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Hydrothermal Catalytic Transformations of Polymeric Wastes over Zeolite Catalysts Modified with Molybdenum and Tungsten

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ABSTRACT

The article is devoted to the study of the adsorption properties and morphology of new composite catalysts based on acid-activated zeolite heulandite-clinoptilolite of the Kazakhstan Taizhuzgen deposit modified with molybdenum salts $(NH_4)MoO \cdot 4H_2O$ and tungsten $(NH_4)_5H_5[H_2(WO_4)_6] \cdot H_2O$, for the process of thermocatalytic hydrogenation of plastic waste. The study of the developed catalyst by the method of adsorption nitrogen porometry demonstrated the presence of typical type IV isotherms, which indicated the formation of a porous adsorbent by multilayer nitrogen adsorption in the mesopores of the catalyst. The adsorption capacity of the structure formed by the catalyst based on zeolite modified with molybdenum and tungsten, due to the presence of predominantly mesoporous cavities, is able to selectively influence the process of hydrothermocatalytic processing of waste polymers based on polyethylene and polypropylene. The pore size distribution indicates the presence of mesopores and an insignificant number of micropores at low pressure. The catalyst samples were tested in the thermocatalytic hydrogenation reaction of polymer waste. Significant gas formation and predominant content of alkanes, isoalkanes, alkenes and aromatic hydrocarbons in liquid products are shown. It is obviously that the main contribution to the transformations made by mesoporous inclusions in the cavities of the zeolite under study formed during their treatment with molybdenum and tungsten salts.

Keywords:
Natural zeolite; Composite catalyst; Polymer waste; Hydrogenation thermocatalytic processing; Adsorption

1. Introduction

One of the results of human activity is the formation of waste, among which waste of plastics and rubber-technical products occupy the first place.

Close attention is paid to the recycling of worn tires, since the toxic effects of tires with expired service life are very negative for the environment and humans. The need to create an effective technology for recycling waste rubber products (tires) is due to the fact that about 1.5 billion used

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tires are thrown out in the world every year, and the main component of tires, synthetic rubber, is very difficult to recycle.

According to the European Tire Recycling Association, the volume of tire recycling does not exceed ten percent. No more than 1/5-1/4 of the collected tires are used as fuel, but most of the used tires are stored or simply left on the territories of car parks or taken to forests, quarries and landfills. Stacks and waste heaps of these wastes are a constant source of increased risk of fire and the development of epidemic diseases due to artificially formed habitats and reproduction of insects and rodents. At the same time, the territories for temporary storage of tires are practically removed from land use [1,2]. The fact that for several decades there has been no certainty about the methods of recycling tire rubber in Kazakhstan is primarily due to the lack of state policy in this direction. It should be noted that by their structure and properties of materials, tires are a strictly unified type of product. The fierce competition for quality and reliability has led to the fact that the composition and properties of rubbers, frame materials, as well as the production technology of these products are very similar from different manufacturers. As a result, modern tires are a complex composite product made of dissimilar materials, which has great resistance to mechanical repetitive loads and destructive environmental factors. Such specific properties of tires, which are very necessary to ensure the safe operation of wheeled vehicles, become unfavorable factors in solving the problem of their elimination after the end of the life cycle. The system of removal from the territory of the region of this type of waste of motor transport activities should provide for a mandatory stage of their collection and processing.

The global production and consumption of plastics is also increasing annually, at the same time the number of wastes is also increasing, among which high- and low-density polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate and polystyrene are the most common [3-9]. With the use of modern equipment and technologies, no more than 1/10 of the raw materials from the bowels and from the surface of the earth are converted into targeted useful products, and more than 85-88% of the raw materials are turned into waste. Polymer waste is mainly stored in landfills of municipal solid waste, and their biochemical, photo- and chemical destruction is accompanied by the release of various toxic impurities into the environment (for example, formaldehyde, phenol, benzene, etc.).

Currently, the problem of recycling waste polymer materials is becoming relevant not only from the standpoint of environmental protection, but also due to the fact that polymer waste can be used in the future as a raw material and energy resource. One of the main sources of plastic waste is waste based on polystyrene (PS) and polyolefins (PO): polypropylene (PP), high-density polyethylene (HDPE), medium (MPPE) and low pressure (LPPE) waste are, % wt.: PE - 34, PS -7.6 and PP -7.4 [10,11].

