ANNOTATION

Dissertation for the academic degree of Doctor of Philosophy (PhD) in the specialty "6D060600-Chemistry"

Shorayeva Kamshat Abitkhanovna

"Development of molybdenum-containing catalysts based of pillared clays for the oxidative dehydrogenation of ethane into ethylene"

General characteristics of the dissertation research. The dissertation work is devoted to the development of new deposited molybdenum-containing catalysts based on modified Al -, Zr -, Al/Zr-columnar clays. The catalytic activity of the synthesized molybdenum-containing catalysts was evaluated during the oxidative dehydrogenation of ethane into ethylene. The influence of synthesized carriers - samples of columnar clays, composition, structure, temperature and other physico-chemical factors on the catalytic activity of molybdenum-containing catalysts is studied.

The dissertation was studied for the first time and presented in the form of articles: one article in the journal with an impact factor, which is included in the database of Thomson Reuters and Scopus; three articles in journals recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan; as well as in the form of one patent of a utility model of the Republic of Kazakhstan.

The dissertation work was carried out within the framework of the following grant projects and programs funded by the Ministry of Education and Science of the Republic of Kazakhstan:

- "Catalytic purification of C1-C4 hydrocarbons for the production of industrially important gas and petrochemical monomers (AP05133881, 2018-2020)";
- "Creation of a base for the production of refined oil and gas products based on domestic catalytic technologies (BR05236739, 2018-2020)";
- "Development of fundamental aspects of the catalytic conversion of renewable natural raw materials-biogas, development of environmentally friendly fuels (AP08855562, 2020-2022)";
- "Development of catalytic systems with controlled properties for the synthesis of valuable commodity products (AP08052090, 2020-2022)".

The relevance of the research topic. It is known that huge reserves of natural resources and their rational use are of great importance for the future of Kazakhstan. Therefore, the synthesis of new environmentally friendly carriers and catalysts based on natural clays is of great interest in modern catalysis. In this regard, it is important to obtain catalysts and carriers-columnar clays based on the placement of variable metal oxides in the interlayer space.

As a result of modification and pillarization of natural clays, the number of non-clay minerals decreases, the number of useful experimental clay particles

increases, the number of active centers increases, which, in turn, increases the sorption capacity of modified clays. The use of natural clays as carriers in catalytic modifications has not yet been fully studied. Columnar clays must have the necessary chemical properties and adhesion to retain the active ingredient in its surface layer, to provide access to the active parts of the catalyst in the reactor.

High characteristics of ethylene can also be achieved by using mixed polyoxide systems. Only the optimal choice of catalysts for the oxidative dehydrogenation of ethane into ethylene can lead to a purposeful process with a predominance of this product. However, the development of new effective catalysts for the selective oxidative dehydrogenation of ethane into ethylene is still at the research and development stage.

Thus, the dissertation work is aimed at the synthesis of new molybdenum-containing catalytic systems/catalysts based on columnar clays and the description of their catalytic properties in the process of oxidative dehydrogenation of ethane into ethylene.

The purpose of the study. Synthesis of new highly selective molybdenum-containing catalytic systems based on columnar clays and their testing in the process of oxidative dehydrogenation of ethane into ethylene to obtain a high yield of industrially important ethylene. The use of columnar clays of montmorillonite and kaolinite from Kazakhstan deposits as carriers and the determination of their catalytic properties.

To achieve this goal, the following tasks were set:

1. Selection, investigation of the properties and structures of carriers used for the synthesis of catalysts for the oxidative dehydrogenation of ethane into ethylene.

- Selection of natural clays from the deposits of Kazakhstan for columning and modification;
- Synthesis of columnar clays with the introduction of polyhydroxocomplexes of zirconium and / or aluminum into the interlayer space of natural clays;
- Modification of layers and surfaces of natural columnar clays with cations of alkaline, alkaline earth, variable and rare metals;
- Selection of the main ratios of cations, the nature of the initial salts, the conditions of their processing;
- Study of the composition and structure of the initial and modified clays using complex physico-chemical methods such as BET, RFA, TEM, RFES, elemental analysis, etc.

