ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
on specialty «6D073900– Petrochemistry»
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«Development of composite catalysts based on modified natural zeolites for polymer waste recycling processes»

General description of the work

The work is devoted to the production of modified new composite catalysts based on natural zeolite for the implementation of the technology of thermocatalytic treatment of carbon-containing waste, such as industrial household waste, plastics and heavy oil waste, into motor fuels and valuable organic compounds and their comprehensive analysis and testing.

The relevance of the study

Currently, a large amount of carbon-containing waste, such as worn tires and plastics, accumulates annually in the Republic of Kazakhstan and in many other countries of the world. On the one hand, they relate to difficult-to-biodegrade and non-destructive waste, which pose a serious threat to the environment. On the other hand, they are large reserves of secondary raw materials for processing them into alternative fuels and organic materials, Many advanced countries of the world are intensively working to improve and create new technologies for recycling tires and plastic waste, as well as improving the performance of recycling processes, which in general significantly increases the effectiveness of the method. At the same time, much attention is paid to the environmental aspects of recycling, namely waste-free and low-waste recycling, as well as resource-saving technologies. Recycling of industrial, household and plastic waste is one of the urgent tasks for the Republic of Kazakhstan.

There are practically no technologies for recycling plastic waste in Kazakhstan. Thermocatalytic treatment of industrial, household and plastic waste into motor fuels and valuable organic compounds is promising. The advantage of this method is associated with an increase in the rate of oil refining and an increase in oil waste in the form of fuel oil and tar – additional raw materials for the production of synthetic fuel products.

In this regard, for environmental protection, rational use of natural resources, production of energy sources and additional types of valuable organic compounds, it is necessary to obtain new modified composite catalysts based on high-efficiency natural zeolite and develop technologies for thermocatalytic treatment of industrial and household waste together with heavy oil waste.

Currently, catalysts for technologically important processes are being imported. In this regard, the development of inexpensive domestic catalysts with high efficiency is an urgent task. Because of their structure, zeolites have the property of molecular selectivity, as a result of which zeolites can only absorb substances with a certain number of molecules. According to these properties, zeolites currently exhibit catalytic activity in the production of synthetic fuels in petrochemical processes.

Purpose of the work is the develop composite catalysts based on natural zeolite modified with transition metals for the processing of polymer waste.

The tasks of the thesis:

- determination of the optimal parameters of the technology of complex processing of industrial and household waste into motor fuel;
- development and testing of composite catalysts based on natural zeolite for the process of thermocatalytic hydrogenation of polymer waste;
- study of the physico-chemical characteristics and catalytic properties of the obtained composite catalysts;
- determination of the main physico-chemical parameters of the target products obtained in the process of hydrogenation thermocatalytic waste treatment;
- pilot production tests and research of technology for the joint processing and manufacture of rubber and plastic waste into fuel materials and valuable products.

The object of the study are new composite catalysts based on natural zeolite modified with molybdenum and tungsten salts, natural zeolite from the Taizhuzgen deposit, tire and plastic waste, and heavy oil residue from the Kumkol field.

The subject of the study is the development of composite catalysts based on modified natural zeolite for the processing of polymer waste.

Research methods

The following physico-chemical research methods and calculations were used in the work: adsorption porometry (BET), IR spectroscopy, X-ray phase and X-ray photoelectron analysis, thermogravimetric analysis, electron microscopy, gas chromato-mass spectrometric analysis.

The main provision for the defense:

1. Optimum conditions for thermocatalytic hydrogenation of plastic waste and automobile tires: plastic waste: $t_{process}$ = 400 ºC, $r_{initial}$ = 0.5 MPa, $\tau_{holding}$ = 15 min, Polymer: Paste-forming agent = 1: 1, m_{cat} = 2%; tire waste: $t_{process}$ = 450 ºC, $r_{initial}$ = 0.5 MPa, $\tau_{holding}$ = 60 min, Tire waste: Paste-forming agent = 1: 1, m_{cat} = 2%.

2. Effective catalysts for thermal catalytic processing of polymer waste: 2.0%Mo/zeolite (61.56%), 2.0%W/zeolite (60.14%), 1%Mo1%W/zeolite (69.71%). The specific surface area of the catalyst increases from 2.1 (activated zeolite) to 6.1 m^2/g (1%Mo1%W/zeolite) and exhibits activity in the mesoporous form.

3. The valence state of metals in the composite catalysts is Mo^{4+}, Mo^{6+}, W^{6+}, with hydrogen sulfide (H_2S) formed in the process, MoS_2 (molybdenite and jordisite), MoS_3 (molybdenum trisulfide) and WS_3 (tungsten sulfide) form sulfides. As a result of the process, the amount of sulfur increases in solid waste (from 2.13% to 2.47%), and decreases in liquid products (0.097 – 0.038% by weight).

Scientific provisions for the defense

The dissertation presents the following original results:

1. Based on natural zeolite, accessible, inexpensive and highly active composite catalysts 2%Mo/zeolite, 2%W/zeolite, 1%Mo1%W/zeolite were synthesized for the first time for the process of thermocatalytic processing of worn-out tires and plastics into alternative motor fuels and valuable organic compounds;

2. A comprehensive study of the developed catalysts was carried out using IR spectroscopy, Raman spectroscopy, adsorption porometry (BET), electron microscopy, X-ray phase and X-ray photoelectron analysis and the effectiveness of catalysts based on natural zeolites modified with transition metals due to their elemental composition, characteristics and the presence of activation centers for the process of thermocatalytic processing of carbon-containing waste into fuel distillates;

3. It was found that the catalytic activity of Mo^{4+}, Mo^{6+}, W^{6+} increases in the presence of hydrogen sulfide formed during the formation of intermediate fragments, and it was also proved that MoS_2 (molybdenum and jordisite), MoS_3 (molybdenum trisulfide) and WS_3 (tungsten sulfide) pass into the active form;

4. The hydrogenation and cracking activity of the composite catalyst based on natural zeolite is confirmed by electron-acceptor properties (aprotic Lewis centers) observed during thermal activation of the initial zeolite (673-723 K).