Recycling of polymer waste is one of the most difficult environmental problems to solve. The use of polymer waste makes it possible to significantly save primary raw materials (primarily oil) and electricity.

Large-scale technological research and development being developed and carried out in the developed countries of the world, provoked by a huge increase in the depletion of raw materials worldwide, should be associated with a reorientation to waste-free technologies that ensure a minimum amount of waste, high economic efficiency of subsequent recycling of production waste. From year to year, environmental standards for industrial emissions are being tightened. The organization of waste recycling with minimal energy and material costs is a grandiose extremely important technical task that requires an integrated approach, including changes or significant correction of the entire set of technical means, equipment and technologies.

Initially, the solution to the problem of industrial waste was carried out mainly by destruction, i.e. by well-known methods, which include burial, i.e. burying, incineration, but with the increase in the degree of environmental pollution in the world, other, more promising ways of waste disposal were brought to the fore: from sorting to reuse, that is, recycling resources. World practice testifies to the need to create state comprehensive programs aimed at organizing the collection, temporary storage, processing and development of the market for the consumption of plastic and tire recycling products. The main areas of plastic waste processing include: thermal decomposition at temperatures of 400-800°C, destruction with the production of initial low-molecular products (monomers, oligomers) and recycling. Most of the plastic waste recycling processes in the world are carried out by their thermal (pyrolytic) splitting.

One of the ways to regulate the conditions of pyrolytic destruction of waste and the properties of the resulting products is to conduct the process in the presence of catalysts. Catalysts affect the yield of pyrolysis products, reduce the temperature and increase the rate of destruction of hydrocarbons [12,13]. Thus, it was shown that catalytic cracking of polyolefins at a temperature of 400-550°C leads to the production of hydrocarbon mixtures completely different from those obtained after thermal high-temperature cracking [14-17]. When processing mono- and mixed plastics, problems arise due to the influence of various factors on their degradation processes.

One of the most promising methods of processing plastic waste into high-quality liquid fuel is hydrocracking. Compared to pyrolysis and catalytic cracking, hydrocracking makes it possible to obtain a highly saturated liquid product that can be used without additional processing as transport fuel or fuel oil. Hydrocracking promotes the breaking of carbon-carbon bonds together with simultaneous or sequential hydrogen hydrogenation of unsaturated molecules formed in the process. It allows you to convert heavy (high-boiling) plastic molecules into lighter (low-boiling) molecules [18-20]. Hydrocracking of model plastic waste on a zeolite catalyst with a mesoporous structure, with nickel deposited, is more efficient than on various micro-mesoporous acid zeolite composites. At the same time, the share of light diesel fuel increases to 1/3. Catalytic hydroforming of polyethylene oil occurs on zeolites and mesostructured aluminosilicates, with nickel deposited. The process of catalytic hydrocracking occurs at lower temperatures and causes lower operating costs [21-28].

Numerous studies of the adsorption and catalytic properties of various catalysts indicate that the adsorption capacity of the zeolite-based catalyst structure, due to the presence of micro-, meso- and macroporous cavities in it, is able to selectively influence the process of hydrothermocatalytic processing of plastics. It is shown that microporous cavities of zeolites prevent the diffusion of larger molecules, and most of the transformation products consist of gases, while catalysts based on mesoporous structure contribute to an increase in the yield of the liquid product. Mesoporous material is a one–dimensional porous formation with a hexagonal set of homogeneous mesopores and, due to the large surface area and acidity, is able to reduce the tendency to coke formation. However, due to the insignificant formation of aromatic compounds and branched olefins, low-quality fuel is obtained. For this reason, for the most efficient transformation of plastics as a result of thermocatalytic processing, it is necessary to modify the catalysts with various active substances.

Zeolites are well known as microporous catalysts, and the presence of micropores can hinder the diffusion of larger molecules. To reduce the content of micropores, methods are used to evaluate the textural properties of zeolites. However, the classical method of analysis can overestimate the surface area of mesopores and underestimate the volume of micropores for the studied micro-mesoporous materials. Measurements of the porous structure of various zeolites made with specially developed mechanical impurities allow making appropriate changes in the structure [29-31]. Mesoporous structures are characterized by low acidity, low cracking ability compared to zeolites with a higher Si/Al ratio [32-34]. The use of zeolites with a mesoporous structure favors an increase in the availability of acid centers and increases the activity of metal-containing centers. This circumstance makes it possible to partially reduce the diffusion restrictions for rapid access of reactants and diffusion of products from the reaction zone. In addition, the possibility of pore blocking by larger particles is reduced/eliminated and the formation of large molecules with a particle diameter d less than 1 nm increases.

