Relevance of the research topic. To solve the problems of nuclear power and industry related to the separation of hydrogen isotopes, the most promising technology in the world is the chemical isotope exchange (ChIE) of hydrogen with water. This process is used to produce heavy water at the final concentration stage, as well as for the detriation of heavy water and light water waste. Currently, this technology is implemented in the CECE (Combined Electrolysis and Catalytic Exchange) variant, a process in which ChIE is combined with energy-intensive electrolysis of the entire water flow circulating in the separation column. The key component of the technology is a hydrophobic hydrogen isotope exchange catalyst (operating temperature 50-80°C). An alternative to this process is a two-temperature scheme, in which water electrolysis is not used, and flow reversal is provided due to the temperature difference in the hot and cold columns: the larger this difference, the higher the efficiency of the separation process. However, for the implementation of the process of separation of hydrogen isotopes according to the two-temperature design, it is necessary to use a hydrophobic catalyst with thermal stability at least up to 180-200°C. The development of such a catalyst, on the one hand, will provide an opportunity for experimental verification of the efficiency of using the two-temperature technology. On the other hand, it will allow the CECE process to be carried out at elevated temperature and pressure, which will significantly reduce the volume of separation columns and, accordingly, the need for the amount of expensive catalyst. In addition, a promising task is the development of a hydrophobic platinum catalyst on an inorganic substrate with heat resistance up to 450-500°C, which will solve another problem of the CECE process: the creation of a reliable low-temperature catalytic reactor for the oxidation of the entire hydrogen flow leaving the ChIE column.

The degree of scientific development of the research topic. Despite a large number of studies devoted to the chemical isotope exchange of hydrogen with water in countercurrent columns, there is currently no industrial implementation of this technology. This is primarily due to the low profitability of existing design: large volumes of columns, expensive catalyst, high operating costs. The use of the developed methods for increasing the efficiency of the isotope exchange process will make it possible to reduce costs and introduce the technology on an industrial scale.

The aim of the work is to select the conditions and optimize the process of isotope exchange of hydrogen with water in countercurrent columns with a combined loading of a hydrophobic catalyst and a hydrophilic packing.

Tasks necessary to achieve the aim:

1. Synthesis of hydrophobic (based on a copolymer of styrene and divinylbenzene, SDVB) and hydrophobized (based on γ-Al_2O_3) platinum catalysts with specified parameters and study their catalytic properties in the isotope exchange reaction in the water-hydrogen system;

2. Development of an experimental methodology for determining the structure of the flows in combined layers of hydrophobic and hydrophilic contact elements based on the analysis of response curves for pulsed injection of a tracer in order to select the optimal conditions for loading and operating separating columns;

3. Get an experimental database on the effect of process parameters (temperature, pressure, launching method) on the efficiency of isotope exchange in the water-hydrogen system in countercurrent columns with a combined loading of the synthesized catalyst and hydrophilic packing.

Scientific novelty of the work:

1. It has been shown that the modification of γ-Al_2O_3 granules with solutions of silanes (methyltrimethoxysilane, phenylsilsesquioxane, methylphenylsilsesquioxane) makes it possible to obtain a hydrophobized hydrogen activation catalyst, comparable in catalytic activity to the RCTU-3SM pilot catalyst, heat-resistant in an inert atmosphere up to 380°C;

2. A method has been developed for the preparation of a hydrophobic platinum catalyst based on SDVB as applied to the hydrogen isotope exchange reaction. It was found that the activity of the platinum catalyst based on SDVB depends on the preparation method of support and increases with increasing pore volume;

3. On the basis of hydrodynamic studies of combined loads of hydrophobic and hydrophilic contact elements into the column by analyzing the response curves during the pulse input of the tracer, a method is proposed for estimating the effect of the volume ratio of hydrophobic and hydrophilic elements and operating conditions of separation columns on the continuity of the liquid flow, which affects the distribution of hold up over the liquid phase between static and dynamic components;

