

ABSTRACT
**thesis for the degree of Doctor of Philosophy (PhD) on educational
program «8D07101 – Petrochemistry»**
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**«Regularities of stabilization of the active component phase in oxide
catalysts in deep oxidation of methane»**

General description of the work. The dissertation is devoted to the synthesis of oxide catalysts in deep oxidation of methane using composite materials based on Co-Mg, their comprehensive characterization, stabilization of the active phase, and catalytic performance testing.

The relevance of the study

At present, atmospheric air pollution and climate change are among the most pressing environmental challenges on a global scale. Among greenhouse gases, methane (CH₄) occupies a special place due to its global warming potential, which is several times higher than that of carbon dioxide. Methane is released into the atmosphere during oil and gas production and transportation, from coal mines, during the decomposition of municipal solid waste, in agriculture, as well as in the exhaust emissions of motor vehicles and power-generating installations. The accumulation of methane in the atmosphere not only intensifies the greenhouse effect but also contributes to the formation of tropospheric ozone, which has adverse impacts on human health and ecosystems.

In large industrial and urbanized regions, including the city of Almaty, atmospheric air quality remains a serious environmental concern. In 2024, according to data from the international organization IQAir, Almaty was ranked among the major cities with high levels of air pollution. This situation is associated with the large number of vehicles, fuel quality, and industrial emissions. Elevated concentrations of methane, carbon monoxide, nitrogen oxides, and volatile hydrocarbons in the atmosphere increase environmental risks. Therefore, the effective abatement of gaseous hydrocarbons, especially methane, represents an important scientific and technical challenge.

Deep catalytic oxidation of methane ($\text{CH}_4 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) is one of the most effective methods for converting it into harmless products. However, the high strength of the C-H bond in the methane molecule (≈ 435 kJ/mol) makes its activation difficult and requires high temperatures. In this regard, there is a need to develop new efficient catalysts that exhibit high catalytic activity and stability at low temperatures.

At present, platinum group metal-based catalysts, particularly those containing Pt, Pd, and Rh, demonstrate high activity in methane oxidation reactions. However, their high cost, limited availability, and susceptibility to sulfur-containing compounds restrict their widespread use on an industrial scale. In this context, catalysts based on transition metal oxides constitute an economically and technologically viable alternative.

Purpose of the work. Synthesis of new highly efficient and thermally stable Co-Mg-based catalysts free of noble metals such as Pt, Pd and Rh for the deep oxidation of methane, their comprehensive characterization, and the investigation of the phase stabilization behavior of the active component.

The tasks of the thesis:

- to synthesize noble-metal-free oxide catalysts with Co:Mg molar ratios of 1:1, 2:1 and 4:1 by thermal treatment for the deep oxidation of methane;
- a comprehensive investigation of changes in the phase composition, structure, morphology, and oxygen-related properties of the synthesized catalysts during thermal treatment will be performed using IR spectroscopy, SEM, XRD, BET, EPR, TPD, and TPR-H₂. Based on the obtained results, the patterns governing the stabilization of the active phase of the catalyst components will be established;
- to study the phase changes in the synthesized catalysts during high-temperature treatment, as well as their redox properties and thermal stability;
- to determine the optimal conditions for the deep oxidation of methane by varying the process temperature.

The object of the study the deep methane oxidation process and oxide catalysts synthesized by thermal treatment.

The subject of the study

Is the synthesis of highly efficient, noble-metal-free oxide catalysts for deep oxidation of methane, investigation of the phase stabilization of the active component, and the study of their physicochemical properties and catalytic performance.

Research methods

The synthesized samples were studied using the following physicochemical methods: infrared spectroscopy (IR), scanning electron microscopy (SEM), X-ray diffraction (XRD), BET surface area analysis, electron paramagnetic resonance (EPR), temperature-programmed desorption (TPD), and temperature-programmed reduction in hydrogen (TPR-H₂). Laboratory-scale testing of the synthesized catalysts was also conducted. The experimental tests were conducted using an automated flow catalytic unit. The reaction products were analyzed using gas chromatography (GC).