2. Conditions for the synthesis and optimization of catalytic compositions, conducting and optimizing the catalytic reaction of oxidative dehydrogenation of ethane into ethylene.

- Development of methods for the synthesis of a series of catalysts with nanoparticles of complex oxides based on columnar clays modified with cations of alkaline and alkaline earth elements, known for their high selectivity and activity in oxidative dehydrogenation reactions.

- Study of the surface layer, structure, morphology, surface properties and reactivity of catalytic materials using a complex of physico-chemical methods.

- Conducting screening catalytic studies of the reaction of oxidative dehydrogenation of ethane into ethylene in flow-through catalytic installations.

- Selection of the most optimal compositions for detailed study.

3. To study the kinetics and mechanism of the reaction of oxidative dehydrogenation of ethane into ethylene using synthesized molybdenum-containing catalysts.

- Study of the effect of the composition of the active phase, modifying additives and carriers on the process of oxidative dehydrogenation of ethane into ethylene;

- Study of the catalytic activity of synthesized catalysts in the process of oxidative dehydrogenation of ethane into ethylene;

- Study of the phase composition, structure, and dispersion of catalysts using physico-chemical methods (BET, RFA, TBT-H2, TEM, etc.).

The object of the research is polyoxide systems embedded in columnar clays obtained by impregnation, capable of catalyzing the reaction of oxidative dehydrogenation of ethane into ethylene.

The subject of the research is synthesis of columnar clays as a carrier. Methods for obtaining polyoxide complexes/catalysts based on columnar clays, studying their structure and catalytic properties.

Research methods. The research of the dissertation was carried out using modern scientific and experimental methods in the field of physical chemistry and catalysis. Modern instruments and equipment were used in the work, such as the transmission electron microscope JOEL (Japan), the automatic diffractometer DRON-3 (Russia), the electronic probe microanalyzer Superprobe 733 JOEL (Japan), the energy dispersion spectrometer OXFORD INSTRUMENTS (England), Sorbtometr-M (Russia), the planetary mill AGO-2 (Russia), etc.

The dissertation work was carried out in the scientific laboratory of Taraz Regional University, the Department of Chemistry and Chemical Technology (Taraz), the Scientific Laboratory of Nanotechnology and Nanochemistry (Taraz), the D. V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry (Almaty), Novosibirsk State University (Novosibirsk, Russia), the G. K. Boreskov Institute of Catalysis (Novosibirsk, Russia).

Scientific novelty. The research carried out in this dissertation is new in the field of catalysis, where, using modern methods of physical chemistry and catalysis, polyoxide molybdenum-containing compounds capable of catalyzing ethane into ethylene by oxidative dehydrogenation were synthesized for the first time on the basis of columnar clays by impregnation. As a result of the research, the following basic rules of protection were analyzed:

- methods for obtaining modified columnar clays;

- methods of preparation of polyoxide molybdenum-containing catalysts, first obtained on the basis of columnar clays;

- for the first time, the process of oxidative dehydrogenation of ethane into ethylene using molybdenum-containing polyoxide catalysts obtained on the basis of columnar clay is being investigated;

- obtaining results on the composition, structure, etc. physicochemical properties of new polyoxide molybdenum-containing catalysts.

The main results submitted for defense. The new scientific results obtained as a result of the dissertation work allow us to draw the following conclusions:

1. It is shown that the rational use of natural clays is of particular interest not only as adsorbents, but also as carriers of new highly efficient catalysts. The physicochemical properties of the synthesized Al, Zr, Al/Zr-columnar clays were studied using the methods of elemental analysis, XPS, BET, TEM and XFA. The use of columnar clay samples in catalysis will help solve the problem of developing domestic production of catalyst synthesis and replacing its expensive imported analogues.