In some studies, the dependence of activity and selectivity on the location and distribution of acid centers in zeolite has been revealed. The activity and selectivity of reactions carried out in the presence of zeolite-containing catalysts are affected by both increased polarization and delocalization of protons [35-38]. Thus, the regulation of acid centers and a well-defined pore structure make it possible to accurately determine and regulate the catalytic activity of zeolites. Mesoporous zeolite materials are excellent promising alternative materials for using the effects of molecular retention in catalytic reactions. One of the ways to enhance these interactions is to regulate the hydrophobic-hydrophilic balance of the surface. In [39] the condensation method was used to control the hydrophobicity of mesoporous silica. It is established that the obtained materials are methyl-/phenyl-containing silica with a pore size of 3-5 nm. The results of the analysis of the chemical composition of the surface of the synthesized zeolite showed improved material characteristics in the case of lysozyme adsorption and the catalytic process on the carrier. The use of mixed catalysts A1-MSM-41 and HZSM-5 in various ratios makes it possible to slightly increase by 5-10% the yield of C_5-C_{20} fractions of hydrocarbons during the destruction of polyolefins in relation to the use of these systems individually [40].

The acidity of the catalyst plays an important role in the selectivity of the macromolecule decomposition process: zeolites and aluminosilicates with a fairly high acidity are not selective with respect to monomer yield; and strongly acidic catalysts of the $AlCl_3$-type contribute to an increase in the rate of thermal decomposition of polyolefins and a decrease in the process temperature [41-44]. It should be noted that the use of the considered catalytic systems in the destruction of contaminated polymers is complicated by the presence of substances capable of deactivating the active centers of the catalyst at a high rate with subsequent loss of catalyst activity. Therefore, an important industrial parameter of the use of the catalyst is the deactivating ability. The activity of catalysts during the destruction of polyolefins varies in the series: HZSM-5 > aluminosilicates > HY, N-mordenite.

Natural and synthetic zeolite catalysts were used in a small experimental reactor for catalytic pyrolysis of four main types of plastic waste, such as polyethylene, polystyrene, polypropylene and polyethylene terephthalate [45-49]. Thus, mesoporous catalysts with induced acidity and micro- and mesoporous composite zeolite-containing catalysts attract the closest attention of researchers to test the activity of such catalysts in the hydrocarbon hydrocracking reaction. Apparently, the addition of nanoparticles to the structure of mesoporous zeolite can lead to an increase in the acidity and stability of such catalytic systems and to an increase in their catalytic efficiency.

The aim of this work is the synthesis of new mesoporous zeolite-containing catalysts modified with molybdenum and tungsten salts, the selection of catalyst compositions with good adsorption properties and texture. The activity and selectivity of the prepared catalysts were studied in the process of thermocatalytic hydrogenation of polymer waste based on polyethylene (PE) and polypropylene (PP).

2. Methodology

Natural zeolite heulandite-clinoptilolite was activated by acid-free treatment. For this purpose, it was preliminarily ground to a powder state, sifted through a sieve with a pore size of 0.25 mm. 100 g of zeolite were taken and then they were decationized with a 1 M solution of NH_4Cl (120 ml) in a round-bottom flask with constant stirring in a boiling water bath for 6 hours. The treated zeolite was separated from the mixture by filtration, washed with distilled water from chlorine ions, and then dried successively, first at room temperature, then at 100°C to a constant weight. Then it was subjected to heat treatment in a catalytic cracking unit with a stationary catalyst bed, successively heating in a stream of air supplied at a rate of 500 mL/min to 100, 200, 300, 400, 500 °C, respectively, for 4 hours.

The activated zeolite was modified by impregnation with a solution of molybdenum $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and tungsten $(NH_4)_5H_5[H_2(WO_4)_6]\cdot H_2O$ salts in a ratio of 1:1. A portion of the zeolite was kept in a 0.1 M salt solution for 3 hours, then the residual solution was decanted off, and the catalyst, 1% Mo(VI)–1% W(VI)/zeolite, was dried in air to a constant weight.