The main provision for the defense:

1. Accessible and highly efficient Co-Mg oxide catalysts free of noble metals were synthesized for the deep oxidation of methane. The catalysts were prepared by thermal treatment, and samples with Co:Mg molar ratios of 2:1 and 1:1 were investigated. It was shown that, despite the absence of noble metals in their composition, the synthesized catalysts exhibit high catalytic activity in the deep methane oxidation reaction.

2. The transition from spinel to solid solution phases was confirmed by significant changes in the TPR-H₂ profiles: the first reduction peak (410-420°C) markedly decreased, while the second peak shifted to a higher temperature range, reaching a maximum at 1010-1080°C. This second peak domain was identified for the first time. A solid-state phase transition from Mg_xCo_{2-x}O₄ spinel to (Co, Mg)O was observed in the 800-900°C range across all Co:Mg ratios studied. A "true" solid solution, obeying Vegard's law, formed only upon spinel decomposition.

3. The deep methane oxidation reaction was conducted in a CH₄:O₂:Ar gas mixture. Using the proposed 50%Co-50%Mg catalyst (optimal Co:Mg = 1:1), a methane conversion of 96.6% was achieved at 600°C.

Scientific provisions for the defense

The originality and novelty of the dissertation are outlined below, based on the first-time achievements:

1. For the first time, phase composition analysis confirmed the occurrence of a phase transition from MgCo_2O_4 spinel to a CoO-MgO solid solution in the temperature range of 650-1000°C, accompanied by changes in catalyst particle size and morphology with increasing thermal treatment temperature. It was established that samples obtained at low thermal treatment temperatures contain a small amount of $\text{Co}^{2+}_{\text{Td}}$ ions, corresponding to the Co_3O_4 spinel phase; their content decreases upon transition to the MgCo_2O_4 solid solution.

2. For the first time, temperature-programmed reduction (TPR) analysis demonstrated that, for samples calcined at temperatures below the phase transition region, two oxygen reduction peaks are observed in the low-temperature region: the first peak (420-470°C) corresponds to the transition of $\text{Co}^{3+}_{\text{Oh}}$ in the octahedral sites of the spinel structure to $\text{Co}^{2+}_{\text{Oh}}$ in the CoO structure, while the second peak (540-620°C) corresponds to the reduction of CoO to metallic Co^0 . In samples calcined at higher temperatures, the first peak decreases significantly, whereas the second peak appears in the 900-1100°C range and corresponds to the reduction of CoO in the structure of a true solid solution to Co^0 .

3. It was established that the phase transition of $\text{Mg}_x\text{Co}_{2-x}\text{O}_4$ spinel to the (Co, Mg)O solid-solution phase occurs in the temperature range of 800-900°C for all investigated Co:Mg ratios and throughout the entire temperature range considered. The cubic phase in low-temperature Co-Mg samples is an anion-modified paracrystalline system and shows only weak dependence on the initial Co:Mg ratio. A true solid solution obeying Vegard's law is formed only after spinel decomposition.

4. Investigation of the activity of the synthesized catalysts in the deep methane oxidation reaction revealed the high activity of spinel-based samples, as well as a linear correlation between the activation energy of the reaction and the thermal treatment temperature. The relatively small change in the activation barrier upon transition from spinel to a true solid solution indicates the similar nature of their active sites. The obtained activation energy values are consistent with the general trends characteristic of Co-Mg oxide systems and their dependence on composition and thermal treatment temperature.

Practical and theoretical significance of the scientific results

The catalytic purification of residual hydrocarbons through deep methane oxidation is of major economic and environmental importance, as it contributes to solving environmental problems by improving the hydrocarbon composition of motor fuels and neutralizing toxic components in exhaust gases. Understanding the mechanism of the deep methane oxidation process is crucial for developing catalysts capable of fully converting CO, CH_4 , SO_2 , NO, and residual hydrocarbons. Furthermore, the study significantly contributes to the advancement of the theoretical foundations for hydrocarbon feedstock utilization, particularly deep methane oxidation. The knowledge gained from this research has potential for commercialization and practical implementation, enabling considerable improvements in environmental quality and addressing atmospheric pollution issues in the future.

