ANNOTATION

of dissertation work,

submitted for the degree of Doctor of Philosophy (PhD) in the specialty "6D072100 - Chemical Technology of Organic Substances"

Yesbol Shaimardan

«Research and conversion of persistent organic pollutants based on polychlorinated biphenyls»

General description of work. The dissertation is devoted to the study and establishment of the scale of distribution and quantitative content of polychlorinated biphenyls (PCBs) related to persistent organic pollutants (POPs) in the territories adjacent to the Ust-Kamenogorsk condenser plant, as well as the development of heterogeneous mono- and bimetallic catalysts for the disposal of PCBs by catalytic dehydrochlorination.

Relevance of the research topic:

The Stockholm Convention has designated certain organochlorines, including polychlorinated biphenyls (PCBs), as persistent organic pollutants (POPs) and are therefore subject to a mandatory detoxification process. On May 22, 2001, the Convention on Persistent Organic Pollutants was signed in Stockholm, which aims to reduce and completely eliminate the production, use, releases and storage of existing stocks of POPs. The Stockholm Convention was ratified by Kazakhstan on June 7, 2007. Within the framework of this Convention, by 2028 it is planned to completely decontaminate and utilize PCBs in used transformers and capacitors. The environmental analytical program of the Stockholm Convention involves monitoring to assess the level of pollution and distribution of POPs as a result of direct or indirect anthropogenic impact on the environment.

As a result of the survey, it was found that in terms of the presence of PCB-contaminated territories and waste PCB-containing equipment, Kazakhstan ranks second (after Russia) among the CIS countries. Eight “hot” spots contaminated with PCBs have been identified in the republic. In the city of Ust-Kamenogorsk, East Kazakhstan region, 80% of PCB waste is concentrated. The currently accumulated reserves of excessively produced halogen-containing by-products and POPs require environmentally safe disposal, which necessitates the development of effective methods for recycling these substances and converting them into less hazardous compounds. Due to the heterogeneity of the composition of PCBs and the variety of methods for their disposal, it is extremely important to select, improve existing ones and develop new effective and environmentally friendly methods for the disposal of POPs in order to transform them into useful products. The selection of neutralization methods depends on the aggregate state of the material to be disposed of, the concentration of POPs, and the technological and environmental features of the processes being carried out. The likelihood of the formation of dioxin-like by-products during the disposal of POPs necessitates the need for strict control of the technological process and, according to Article 5 of

the Stockholm Convention, it is necessary to ensure the use of modern disinfection methods.

In modern methods for neutralizing industrial waste containing PCBs, the lion's share is occupied by catalytic dehydrochlorination of PCBs due to the possibility of using new types of catalysts obtained using nanomaterials and nanotechnologies. In addition, reductive methods for removing halogen or replacing it with hydrogen make it possible to regenerate the hydrocarbon component of halogenated molecules for reuse, which meets the objectives of resource conservation, and the use of catalytic methods contributes to a significant reduction in energy costs. The most common catalyst systems used for the dehydrochlorination of PCBs are palladium-containing supported catalysts. The palladium content in such catalysts reaches up to 10%. Therefore, research conducted to reduce the palladium content by “diluting” the noble metal with other metals with low cost characteristics is relevant.

Goal of the work. Analytical control of PCBs and study of its distribution in environmental objects of the city of Ust-Kamenogorsk, as well as the development of mono- and bimetallic catalysts deposited on a carrier for the catalytic dehydrochlorination of PCBs.

In order to achieve this goal, the following tasks were set:

- Establishment of the optimal modifier (hydrochloric, phosphoric, nitric, sulfuric and acetic acids, sodium hydroxide, hydrogen peroxide) of commercial activated carbon of the BAU-A brand for the purpose of use as a carrier in the production of monometallic catalysts based on Pd, Cu, Ni and bimetallic heterogeneous Pd-Cu, Pd-Ni catalysts and study of the physico-chemical properties of modified activated carbon (AC_m);
- Synthesis of catalysts $10Cu/AC_m$, $10Ni/AC_m$, $5Pd/AC_m$, $3Pd\text{-}7Cu/AC_m$, $3Pd\text{-}7Ni/AC_m$ for reductive dehydrochlorination of persistent organic pollutants (POPs) containing metals (wt., %): Pd – 5%; Cu – 10%; Ni – 10%; Pd-Cu – 3:7% respectively; Pd-Ni – 3:7%, respectively, and the study of their physicochemical properties;
- Development of methods for the synthesis of $1Cu/AC_m$ and $3Cu/AC_m$ catalysts with copper contents of 1% and 3% and study of their physicochemical properties;
- Study of the congeneric composition of PCBs in soil and bottom sediment samples and study of their distribution area in the city of Ust-Kamenogorsk, where 80% of PCB wastes of the Republic of Kazakhstan are concentrated, as well as the extraction of PCBs from contaminated samples;
- Establishment of the optimal mode for the conversion of PCBs and chlorobenzene by catalytic dehydrochlorination with catalysts $10Cu/AC_m$, $10Ni/AC_m$, $5Pd/AC_m$, $3Pd\text{-}7Cu/AC_m$, $3Pd\text{-}7Ni/AC_m$ and $1Cu/AC_m$ $3Cu/AC_m$.

