

ANNOTATION

of the dissertation on the topic "Development and research of physico-chemical properties of highly efficient Co-containing catalysts for the synthesis of alcohols from syn- gas" for the degree of Doctor of Philosophy (PhD) in EP 8D05311- "Chemistry" by Gulim Danebaevna Dzhetsisbaeva

General Characteristics of the Work

The dissertation is aimed at the development of highly active and selective cobalt-containing catalysts with a perovskite structure for the production of alcohols from synthesis gas, the investigation of the influence of synthesis methods on their catalytic properties, as well as the identification of the relationships between the physicochemical characteristics of the catalysts and the methods of their synthesis.

Relevance of the Work

The catalytic conversion of synthesis gas into hydrocarbons and alcohols via the Fischer–Tropsch process is considered an environmentally friendly approach for the production of valuable chemical products. Synthesis gas obtained from the processing of natural and associated gas, biomass, and coal is of significant interest due to its potential for conversion into synthetic alcohols that enhance the octane and cetane numbers of neat fuels and fuel blends. Over the past three decades, intensive research has been carried out on shifting the synthesis from methanol toward higher alcohols (C_2^+OH). Higher alcohols are widely used in various fields, including alternative fuels, fuel blends, and as industrial feedstocks or intermediates for chemical production. To date, no commercial process for the production of C_2^+ alcohols from synthesis gas has been implemented. This is primarily due to the fact that selectivity toward the desired products remains an unresolved issue. The method of catalyst preparation, its composition and structure, as well as the reaction conditions, are the key factors determining the selective formation of intermediate products in this process. Previous studies have demonstrated that the nature of the precursor significantly affects the physicochemical and catalytic properties of the reduced nanoparticles of active metals.

At present, cobalt-based catalysts are the most economically efficient systems for the Fischer–Tropsch synthesis of hydrocarbons and alcohols. Their active component consists of metallic cobalt (Co^0) nanoparticles stabilized on the surface of oxide supports (Al_2O_3 , SiO_2 , TiO_2). The formation of such nanoparticles is achieved through specific methods for the preparation of oxide systems with a highly developed surface area.

Among the stable compounds that promote the formation of active particles on the surface of stable oxides are mixed oxides with spinel-, delafossite-, and perovskite-type structures. The latter, owing to the possibility of flexible variation in chemical composition, enables the selection of an optimal catalyst composition and surface characteristics, thereby allowing effective control over product selectivity. Complex oxides with a perovskite-type structure can therefore be

considered promising precursors for the formation of active and stable cobalt nanoparticles in the synthesis of C_2^+ alcohols.

Purpose of the study: Synthesis of highly active and selective perovskite-like cobalt-containing catalysts for the synthesis of alcohols from syn-gas and a study of the influence of synthesis methods on their catalytic properties.

Research objectives:

1. Synthesis of a complex oxide with the perovskite structure $LaCoO_3$ with different ratios of lanthanum and cobalt by the coprecipitation method in the presence of a soft template - ethylene glycol, as well as by the citrate method in the presence of a hard template - mesoporous silica KIT-6.

2. Study of the influence of the synthesis method on the structural, textural and surface characteristics of the samples.

3. A study of the catalytic properties of samples in the synthesis of alcohols from syngas as a function of temperature. Establishing the relationship between the catalytic properties of the samples and their physicochemical characteristics.

4. Study of the physical and chemical state of catalyst samples after catalytic studies.

Research Methods

The methodology and research methods of this dissertation are based on the works of both domestic and foreign scientists in the field of synthesis and investigation of the physicochemical properties of catalysts used in the production of alcohols from synthesis gas (Fischer–Tropsch synthesis). The information sources included periodicals, scientific publications, and state standards.

To study the physicochemical characteristics of cobalt-containing catalysts with a perovskite structure, the following analytical techniques were applied: atomic emission spectroscopy (AES), nitrogen physical adsorption using the Brunauer–Emmett–Teller (BET) method, powder X-ray diffraction (PXRD), high-resolution transmission electron microscopy (HRTEM) compatible with energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA).