The morphology of natural zeolite and composite catalysts based on it was studied using a low-vacuum scanning electron microscope (SEM) Quanta 200i 3D (FEI, USA). The range of microanalysis systems of determined images was in the b-U region, and the energy distribution was 132 EV (Mn Kα). Heating modules were - up to 1000°C. The voltage across the electron optics was varied from 200 to 30 kV. Separation in low vacuum mode - 10-130 Pa (0.1-1.0 Torr).

The specific surface area of samples of natural zeolite and composite catalysts based on it was studied by low-temperature nitrogen adsorption on an ASAP 2400 Micrometrics specific surface analyzer (USA). An analyzer (10 mm Hg) was used, providing accurate and reproducible pressure resolution. It is equipped with a turbomolecular brake pump providing the high vacuum required for krypton pressure analysis.

Specific surface analyzers were used, which made it possible to carry out multipoint measurements of solid samples according to the BET adsorption isotherm. The Horiba SA-9600 analyzer measured the BET surface area of the catalyst in the range from 0.10 to > 2.000 m^2/g. The Thermo Scientific Surfer analyzer allowed the use of static volumetric gas adsorption methods to determine the amount of gas interacting with free areas of a solid surface.

Analysis of the composition and intensity of the composite catalyst was carried out on an X-ray fluorescence spectrometer (XRF) with a wavelength dispersion similar to an electron microprobe (EPMA). With the S2 PUMA Series 2 with a mapping step, multi-point quality monitoring has been simplified. To measure the dimensions of the samples, available inserts from 40 to 152 mm in diameter were used.

Resin-asphaltene oil refinery wastes (fuel oil with a boiling point above 350 °C) were used as an additional binder - a paste-forming agent, a source of hydrogen and carbon-containing raw materials. Plastic waste was pre-crushed to the state of crumbs, varying the particle size no more than 3-6 mm in diameter.

Thermocatalytic hydrogenation processing of raw materials based on plastic waste was carried out at an installation where a hollow cylindrical stainless-steel vessel with a built- in chromel-alumel thermocouple and a nozzle for a pressure gauge served as a reactor. The reactor was operated in the mode of periodic shaking in a nitrogen atmosphere, under pressure. The temperature was regulated in the range from 400 to 450°C, the pressure from 0.5 to 0.6 MPa.

The mixture of feedstock, catalyst, and fuel oil preheated to 80°C was loaded into the reactor and purged with nitrogen. Heating to the required reaction temperature was carried out using an alternating current heater controlled by a transformer and an ammeter. The contact time varied from 15 to 30 min. During the reaction, the temperature, pressure, and volume of the evolved gas were controlled. The gas was collected in a gasometer attached to the installation with a saturated sodium chloride solution.

After the reactor was cooled to room temperature, it was connected using a nozzle through a straight cooler and a three-way allonge with receivers. Then, when heated, fractional distillation was carried out, separating fractions boiling up to 180 °C, from 180 to 250°C, and from 250 to 320°C. The dry residue after distillation was weighed and the material balance of the process was calculated. The products obtained in the course of the reaction were analyzed by nitrogen adsorption porosimetry, SEM, gas-liquid chromato-mass spectroscopy, and energy-dispersive spectroscopy.

The fractional composition of the analyzed distillates was determined on an Agilent 7890A/5975C chromato-mass spectrometer (USA). The mobile phase of the chromatograph was gaseous helium grade A, the volume fraction of which was at least 99.995 vol. %. Mass spectra were taken in the scanning mode. For chromatographic separation, an HP-5MS capillary column with a length of 30 m and an internal diameter of 0.25 mm was used. The stationary phase was dimethylpolysiloxane 95 wt. % and methylphenylpolysiloxane 5 wt. % with a layer thickness of 0.25 µm.