Object of study. Samples of soils and bottom sediments contaminated with PCBs; activated carbon of BAU-A grade modified with hydrochloric acid; catalytic activity towards PCBs of synthesized mono- and bimetallic ($10Cu/AC_m$,

10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, 3Pd-7Ni/AC_m) catalysts, synthesis method and degree of chlorobenzene conversion by 1Cu/AC_m and 3Cu/ catalysts AC_m.

Subject of study. Dehydrochlorination of PCBs and chlorobenzene using mono- and bimetallic (10Cu/AC_m, 10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, 3Pd-7Ni/AC_m) catalysts supported on BAU-A grade activated carbon modified with hydrochloric acid and catalysts 1Cu/AC_m and 3Cu/AC_m, with a metal content of 1% and 3%, respectively.

Scientific and technical level of research and metrological support of research work. In the process of performing the dissertation work, classical and modern physical and chemical research methods were used. The congeneric composition of PCBs in soil and bottom sediment samples, the composition, structure of the carrier also the synthesized catalysts were studied by physical and chemical methods on the basis of the engineering laboratory of the Kazakh National Research Technical University named after K. Satpayev, the School of Engineering and Digital Sciences of Nazarbayev University and the national scientific laboratory for collective use East Kazakhstan University named after S. Amanzholov.

In particular, the following methods of sample preparation and research were applied:

- Soil sampling was carried out in accordance with state standard (STST) 28168-89 « Soils. Sample selection»;
- Samples of bottom sediments were taken from the Irtysh River in the area of the epicenter of local PCB contamination (Ust-Kamenogorsk capacitor plant area), according to STST 17.1.5.01-80 «Protection of Nature. Hydrosphere».;
- In order to obtain concentrates from solid matrices, extraction was carried out in a Soxhlet apparatus «Behr R 104S-SK» (Germany);
- Identification of PCBs in extracts of soils and bottom sediments was carried out using an Agilent GC 7890A MS 5975C gas chromatograph (GC/MS) with a quadrupole mass spectrometric detector (GC-MSD) (USA);
- The optical characteristics of Pd, Cu, Ni and Pd-Cu, Pd-Ni were determined by UV spectroscopic method (Specord 210 plus BU, Germany);
- Structure and morphology of 10Cu/AC_m, 10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, 3Pd-7Ni/AC_m and 1Cu/AC_m and 3Cu/AC_m catalysts with copper content of 1%, 3% precipitated on a modified AC_m carrier , studied on a Panalytical X'PERT PRO MRD X-ray diffractometer (Netherlands) and on a high-vacuum scanning microscope with an energy dispersive analyzer (Auriga Crossbeam 540, Germany);
- Chemical structure of 10Cu/AC_m, 10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, 3Pd-7Ni/AC_m and 1Cu/AC_m and 3Cu/AC_m catalysts with a copper content of 1%, 3% precipitated on a modified AC_m carrier, studied by IR-Fourier spectroscopy on FT-801 (Russia);

- Microphotographs of 10Cu/AC_m, 10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, 3Pd-7Ni/AC_m and 1Cu/AC_m and 3Cu/AC_m catalysts were obtained using electron microscopy (TEM) JEM 1400 (JEOL, Japan) with digital camera CCD Morada (OLYMPUS);
- The porosity and surface characteristics of the catalysts were determined by the BET method on an automatic gas sorption analyzer (Nitrogen Porosimeter, Anton Paar, Austria);
- The product obtained in the course of catalysis was identified on a gas chromatograph (GC/MS) brand Agilent GC 7890A MS 5975C with a quadrupole mass spectrometric detector (GC-MSD) (USA).

Scientific novelty of the obtained experimental results.

- For the first time, the optimal modifier (hydrochloric, phosphoric, nitric, sulfuric and acetic acids, sodium hydroxide, hydrogen peroxide) was studied and selected for the use of BAU-A brand activated carbon as a carrier for the production of Pd, Cu and Ni mono- and Pd-Cu, Pd -Ni bimetallic heterogeneous catalysts for the purpose of dehydrochlorination of persistent organic pollutants based on PCBs and the physicochemical properties of modified activated carbon were studied;
- For the first time, catalysts on an AC_m support were synthesized with a reduced amount of palladium (wt. %) to 5% in monometallic catalysts and up to 3% in bimetallic catalysts, “diluted” with transition metals based on copper and nickel, and monometallic catalysts based on copper and nickel were obtained 10Cu/AC_m and 10Ni/AC_m, with a metal content of 10% and their physicochemical properties were studied;
- A method has been developed for the synthesis of monometallic catalysts 1Cu/AC_m and 3Cu/AC_m, with a copper content of 1% and 3%, deposited on an ACm support;
- The congeneric composition of PCBs, belonging to the group of persistent organic pollutants, was studied in environmental objects of the city of Ust-Kamenogorsk, in particular in samples of soils and bottom sediments, and the areas of their distribution were determined;
- The optimal mode for the catalytic dehydrochlorination of PCBs using catalysts 10Cu/AC_m, 10Ni/AC_m, 5Pd/AC_m, 3Pd-7Cu/AC_m, and 3Pd-7Ni/AC_m has been determined;
- The catalytic activity of monometallic catalysts 1Cu/AC_m and 3Cu/AC_m in the process of catalytic dehydrochlorination of model chlorobenzene was studied.

