ANNOTATION

Dissertation for the degree of Doctor of Philosophy (PhD)
8D07103 - "Chemical technology of explosives and pyrotechnics"

KORKEMBAY ZHANIBEK
PROMOTION OF PERCHLORATE AMMONIUM COMBUSTION BY Ti_3C_2 (MXENE) ADDITION

General characteristics of the work.

This dissertation focuses on the synthesis of Ti_3C_2 (MXene**)** material selected as a catalyst and the study of its physicochemical properties. The synthesized multilayer nanosheets possess a large specific surface area and active sites, which enable their use as a catalyst. During the research, a Ti_3C_2(MXene)/ammonium perchlorate (AP) composite was prepared, and its thermal decomposition was characterized using Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)**.** Based on the obtained data, key kinetic parameters such as activation energy and exponential coefficient were calculated using Kissinger's graphical method. Furthermore, the influence of the Ti_3C_2 (MXene) catalyst and pressure on the combustion process of solid rocket fuel based on ammonium perchlorate was investigated, and the catalyst's efficiency was scientifically substantiated.

Relevance of the research topic.

The relevance of this research lies in utilizing the catalytic properties of titanium carbides Ti_3C_2 (MXene) as a catalyst for solid rocket fuel based on ammonium perchlorate. This approach optimizes combustion and increases energy release. Considering the importance of solid fuels in space transportation, their improvement is essential. Enhancing catalyst activity reduces negative effects from combustion products. The unique structure of two-dimensional titanium carbides Ti_3C_2 (MXene) has attracted significant interest. MXene can serve as an effective catalyst, replacing transition metal oxides. Ammonium perchlorate is capable of self-deflagration, since its decomposition produces ammonia and hydrochloric acid that sustain a gas-phase flame at about 1400 K. It also exhibits distinctive low-temperature decomposition behavior under pressure. These properties have made ammonium perchlorate the main component of composite solid fuels for space propulsion. Nevertheless, optimizing its combustion still requires further research. Modern high-energy engines are "composite," consisting of oxidizers (65–70%), metallic fuels (10–20%), binders (8–15%), and burning-rate catalysts (2–5%). Ammonium perchlorate is most often used as the oxidizer, while aluminum serves as the metallic fuel. The use of Ti_3C_2 as a catalyst provides momentum for developing powerful, fast-propelling rocket engines.

The purpose of the work.

The use of titanium carbide (Ti_3C_2 (MXene)) as a catalyst enables the optimization of the combustion process of ammonium perchlorate-based solid rocket propellants, namely by increasing the burning rate, enhancing heat release efficiency, and controlling the formation of reaction products, thereby improving the energetic and operational characteristics of the propellant system.

The tasks of the work.

To achieve the stated objective, the following tasks were accomplished:

- Characterize the elemental composition and structural features of titanium carbide Ti_3C_2 (MXene) used as a catalyst.
- Develop formulations to determine the most effective mass fraction of titanium carbide Ti_3C_2 (MXene) influencing the thermal decomposition of ammonium perchlorate, and perform DTA and TG analyses of these formulations.
- Based on the identified mass fraction of titanium carbide Ti_3C_2 (MXene), prepare the composition of solid rocket propellant based on ammonium perchlorate.
- Monitor the combustion process of the composite solid propellant in a high-pressure device and analyze the recorded data.

The objects of research – Ti_3C_2 (MXene), is a composite composition of solid rocket fuel based on Ti_3C_2 (MXene), AP titanium carbite synthesized by adding Ti_3AlC_2(MAX) powder to Ti_3C_2 hydrofluoric acid.

The subject of research is the thermal and kinetic parameters (physico-chemical properties) of solid propellant based on AP.

Research methods. To solve the tasks necessary to achieve the goal, the following research methods were used: thermogravimetric analysis, thermal analysis of differentiation, elemental analysis, X-ray phase analysis, optical microscope, scanning electron microscopy .

The scientific novelty of the research.

- The synthesized Ti_3C_2 (MXene) consists of multilayered nanosheets with a large specific surface area and active sites, which makes it suitable for use as a catalyst.
- During the thermal decomposition of ammonium perchlorate, a 2% mass fraction of Ti_3C_2 (MXene) was found to exhibit the highest catalytic activity.
- In the combustion of ammonium perchlorate-based solid rocket propellant, Ti_3C_2 (MXene) interacts in the high-temperature region with the thermal decomposition products of ammonium perchlorate, forming catalytically active compounds such as TiO_2, TiC, and TiN.
- As a result of the catalytic activity of Ti_3C_2 (MXene) during the decomposition and combustion stages, the burning rate of ammonium perchlorate-based solid propellant increases, and a rise in temperature is recorded.

The main provisions submitted for protection:

1. In the presence of hydrofluoric acid, aluminum in the Ti_3AlC_2 (MAX) phase can be removed through chemical treatment as AlF_3. As a result, the structure of titanium carbide Ti_3C_2 (MXene) is exfoliated into layered nanosheets. This morphology significantly increases the material's specific surface area and the number of active sites.

2. Composite samples of Ti_3C_2(MXene)/ammonium perchlorate (AP) with mass fractions of Ti_3C_2(MXene) at 1%, 2%, 5%, and 10% were prepared. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) results showed that the optimal mass fraction of Ti_3C_2(MXene) for facilitating thermal decomposition is 2%. At higher fractions (5–10%), particle agglomeration, i.e., clustering and uneven heat transfer, reduces catalytic efficiency.