2. Various methods of synthesis of polyoxide catalysts for use in the process of oxidative dehydrogenation of ethane into ethylene have been developed. MoVTeNbO mixed polyoxyl catalytic composites were prepared by impregnating them in samples of columnar clay and further calcining. This is an important factor in determining the catalytic properties of catalysts, and compared to the prototype, it was noticed that the selectivity for ethylene was significantly higher when using MoVTeNbO/PilC catalysts. Thus, using physicochemical methods for further research, we chose MoVTeNbO polyoxide catalysts containing 10 wt.% columnar clay, since these catalytic systems have shown better catalytic activity in the oxidative dehydrogenation of ethane into ethylene.

3.The phase compositions, structures and dispersions of MoVTeNbO/PilC catalysts synthesized for effective use in the ODE process using physicochemical methods, such as XFA, TPV-H2, TEM, TEM equipped with EDX, were studied and conclusions were made.

4. When studying MoVTeNbO polyoxide catalysts based on columnar clays by TEM methods equipped with EDX, XPA, TPV-H2, PEM, it turned out that despite the strong chemical interaction between the components, it is the M1 phase in the composition of the catalysts that affects the high activity and selectivity during the oxidative dehydrogenation of ethane into ethylene.

5.Kinetic studies of MoVTeNbO/PilC catalysts were carried out to understand the catalytic properties and the mechanism of oxidative dehydrogenation of ethane into ethylene.

Assessment of the completeness of solutions to the tasks set. The goals and objectives set in the dissertation work have been fully solved:

- columnar clays activated by Al -, Zr -, Al/Zr-ions were synthesized from samples of natural clays;

- on the basis of columnar clays, catalysts with nanoparticles of metal polyoxides Mo, La, Nb, Te, etc., were prepared;

- some properties of the obtained catalysts were studied by physicochemical methods such as: TEM, TEM (equipped with EDX), TPV-H2, XPA, XPS and elemental analysis;

- The kinetics and mechanism of the reaction of oxidative dehydrogenation of ethane into ethylene in the presence of new molybdenum-containing catalysts have been studied.

Practical significance. Methods for obtaining Al-, Zr-, Zr/Al-columnar clays obtained from natural clays of montmorillonite and kaolinite from Kazakhstan deposits have been developed. A method for producing molybdenum-containing polyoxide catalysts based on columnar clays, which are capable of catalyzing the oxidative dehydrogenation of ethane into ethylene with high efficiency and selectivity, has been developed and proposed.

The results of the dissertation work allow us to solve a wide range of theoretical problems of catalysis, ecology and green chemistry of the Republic of Kazakhstan, in particular, the development and testing of domestic highly effective catalysts for the oxidative dehydrogenation of ethane into ethylene.

Personal contribution of the author. It consists of an analysis of literature and patent research, experimental research and calculations, analysis of the data obtained and generalization of the results.

Approbation of the work. The main results of the dissertation were presented and discussed at the following international scientific conferences: "DIGITAL KAZAKHSTAN: Global digitalization trends and international experiences", 15 March, 2019, Taraz, Kazakhstan; XI International Conference "Mechanisms of Catalytic Reactions", 7-11 October, 2019. Sochi, Russia; X International Beremzhanov Congress on Chemistry and Chemical Technology. October 24-25, 2019. Almaty, Kazakhstan; XIII International Scientific Conference "Innovative development and relevance of science in modern Kazakhstan". November 7-8, 2019, Taraz, Kazakhstan.

Publications. The following scientific articles have been published based on the results of the work:

- 1 articles-in journals included in the international citation database Scopus, with a percentile of at least 35%;

- 4 theses in the materials of domestic and foreign international scientific conferences;

- 4 articles-in journals recommended by the Committee for Control in the Sphere of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan.

The structure and scope of the dissertation. This dissertation work is presented on 113 pages of typewritten text. Consists of an introduction, the main part, the experimental part, the results and their discussion and the conclusion. The work is illustrated with 23 tables, 5 diagrams, 40 figures and the list of literatures includes 176 sources, consisting of foreign and domestic scientific articles and educational materials.