3. Results

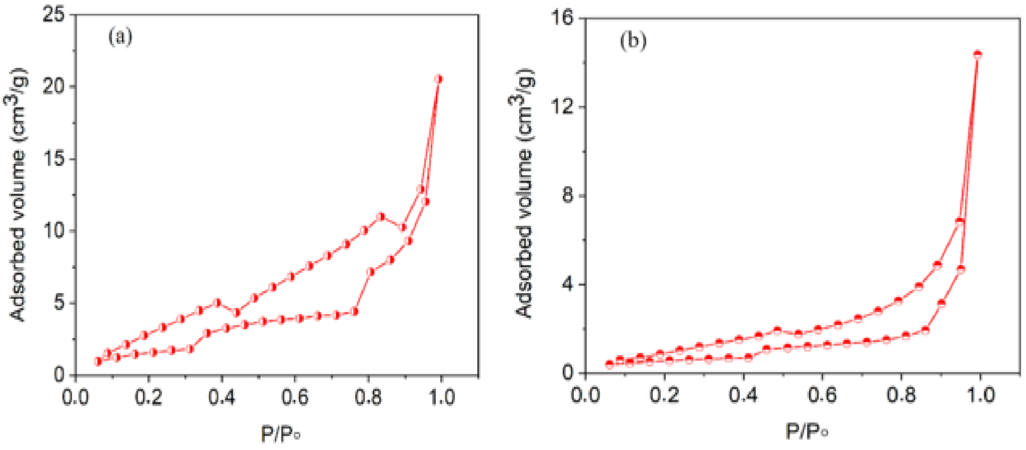
It has been established by the BET method that the multipoint distribution of pores in the activated zeolite sample is more than two orders of magnitude higher than in the 1%Mo(VI)–1%W(VI)/zeolite composite. This is probably due to the partial destruction of mesopores and their uneven distribution in the catalyst sample. The total desorption surface area determined by the BJH method in the 1%Mo(VI)–1%W(VI)/zeolite composite is two orders of magnitude larger than in the activated zeolite sample, which causes the presence of a porous surface.

The total desorption pore volume indicates a possible narrowing of the pores due to the treatment of the activated zeolite with metals and the formation of a surface amorphous mesoporous phase. The desorption pore diameter determined by the BJH method is approximately comparable for both catalyst samples, which suggests that the adsorption characteristics of the surface of the studied adsorbents with a wide pore size distribution can directly affect the efficient and selective conversion of hydrocarbons due to the high adsorbent–adsorbate interaction energy on investigated catalysts.

The results of determining the texture properties of the surface of catalyst samples by the BET and BJH methods are shown in Table 1. Figure 1 shows pore size distribution curves on the surface of an activated zeolite and a 1%Mo(VI)-1%W(VI)/zeolite composite catalyst. It can be seen that for each of the studied catalysts, the phenomenon of hysteresis is observed. A steep increase in the adsorption branch of the isotherm to the region of higher relative pressures was observed with approaching the saturation pressure, which is limited by the final adsorption characteristic of porous adsorbents. The results are consistent with the data obtained from the study of the specific surface area and pore size distribution presented in Table 1.

Table 1
Structural properties of the catalysts

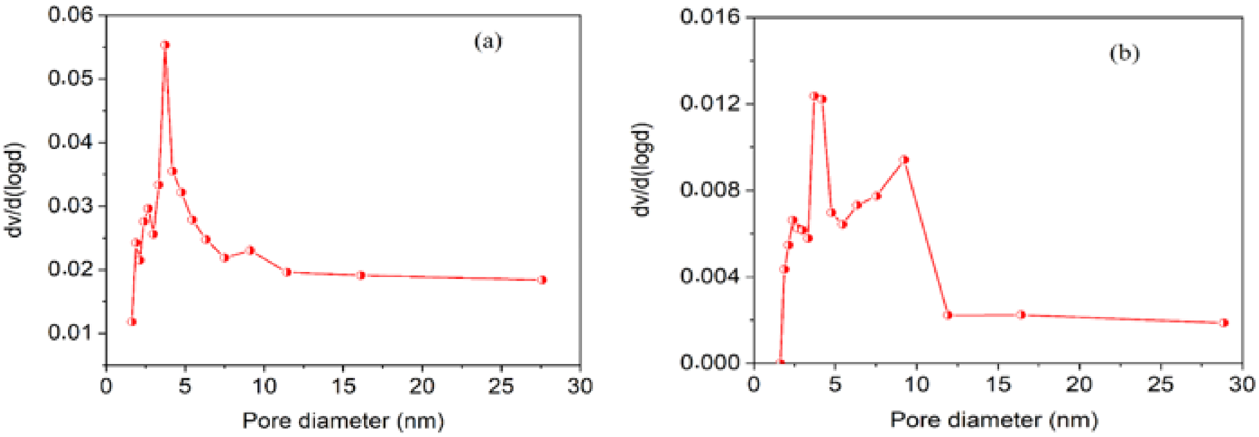
Catalyst	Texture properties of the surface			
	Multipoint BET, m²/g	BJH Method cumulative desorption surface area, m²/g	BJH Method cumulative desorption pore volume, cc/g	BJH Method desorption pore diameter (mode), Å
Zeolite	6.13	2.50	4.01	3.73
1%Mo(VI)-1%W(VI)/ zeolite	2.07	6.72	2.39	3.71



(a) (b)

Fig. 1. Pore size distribution of the catalysts: a) zeolite, b) 1%Mo(VI)-1%W(VI)/zeolite

Figure 2 shows N_2 adsorption/desorption isotherms on samples of activated zeolite and catalyst based on 1%Mo(VI)-1%W(VI)/zeolite composite.