The catalytic properties of the synthesized samples in the reaction of alcohol synthesis from synthesis gas were studied in a fixed-bed stainless steel flow reactor, with chromatographic analysis of both gaseous and liquid products.

The research presented in this dissertation was carried out in the Laboratory of Physicochemical Studies of the Department of Chemistry and Chemical Technology at M.Kh. Dulaty Taraz University, as well as at the Research Center of Novosibirsk State University (Novosibirsk, Russia).

Objects of Research

Cobalt-based perovskite-like catalysts capable of synthesizing alcohols from synthesis gas, prepared by the co-precipitation method in the presence of a soft template under hydrothermal conditions, as well as by the citrate method in the presence of a hard template.

Subject of the Research. The subject of this research is to determine the influence of synthesis methods on the physicochemical properties of Co-containing catalysts

and their relationship with the catalytic activity of the obtained materials in the process of alcohol synthesis from synthesis gas. In addition, the factors governing the activity and selectivity of the synthesized catalyst samples are identified.

The main provisions submitted for defense:

1. The method of co-precipitation under hydrothermal conditions in the presence of a soft template of ethylene glycol allows to obtain complex oxides with the perovskite structure LaCoO_3 (JCDD PDF2 00-025-1060).
2. The use of the hard template of mesoporous silica KIT-6 allows for an increase in the specific surface area of the LaCoO_3 sample from 9.5 to 220 m^2/g .
3. LCO/KIT-6 with an increased specific surface area exhibits significantly higher activity in the catalytic reaction conducted at a constant temperature of 240 °C. Although its selectivity toward alcohols is somewhat lower (61%), a substantial shift toward the formation of valuable higher alcohols is observed (80 $\text{mg}/\text{g}\cdot\text{cat}\cdot\text{h}$).

Main Results of the Research

Justification of the Scientific Novelty and Significance of the Obtained Results

Cobalt-containing complex oxides LaCoO_3 with a perovskite structure were synthesized by the co-precipitation method under hydrothermal conditions in the presence of a soft template — ethylene glycol.

The influence of synthesis methods on the physicochemical characteristics of complex oxides with a perovskite structure, LaCoO_3 and $\text{LaCoO}_3/\text{KIT-6}$, was studied using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA).

The catalytic activity and selectivity of LaCoO_3 and $\text{LaCoO}_3/\text{KIT-6}$ catalysts in the synthesis of alcohols from synthesis gas were investigated, and their relationship with the physicochemical properties of the catalysts was established.

Main Research Results.

1. The catalyst samples LCO-1 and LCO-2 were synthesized by the co-precipitation method in the presence of the soft template ethylene glycol under hydrothermal conditions, while the LCO/KIT-6 sample was synthesized by the citrate method in the presence of the hard template KIT-6. After calcination at 750 °C, X-ray diffraction analysis confirmed the formation of the perovskite phase LaCoO_3 . (JCDD PDF2 00-025-1060).

2. The influence of synthesis methods on the structural, textural, and surface properties of the synthesized catalyst samples (LCO-1, LCO-2, LCO/KIT-6) was investigated using atomic emission spectroscopy (AES), Brunauer–Emmett–Teller (BET) nitrogen adsorption, X-ray diffraction (XRD), energy-dispersive X-ray microanalysis (EDX), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA).

3. The study of perovskite cobalt-containing catalysts in the synthesis of alcohols from synthesis gas showed that the most active sample was LCO/KIT-6, synthesized by the citrate method (alcohol yield of 80 $\text{mg}/\text{g}\cdot\text{cat}\cdot\text{h}$). The use of the hard template silica oxide KIT-6 as a support increased the catalyst's surface area

to 220 m²/g, and despite a slight decrease in overall alcohol selectivity (61%), a significant shift toward the formation of valuable higher alcohols was observed.