3. Using the peak values of DTA curves for pure ammonium perchlorate and the 2% Ti_3C_2(MXene)/AP composite at heating rates of 5°C/min, 10°C/min, 20°C/min, and 30°C/min, the activation energy was calculated by the Kissinger graphical method. It was found that in the high-temperature decomposition stage (HTD), the activation energy decreases to 75 $kJ \cdot mol^{-1}$. Catalytically, this indicates that the expanded surface of Ti_3C_2(MXene) nanosheets facilitates the adsorption of reacting molecules and accelerates electron transfer.

4. When burning ammonium perchlorate-based solid propellant with 0%, 2%, 3%, and 5% titanium carbide Ti_3C_2(MXene) in a high-pressure chamber, the mixture containing 2% Ti_3C_2(MXene) exhibited higher burning rate and recorded temperature compared to other formulations. This phenomenon is explained by Ti_3C_2(MXene) participating in the exothermic process in the high-temperature region, maintaining its initial structure while forming catalytically active compounds TiO_2, TiC, and TiN.

Theoretical significance.

This study addresses the enhancement of combustion efficiency of composite solid rocket fuel based on ammonium perchlorate by modifying its thermochemical and kinetic characteristics with a Ti_3C_2 (MXene) catalyst. The results provide deeper insights into the combustion mechanisms of solid fuel systems, enabling molecular-level characterization of proton transfer and redox processes. These theoretical foundations contribute to the design and optimization of modern catalytic systems. From a practical perspective, the findings help improve the efficiency of solid fuels used in rocket and energy devices, refine control over burning rates and heat release. The outcomes support important technical decisions in the design, production, and safe utilization of rocket propellants.

Practical significance.

The addition of titanium carbide Ti_3C_2 catalyst to ammonium perchlorate-based solid rocket propellants positively affects the thermal decomposition of AP, accelerates the combustion of composite solid propellant, and ensures high-temperature release.

Implementing this work contributes to increasing the speed and thrust power of rocket engines in the field of space transportation.

Author's personal contribution.

The researcher's work involved conducting experiments, developing scientific calculations and models, analyzing the obtained results, drawing conclusions and providing scientific explanations, as well as directly participating in writing articles and scientific reports based on the research findings. These activities required active involvement at all stages of the research process and a high level of professional competence.

Publications.

Based on the results of the dissertation research, a total of 6 scientific works were published, including 2 articles in scientific journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan, 2 articles in journals indexed in the international databases Scopus and Web of Science, and 2 articles in the proceedings of international and national scientific conferences.

In a scientific publication recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan

1. Коркембай Ж., Тоштай К., Алипбаев, А., Атаманов М., & Мальчик, Ф. (2023). Влияние добавок Ti_3C_2(MXene) на разложение перхлората аммония . *Горение и плазмохимия*, *21*(4), 257–263. https://doi.org/10.18321/cpc21(4)257-263
2. Ж. Коркембай*, А.Н. Алипбаев, З.А. Мансуров. Процесс сгорания в присутствии твердотопливного катализатора Ti_3C_2(MXene) на основеперхлората аммония. Л.Н. Гумилев атындағы Еуразия ұлттық университетінің ХАБАРШЫСЫ Vol. 149 No. 4 (2024) 67-78. DOI: https://doi.org/10.32523/2616-6771-2024-149-4-67-78

Publications indexed in Scopus and Web of Science databases with a non-zero impact factor.

1. Korkembay, Z., Auyelkhankyzy, M., Atamanov, M., Mansurov, Z., & Bykov, V. (2025). Mechanism of Catalytic Thermal Decomposition of Ammonium Perchlorate in the Presence of Ti3C2Tx. Eurasian Chemico-Technological Journal, 27(3), 173–179. https://doi.org/10.18321/ectj1664
2. Zh. Korkembay, K. Toshtay, M. Atamanov, F. Malchik, R. Amrousse, Y. Merkibayev, A. Z. Mansurov. Determination of the Catalytic Activity of the MXene in the Combustion of Amonium Perchlotrate //Journal of Engineering Physics and

Thermophysics . Volume 97, pages 985–992, (2024). doi:10.1007/s10891-024-02968-1

Publications at international and national conferences and symposiums:

1. Zh. Korkembay F. Malchik1 , Z. A. Mansurov , V. V. Bykov.(2024) The catalytic effect of Ti_3C_2(MXene) on the thermal decomposition of ammonium perchlorate. “Combustion and plasma chemistry. Physics and chemistry of carbon and nano energetic materials” dedicated to the 95th anniversary of the birth of Professor G.I. Ksandopulo and to the memory of Academician of the Russian Academy of Science Professor Z.R. Ismagilov, pages 182–184
2. Zh. Korkembay, M. Atamanov, S. Tursynbek, Z.A. Mansurov.(2025) Combustion process in the presence of Ti_3C_2(MXene) as a solid fuel catalyst based on ammonium perchlorate (AP). Proceedings of the IX International Student Scientific and Practical Conference on«CHEMICAL PHYSICS AND NANOMATERIALS»,dedicated to the memory of three-time Hero of Socialist Labor,Corresponding Member K.I. Shchelkin. pages 133–135

Reliability and validity of the results obtained

The reliability of the dissertation results is confirmed by the scientific validity and accuracy of the data obtained through a complex of modern physico-chemical methods. The research was carried out in the laboratories of the Non-commercial Joint Stock Company “Al-Farabi Kazakh National University,” at the scientific base of the RSE “Institute of Combustion Problems,” and in the laboratory facilities of the “Karlsruhe Institute of Technology” in Germany.