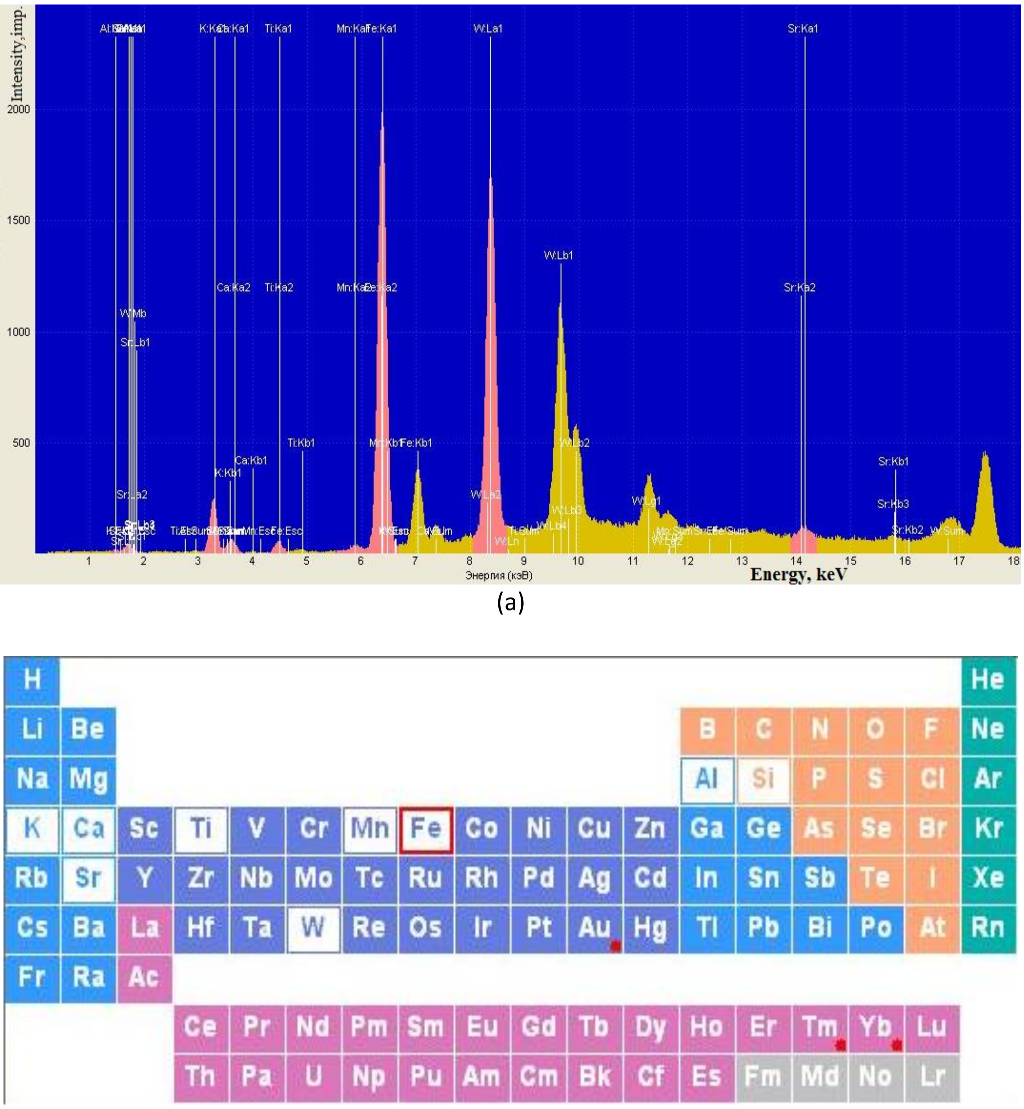
(a) (b)

Fig. 2. N2-adsorption isotherms of the catalysts: a) zeolite, b) 1%Mo(VI)-1%W(VI)/ zeolite

Catalysts based on 1%Mo(VI)-1%W(VI)/zeolite and activated zeolite show typical type IV isotherms characteristic of saturation pressure, which corresponds to the formation of a porous adsorbent-catalyst. This is explained by the possibility of multilayer adsorption of N_2 in the mesopores of these catalysts, which corresponds to a high interaction energy of the adsorbent-catalyst and N_2 as an adsorbate. A type IV hysteresis loop is evident both in the activated zeolite and in the 1%Mo(VI)–1%W(VI)/zeolite composite, which proves the possibility of the formation of a large number of mesopores.