The practical significance of the work.

The congeneric composition of PCBs and their distribution areas in the area of the Ust-Kamenogorsk Capacitor Plant (UKCP) and the storage pond of the UKCP can serve as additional material when taking elective courses in chemistry, biology and ecology in secondary and higher educational institutions, as well as when conducting research work on monitoring and neutralization of POPs by specialized environmental organizations.

The work on identifying the optimal modifier of activated carbon grade BAU-A for use as a carrier of mono- and bimetallic catalysts will expand the area of theoretical knowledge on the use of carbon materials in the field of catalysis. The usage of catalysts on an AC_m carrier with a reduced amount of palladium (wt.%) up to 5% in monometallic catalysts and up to 3% in bimetallic catalysts "diluted" with transition metals based on copper and nickel will allow developing a cost-effective green technology for the neutralization of POPs. In addition, the established optimal technological regime for the catalytic dehydrochlorination of PCBs expands theoretical knowledge in the field of "green" catalysis.

Main provisions submitted for defense:

- In soil samples located near emission sources (UKCP territory), the congeneric composition of PCBs was determined: 244'-trichlorobiphenyl (TCB), 22'55'-tetrachlorobiphenyl (tetraCB); 22'455'-, 23'455'-, 23'44'5-pentachlorobiphenyl (PentaXB); 22'44'55'-, 22'344'5' - hexachlorobiphenyl (HexaCB) and 22'344'55'-heptachlorobiphenyl (HpCB). PCB congeners in sediments are limited to 244' – TCB. A high degree of soil contamination is observed in the areas of the storage pond (UKPZ) and the mining and metallurgical complex, which, respectively, in terms of the content of PCB congeners is 2.26 and 4.83 times higher and in terms of the amount of TCB is 3.01 and 1.87 times higher than the MPC. A high level of contamination of bottom sediments has been established on the territory of the UKCP and exceeds the MPC by 3 times. The completeness of PCB extraction from contaminated objects is achieved maximum when using a mixture of DMSO and hexane as an extractant in a ratio of 1:4.
- The optimal modifier for activated carbon BAU-A from among the reagents used (hydrochloric, phosphoric, nitric, sulfuric and acetic acids, sodium hydroxide, hydrogen peroxide) is concentrated hydrochloric acid, which leads to the dissolution of the mineral components of Ca, Mg, Na and K, and also increasing adsorption capacity and polarity, which in turn contributes to an increase in oxygen functional groups, in particular the carboxyl group. When activated carbon is modified with hydrochloric acid (AC_m), the surface area of the carrier, the volume of micropores and mesopores changes, and HCl interacts with the surface groups of AC_m.
- The optimal metal content in heterogeneous catalysts for the transformation of persistent organic pollutants based on PCBs by catalytic dehydrochlorination is: for monometallic Pd - 5%; Cu – 10%; Ni – 10%; for bimetallic Pd-Cu – 3:7%, respectively; Pd-Ni – 3:7% respectively. The bond between Pd, Cu, Ni and Pd-Cu, Pd-Ni and modified activated carbon (AC_m) occurs through the carboxyl functional group in AC_m. The use of methanol in the hydrodechlorination of PCBs with catalysts $5Pd/AC_m$, $10Cu/AC_m$, $10Ni/AC_m$, $3Pd\text{-}7Cu/AC_m$ and $3Pd\text{-}7Ni/AC_m$ makes it possible to reduce the temperature of the conversion process by half, carry out the dehydrochlorination process without using high pressure and reduce the amount of catalyst used twice. At the same time, the degree of conversion of PCBs into biphenyl increases by 1.02-20 units.

- A method has been developed for the synthesis of catalysts $1Cu/AC_m$ and $3Cu/AC_m$, where $3Cu/AC_m$ is an effective catalyst in the catalytic dehydrochlorination of chlorobenzene to benzene, the conversion of which is 94.46%.

Relationship of work with research programs. The dissertation work was carried out in the laboratory of the engineering profile of the Kazakh National Research Technical University named after K.I. Satpayev within the framework of program-targeted funding № BR05236302 "Scientific and technical justification for innovations in the chemical cluster in the field of creating new materials and technologies to improve the efficiency and environmental sustainability of industrial production" for 2018-2020.

Publications. Based on the results of the study, 8 works were published, of which 1 article in peer-reviewed scientific publications indexed in the Scopus and Web of Science databases, 3 articles in journals recommended by the Control Committee in the field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan and 4 articles in materials of republican and international conferences.

The structure and volume of the dissertation. The dissertation consists of an introduction, 3 chapters, a conclusion and a list of references. The dissertation consists of 121 pages, 24 tables, 90 figures. Bibliography contains 171 sources.