4. The physico-chemical state of the catalysts after the reaction of obtaining alcohols from synthesis gas was studied by the methods of X-ray diffraction phase analysis, SEM and TEM. During the reaction, the complex oxides with a perovskite structure underwent phase and morphological transformations: the perovskite phase was destroyed, and cobalt nanoparticles with a diameter of 9–20 nm were formed on the surface of the resulting La(OH)₃ and La₂O₃ phases. After the catalytic reaction, all catalysts experienced irreversible degradation.

The dissertation was completed based on the state grant funding for research by young scientists "Жас Ғалым" for 2025-2027 as part of the project AR25794577 "Development and research of a cobalt-containing catalyst for synthesis gas conversion".

The dissertation aligns with the priority scientific development areas of "Ecology, Environmental Protection, and Rational Use of Natural Resources" and "Energy, Advanced Materials, and Transport."

Author's Contribution. The main contribution of the author consists in the collection and analysis of domestic and international publications related to the research topic, the synthesis of catalyst samples, the analysis and establishment of correlations between the activity and selectivity of the catalysts in the alcohol synthesis reaction from synthesis gas and their physicochemical properties, as well as the preparation of publications for submission based on the obtained results.

Description of the doctoral student's contribution to the preparation of each publication:

Based on the results of the dissertation research work, 10 papers were published, including: *1 article (Open Chemistry, percentile 54, Q3) was published in an international scientific journal included in the scientific metrics database Scopus:*

1. LaCoO₃ perovskite-type catalysts in syngas conversion. Open Chemistry. – 2020. – 18 (1). – P. 482-487. Methodology, concept development, formal analysis, manuscript writing.

5 articles published in publications recommended by the Committee for Quality Assurance in Education and Science and the Ministry of Higher Education of the Republic of Kazakhstan:

1. Synthesis of perovskite-like Co-containing catalyst. Bulletin of the National Academy of Sciences of the Republic of Kazakhstan. Series "Chemistry and Technology". - 2020. - 440 (2). - P. 115-119. Concept development, conducting the research, writing (the initial draft of the manuscript).

2. A review of co-containing perovskite-like catalysts. Synthesis and application. Bulletin of the Kazakh-British Technical University. – 2020. – №3(54). – P. 54-63. Research methodology, concept development, formal analysis and manuscript writing.

3. The influence of temperature change on the process of obtaining higher

alcohols from syngas. Reports of the National Academy of Sciences of the Republic of Kazakhstan. – 2021. – № 340 (6). – P.126-130. Concept development, research methodology, formal analysis, and writing of the original manuscript.

4. A study of perovskite-like complex oxides using transmission electron microscopy. Bulletin of the National Academy of Sciences of the Republic of Kazakhstan. Chemistry and Technology Series.. – 2024. – №459(2). – P. 62-69. Conceptualization, methodology, formal analysis, investigation, writing — original draft.

5. The Effect of Preparation Methods on the Selectivity and Stability of Co-Containing Catalysts for Fischer-Tropsch Synthesis. Academic scientific journal of chemistry. – 2025. – Vol.3(464). –P.64-74 Formal analysis, investigation, writing — original draft.

Three abstracts of reports were published in the proceedings of the international scientific and practical conference:

1. Synthesis of a perovskite-like catalyst and its physicochemical properties. Proceedings of the 6th International Russian-Kazakh Scientific and Practical Conference "Chemical Technology of Functional Materials." Almaty, 2020. P. 52–55.

2. Syngas conversion on perovskite-like LaCoO_3 catalysts. Proceedings of the International Scientific and Practical Internet Conference "Trends and Prospects for the Development of Science and Education in the Context of Globalization," Pereyaslav, December 22, 2020. Issue 66. P. 282-285

3. Preparation of catalysts with a perovskite structure in the presence of monosaccharides. Proceedings of the XI International Birimzhanovsky Congress on Chemistry and Chemical Technology. – Almaty. – 2021. – P. 153-154.

Structure and scope of the work. The dissertation consists of standard sections: normative references, notations and abbreviations, introduction, literature review, practical section, experimental results and their discussion, bibliography, and appendix.