At low pressures, the N_2 adsorption isotherm on the 1%Mo(VI)–1%W(VI)/zeolite composite is similar to the type I-st isotherm, which is typical for microporous solid catalysts with a small fraction of the outer surface. However, as the pressure increases, a large amount of N_2 is adsorbed, which is typical for mesoporous catalysts. The nitrogen ad-sorption isotherm confirms the presence of mesopores in the composite catalysts along with some microporous regions.

The results of X-ray fluorescence spectroscopy (XRF) of catalysts based on activated zeolite and 1%Mo(VI)–1%W(VI)/zeolite composite are shown in Figure 3 and Table 2. The present study also determined the qualitative and quantitative composition of the initial and composite catalysts. The analysis data coincide with the previously obtained X-ray fluorescence spectroscopy data.



(a)

(b)

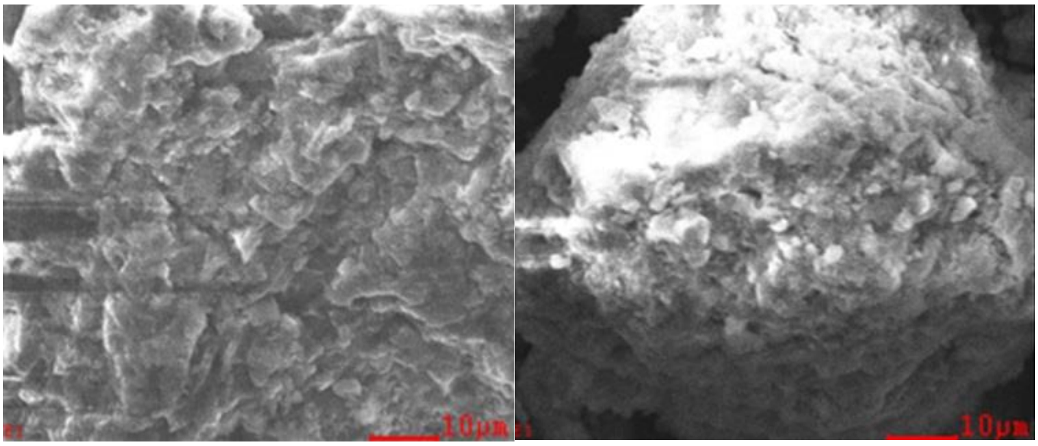
Fig. 3. X-ray fluorescence spectroscopy of catalysts: a), b) catalyst based on activated zeolite; c), d) catalyst 1%Mo(VI)–1%W(VI)/zeolite composite

Using the method of electron microscopy at a 10-fold increase, samples were studied based on the original and acid-activated zeolites (Figure 4). As can be seen from Figure 4, on the surface of the sample of non-activated zeolite (a) and activated zeolite (b), finely dispersed loose formations of a porous structure are observed.

After acid-free treatment in zeolite (b), there is a slight decrease in the aluminum content at a constant silicon content and a visually distinguishable densification of the zeolite with the formation of smoothed fine areas, which may indicate a decrease in the number of mesopores localized in its internal channels, and an increase in the number of micropores, as well as a decrease in acidity inside the pores due to compression and destruction of mesopores.