Reliability and validity of the results

The conclusions and propositions of this study are validated by a substantial volume of experimental data obtained using modern analytical techniques and certified

instrumentation. The reliability of the results is further confirmed by publications in high-impact scientific journals, journals recommended by the Committee for Quality Assurance in the Field of Education and Science (CQAFES) of the Ministry of Science and Higher Education of the Republic of Kazakhstan, a utility model patent of the Republic of Kazakhstan, and a publication as part of the CIS “Best Young Scientist” competition. Additional validation is provided through presentations at both national and international scientific conferences.

The sources of the research are original scientific works indicated in the list of used literature.

The author's personal contribution includes conducting the literature review, planning the research objectives, synthesizing Co-Mg-based oxide catalysts, performing comprehensive characterization, and investigating the mechanisms of phase stabilization of the active components. The author also carried out analysis of the experimental data and prepared research articles and conference abstracts based on the results. The formulation of key research tasks and interpretation of the findings were performed in consultation with scientific supervisors.

1. Cobalt–Magnesium Oxide Catalysts for Deep Oxidation of Hydrocarbons – Research article published in Catalysts (data collection, processing of results, and manuscript preparation).

2. Patterns of Formation of Binary Cobalt–Magnesium Oxide Combustion Catalysts of Various Composition – Research article published in Catalysts (data collection, processing of results, and manuscript preparation).

3. Regularities of Stabilization of the Active Component of Oxide Catalysts in the Deep Oxidation of Methane // News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology (literature review preparation, acquisition of experimental data, data processing and interpretation).

4. Cobalt–Magnesium Oxide Catalysts for Total Oxidation Processes of Hydrocarbons // International Competition “Best Young Scientist” – Endless Light in Science (collection of experimental data, processing of results, and presentation in the form of scientific publications).

5. Method for Preparing an Oxide Catalyst for Deep Methane Oxidation // Utility Model Patent of the Republic of Kazakhstan (experimental data collection, processing, and characterization).

Publications

The research findings were published in the following scientific platforms:

News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology (Vol. 3. 456. 2023), a journal recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan. Catalysts (indexed in Scopus, 2024, Vol. 14(2), Article 136; Vol. 14(7), Article 425). The international competition “Best Young Scientist” – Endless Light in Science (2024). utility model patent of the Republic of Kazakhstan (№10113, Bulletin №4, 24.01.2025).

Approbation of the dissertation.

The main results of the dissertation were presented and discussed at the seminars of the Faculty of Chemistry and Chemical Technology at Al-Farabi Kazakh National University, and at the following international scientific conferences:

- “The World of Farabi” – International Conference of Students and Young Scientists (2023, Almaty, Kazakhstan);
- “Chemical Technology of Functional Materials” – 9th International Russian-Kazakh Scientific-Practical Conference (2023, Novosibirsk, Russia);
- “Chemical Technology of Functional Materials” – 10th International Russian-Kazakh Scientific-Practical Conference (2024, Almaty, Kazakhstan).

Relation of the thesis with research and government programs

The dissertation was carried out within the framework of research projects conducted at the laboratory of oxidation catalysis of the D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, according to the following funded projects:

AP08052090: Development of Catalytic Systems with Tunable Properties for the Synthesis of Valuable Commodity Products (2020–2022); AP14869966: Development of Theoretical Aspects of Catalytic Synthesis of “Blue” Hydrogen as a Step Toward Future Carbon Neutrality (2022–2024); AP19677006: Catalytic Processing of Renewable Bioalcohol Feedstocks – Biomethanol, Bioethanol, and Biopropanol – into Valuable Petrochemical Products (2023–2025).

Volume and the structure of the thesis

The dissertation consists of 113 pages and references 272 sources from the scientific literature. The work includes 12 tables and 46 figures. The dissertation is structured as follows: Introduction, literature review, experimental section, results and discussion, conclusion.