would allow to adjust the main parameters, such as the initial decomposition temperature, ignition delay time, burning rate, the formation of toxic gases and pressure increase (in order to prevent transition combustion process in explosive mode). To optimize the characteristics of pyrotechnic compositions, the most promising materials as catalytic additives are metal oxides nanoparticles. In turn, the process of adding nanosized additives to a powdery material is always complicated by the processes of aggregation and agglomeration of introduced nanoparticles, which leads to uneven distribution in the bulk of the powder material. To prevent the agglomeration process, methods of fixing nanoparticles in the pores can be used. Carbon porous materials are characterized by a fairly ordered structure, and the content of many surface defects allows various metal centers to be embedded in their structure and thus create metal-organic framework structures (MOFs) based on them, which have a number of unique properties, such as ordered crystalline structure, strong metal-ligand interaction, high porosity and high specific surface area. Moreover, the use of highly porous systems with an ordered structure also helps to achieve a uniform local distribution of active centers on their surface, which can significantly increase the efficiency of the catalysts. Thus, the possibility of changing the catalytic activity of MOF by introducing specified metal centers into their structure defines these materials as the most promising as catalytic additives for improving the performance of pyrotechnic compositions.

A promising and economically effective method for the production of porous carbon materials with a high specific surface is to obtain it from renewable plant waste. In this connection, research was conducted on the development of new MOFs based on renewable raw materials such as rice husk with addition of nanosized metal oxides and their influence on the main characteristics of the combustion process of pyrotechnic compositions was studied.

The purpose of research. To develop metal-organic framework structures (MOF) based on waste plant materials and metal oxide nanoparticles and explore the possibilities of their use to increase the burning rate, lower the decomposition temperature of pyrotechnic compositions.

Tasks of research. To achieve this goal, the following tasks were set:

1. To develop a metal-organic framework structure (MOF) based on waste plant materials with addition of metal oxide nanoparticles;

2. To study the kinetics of thermal decomposition of a pyrotechnic composition based on ammonium nitrate with addition of various metal oxides in the presence of metal-organic framework structure (MOF);

3. To determine the effect of a metal-organic framework structure (MOF) with addition of various nanoparticles of metal oxides on the combustion conditions of pyrotechnic compositions at initial pressures from 1 to 3.5 MPa;

4. To study the possibilities of initiating the combustion process of a pyrotechnic composition by laser radiation with the addition of a metal-organic framework structure (MOF);

5. Determine the effect of the metal-organic framework structure (MOF) on the activation energy of the AN/Mg/NC pyrotechnic composition.

The main provisions for the thesis defense.

1. Prevention of the process of agglomeration of metal oxide nanoparticles by the isolated distribution of nanoparticles in a porous carbon matrix increases the catalytic activity of the developed metal-organic framework structures (CRH/Me_xO_y).

2. Achieving a high burning rate of the pyrotechnic composition to 20.5 mm/s, with a low-pressure value *n*=0.42 by adding a metal-organic framework structure (CRH-CuO) at an initial pressure in the system of 3.5 MPa.

3. Ensuring the reduction of the activation energy of the pyrotechnic composition to 8 kJ/mol by the introduction of an additive of a metal-organic framework structure (CRH-CuO).

4. Ensuring the ignition of the pyrotechnic composition by laser initiation using a metal-organic framework structure without adding optical sensitizers with an ignition delay time of 506 ms at a laser energy of 4.35 J.

Object of the study. Metal-organic structural composites (MOF) based on carbonized rice husk with the addition of nanosized transition metal oxides (CuO, NiO, FeO, TiO, Zr_2O) and pyrotechnic compositions based on them containing ammonium nitrate, magnesium, and cellulose nitrate (AN/Mg/NC).

Subject of study. Study of the specific effect of MOF (CRH/Me_xO_y) on the kinetics of thermal decomposition of the pyrotechnic composite (AN/Mg/NC) and the promoting effect of MOF (CRH/Me_xO_y) on the AN/Mg/NC combustion process.

Research methods: To achieve the necessary goals and solve the tasks, the following research methods were used: BET analysis (low-temperature nitrogen adsorption) to determine the specific surface area of activated carbons; scanning electron microscopy (SEM) to study the characteristics and surface morphology of activated carbons; energy dispersive analysis to study the elemental composition; adsorption capacity of methylene blue to study the adsorption capacity; differential scanning calorimetry (DSC); differential thermal and thermogravimetric analysis to study the kinetics of decomposition of compositions (DT-TGA); high-speed camera (MotionXtra HG-100K); NASA-CEA software (chemical equilibrium and application) for thermodynamic calculations of adiabatic combustion temperatures.