Practical and theoretical significance of the scientific results

Thermal catalytic processing of worn-out automobile tires, plastic waste and heavy oil waste as secondary raw materials allows solving the problems of environmental protection, rational use of raw materials and development of technologies for obtaining alternative types of energy sources. The prospects of the problem under study are due to the growth in demand for synthetic motor fuels, the intensification of work to solve the problems under consideration in the world and in Kazakhstan.

Reliability and validity of the results

The reliability of the conclusions and provisions made in the work is confirmed by numerous experimental data obtained using modern methods of analysis and research on certified equipment. The results obtained were published in leading scientific journals with a high impact factor, as well as in journals recommended by the Education and Science Committee of the Republic of Kazakhstan and in collections of materials of domestic and foreign international scientific conferences.

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

The author's personal contribution consists of conducting a literature review, compiling a laboratory setup for the process of thermal catalytic treatment of carbon-containing household waste, planning the objects of study. The author also produced new catalysts based on zeolite from the Tayzhuzgen deposit, modified them with transition metals, and studied their acidic and catalytic properties. An analysis of the obtained experimental data was conducted, and articles and abstracts of reports were published based on the results of the study. The definition of tasks that reveal the topic and the examination of the results obtained were developed by the author together with the supervisors of.

1. Thermo-catalytic processing of polymer waste over catalysts on the basis of natural zeolite from the Tayzhuzgen field (Kazakhstan) modified by molybdenum / Research article published in Rasayan Journal of Chemistry (collection of experimental data, processing of results, preparation of the article).

2. Табиғи цеолитке отырғызылған молибден катализаторы қатысында полимер қалдықтарын гидрогенизациялық термокатализдік өңдеу // Herald KBTU. (direct participation in the collection of experimental data, processing and interpretation of results, preparation of the article).

3. Полимер қалдықтарын гидрогенизациялық термокатализдік өңдеу процестері үшін Тайжүзген табиғи цеолиті негізіндегі катализаторларды зерттеу // Herald KazNRTU (conducting experiments, processing and interpreting the results obtained, and presenting them in the form of scientific papers).

4. Research of composite catalysts for the process of thermocatalytic hydrogenation processing of plastic waste // International Journal of Biology and Chemistry (collection of experimental data, processing of results, formalization in the form of scientific papers).

5. Көмірсутекті қалдықтарды термокаталитикалық гидрогендеу процесі үшін табиғи цеолитке отырғызылған вольфрам катализаторларын зерттеу // Herald KBTU (collection of experimental data, processing and interpretation of the obtained results, preparation of the article).

6. Определение кинетики потери массы образцов отхода автошины и тяжелого остатка нефти по результатам тга с использованием интегрального метода coats-redfern // Herald KBTU (collection and description of experimental data, discussion of analysis results, preparation of the article).

7. Recycling of waste plastics to liquid fuel mixture over composite zeolites catalysts. Chemical Bulletin of Kazakh National University (collection and description of experimental data, processing of results, preparation of the article).

Publications

The results of the study are presented by scientific publishers of the Ministry of Education and Science of the Republic of Kazakhstan in the Bulletin of KBTU ISSN 1998-6688 (Almaty, (T 15, No. 1, 2018), in the Bulletin of KazNRTU (No. 5 (135), 2019), ISSN 1998-6688 in the Bulletin of KBTU (Almaty, (T 17, No. 2, 2020), ISSN 1998-6688 in the Bulletin of KBTU (Almaty, (T 17, No. 3, 2020), in the International Journal of Biology and Chemistry (No. 1, 2020), Bulletin of Kaznu series of chemistry ISSN 1563-0331 (T 101, No. 2, 2021) and "Rasayan journal of chemistry" ISSN 0974-1496 (2019, Vol. 12, No. 4).

Approbation of the dissertation.

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

– at the International Scientific Conference of Students and Young Scientists "Farabi alemi", Almaty, 2018;

– "Chemical technology of functional materials" - the 4th International Russian-Kazakh Scientific and Practical Conference (2018, Almaty, Kazakhstan);

– at the International Scientific Conference of students and Young Scientists "Farabi Alemi", Almaty, 2019

Relation of the thesis with research and government programs

This work was carried out in accordance with the projects for grant funding of scientific research on the topic: "Resource-saving technologies for joint processing

of solid fossil fuels and industrial and household waste into liquid motor fuels" (4434 / GF-4, 2015-2017) and for grant funding of research of young scientists under the project "Zhas Galym" on the topic "Development of composite catalysts for the process of thermal catalytic treatment of worn-out polymer waste into fuel distillates" (AP25794283, 2025-2027).

Volume and the structure of the thesis

The dissertation work consists of a review of the literature, objects and methods of research, results and discussion, conclusion, a list of used sources from 131 titles. The work contains 122 pages, 64 figures and 26 tables.