4. For the analysis of experimental data, a mathematical description of the movement of a liquid flow through a mixed packed catalytic layer using the random walk method is proposed. It has been confirmed that from a hydrodynamic point of view, to ensure the continuity of the liquid flow, the maximum proportion of the Pt/SDVB catalyst (granule diameter 0.8-1.2 mm) in a mixture with a hydrophilic packing (SPP 3x3x0.2 mm) should not exceed 20 vol. %, and the method of launching the column has the greatest influence on the nature of the movement of the liquid;

5. Using the obtained database of physicochemical data on the components of the process of catalytic isotope exchange in the water-hydrogen system, the regularities of the influence of the parameters of its implementation of the process on the efficiency of mass transfer were revealed. A significant effect of the competitive adsorption of water and hydrogen vapor on the active sites of the catalyst on the rate of the catalytic component of the process has been found, and it has also been shown that a decrease in the ratio of water vapor/hydrogen flows leads to a decrease in the mass transfer coefficient.

The practical significance of the work.

1. The database of physicochemical and hydrodynamic data obtained in the work expands the possibilities of practical application of the technology under study for the separation of isotopic mixtures of hydrogen.

2. The results of this work were used to produce an experimental batch of a hydrophobic catalyst for the system for normalizing the isotopic composition of the heavy water moderator of the PIK reactor (Agreement No. 26.05-D-1-1/2018 dated December 29, 2017).

3. A method is proposed for studying the structure of flows in a column, which makes it possible to determine the optimal ratio of the hydrophobic and hydrophilic components for loading a countercurrent isotope exchange column.

Methodology and research methods.

The methodological basis of the dissertation is presented by an analysis of modern scientific literature on the topic of work, as well as generally accepted methods for conducting laboratory research and processing experimental data. In this work, the methods of low-temperature nitrogen adsorption, differential thermal analysis, and mass spectrometry were used to study catalyst carriers. To study the parameters of the packed catalytic layer, the method of pulsed tracer injection was used, and to study the mass

transfer characteristics of the isotope exchange process, modern physicochemical methods of isotope analysis were used.

The main provisions for defense:

- influence of the composition of hydrophobizing impregnation with polymers from the class of silanes on the hydrophobicity and thermal stability of Pt catalysts based on Al_2O_3;

- the influence of the method of synthesis and preliminary preparation of the carrier of SDVB on the activity of the Pt catalyst based on it in the reaction of isotopic exchange of hydrogen with water vapor;

- influence of column packing parameters with a mixture of a hydrophobic catalyst and a hydrophilic packing, the way it is started and the conditions of the experiment (reflux density, gas flow) on the hydrodynamic conditions of liquid movement in the packed catalytic layer;

- influence of the process parameters (temperature, pressure, start method) on the overall efficiency of the ChIE process in the water-hydrogen system and the rate of its stages of phase and catalytic isotope exchange (PhIE and ChIE).

Approbation of work.

The materials of the work were reported and discussed at the XVII International Scientific Conference and School of Young Scientists "Physical and Chemical Processes in Atomic Systems", at the XIII International Congress of Young Scientists in Chemistry and Chemical Technology ICCT-2017, at the 13th International School of Young Scientists and Specialists named after A.A. Kurdyumov "Interaction of hydrogen isotopes with structural materials" (IHISM'19 JUNIOR), at the 7th International Conference and the 14th International School of Young Scientists and Specialists named after A.A. Kurdyumov "Interaction of hydrogen isotopes with structural materials" (IHISM'21), at the international conference Tritium 2019: 12th international conference on tritium science & technology and at the International conference 3rd Asia Pacific Symposium on Tritium Science APSOT-3.

Publications:

A total of 16 scientific papers were published on the topic of the dissertation, including 9 in publications recommended by the Higher Attestation Commission (8 of them

in publications indexed by Scopus, Web of Science and Chemical Abstracts), in collections of abstracts of reports of scientific conferences - 6. Received 1 RU patent.