Scientific novelty of the work. The scientific results presented in this work contain new experimental and theoretical data on the influence of metal-organic framework structures MOF (CRH/Me_xO_y) on the combustion and thermal decomposition of pyrotechnic compositions based on ammonium nitrate.

The following results were obtained for the first time:

1. Activated carbon-based MOF (CRH/Me_xO_y) metal-organic frameworks have been developed based on carbonized rice husk with addition of transition metal oxide nanoparticles, which were first used as a combustion catalyst in pyrotechnic compositions.

2. It was found that the additives MOF (CRH-CuO) provide the pyrotechnic composition AN/Mg/NC with a high burning rate of 11.6 to 20.5 mm/s at an initial pressure in the system of 1 to 3.5 MPa, while the calculated value of the indicator pressure n is in the range of 0.53-0.42. From the results obtained, an important conclusion follows that the addition of MOF provides the opportunity to significantly increase the burning rate of the pyrotechnic composition without the transition of the combustion process to explosive mode.

3. It was revealed that the additives of MOF (CRH-CuO) have a direct effect on the decomposition mechanism of the pyrotechnic composition AN/Mg/NC and reduce its activation energy to 8 kJ/mol.

4. It was established that the developed pyrotechnic compositions AN/Mg/NC/CRH/Me_xO_y are highly energy-efficient materials suitable for direct ignition by laser radiation. The developed combustible composition does not require the addition of optical sensitizers to ensure stable ignition by laser radiation, which means the preservation of its chemical properties. The pyrotechnic composition AN/Mg/NC/CRH-CuO stably ignites at a laser energy of ≥4.35 J (without MOF, the

laser energy was 25.97 J), the ignition delay time is 506 ms (without MOF, the ignition delay time was 902 ms).

The theoretical significance. The theoretical significance of the work is to establish the basic laws of the influence of metal-organic framework structures (MOF) on the characteristics of thermal decomposition and combustion of energy-intensive materials. The obtained scientific results can be used in fundamental and applied research related to the composition and properties of energy materials.

The practical significance. The developed metal-organic framework structures (MOF) are promising materials for use as effective additives for improving the useful characteristics of energy-intensive materials. The results can be used in applied research related to the development of high-energy energy-intensive materials.

Approbation of the work results. The results of the dissertation were reported and discussed in the following international scientific conferences:

• Proceedings of IV Conference of Students and Young Scientists «Chemical Physics and Nanomaterials» (Almaty, March 19, 2019);

• Proceedings of the Conference of the Students and Young Scientists dedicated to the 30th anniversary of the Institute of Combustion Problems creation (Almaty, November 30, 2017);

• X International Symposium «The Physics and Chemistry of Carbon and Nano energetic Materials» (Almaty, September 12-14, 2018);

• International Scientific Conference Modern Problems of Condensed Physics States, Nanotechnologies and Nanomaterials (Almaty, May 17-18, 2018);

• The First International Conference on Defense Technology Proceedings (Beijing, China, October 21-25, 2018);

• The 4^{th} International Nano-Structured Energetic Materials Workshop (Nanjing, China, November 2-4, 2018);

Experimental results were obtained using modern research methods and equipment provided by a foreign supervisor at Nanjing University of Science and Technology (Nanjing, China).

The personal contribution of the author consists in the formulation and conduct of experiments, the synthesis and interpretation of the obtained results, the writing of articles and reports. Goals and objectives, experiment planning, discussion of the results and the main points of defense were discussed with both scientific consultants.

Publications. The main results of the thesis were published in 12 publications: 2 articles is included in the Scopus database and 1 article included in the Thomson Reuters database, 4 publications were published in journals recommended by the Committee on Control in Education and Science of the Republic of Kazakhstan, 4 - in the collections of international scientific conferences, and 1 application for utility model No. 2019/0488.2.

The scope and structure of the work. This dissertation work is presented on 94 pages of printed text and contains 64 figures and 16 tables. The work consists of introduction, review of literature, description of research objects and methods, results and discussion, conclusion, list of references contain 116 names.