Table 2
Results of X-ray spectral analysis of catalysts

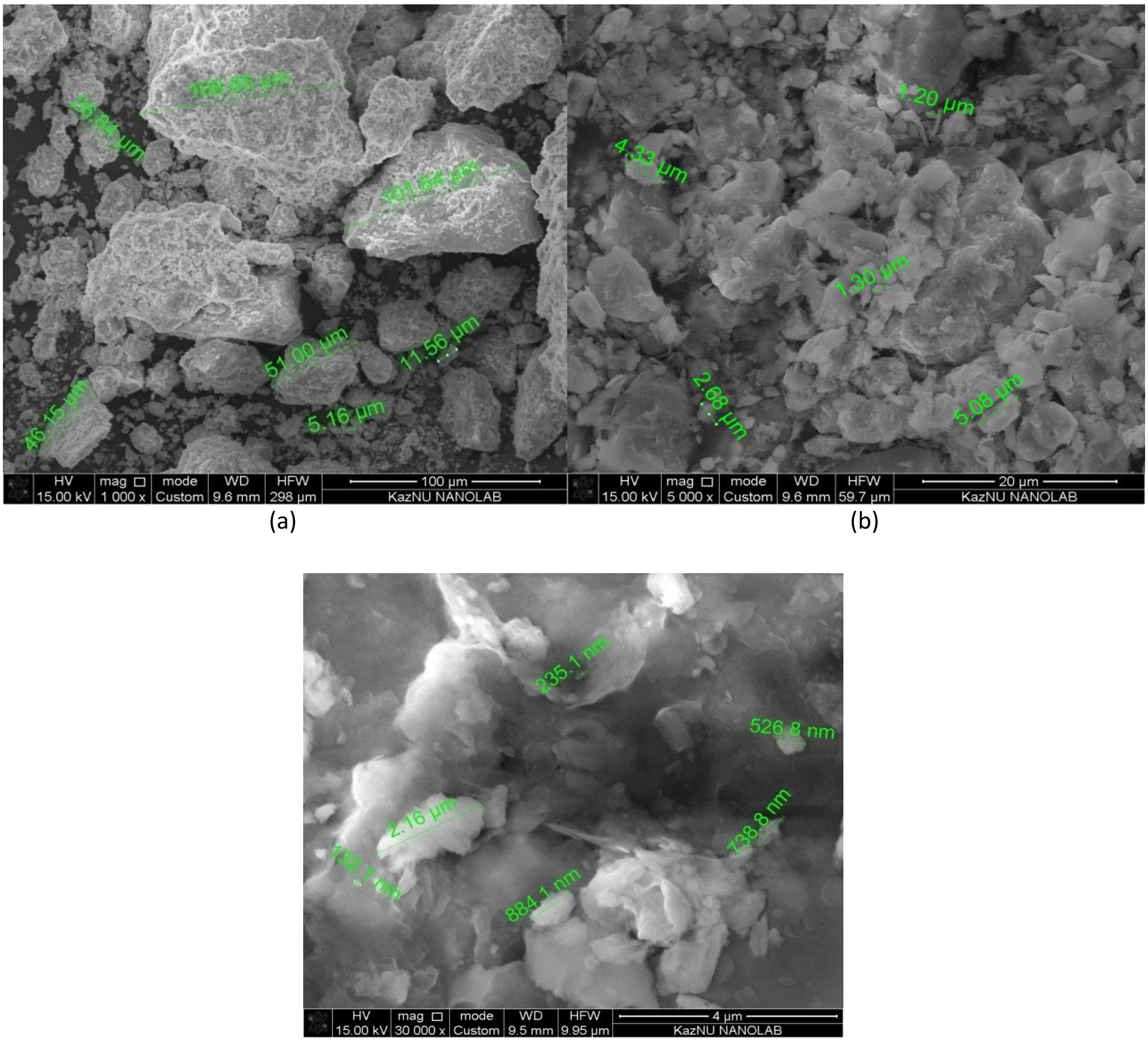
No	Element	Concentration, %	Interval, cps
Catalyst based on activated zeolite			
1	Iron	31.14	344.4
2	Silicon	26.00	1.00
3	Calcium	0.337	4.60
4	Titanium	0.925	5.8
5	Manganese	0.232	2.3
6	Potassium	17.36	25.5
7	Aluminium	22.88	0.33
8	Strontium	1.12	8.2
Catalyst 1%Mo(VI)–1%W(VI)/zeolite composite			
1	Iron	9.97	183.2
2	Aluminium	20.81	0.43
3	Silicon	31.52	2.5
4	Titanium	0.517	4.2
5	Potassium	10.88	18.1
6	Calcium	0.543	4.9
7	Manganese	0.181	2.9
8	Tungsten	24.75	165.6
9	Strontium	0.828	6.3



(a) (b)

Fig. 4. Microelectronic photographs of the original (a) and activated (b) zeolites

Further treatment of the activated zeolite with a solution of salts of molybdenum (VI) and tungsten (VI) possibly leads to the formation of a disordered structure with a large spread of micro-, meso- and macropores, as evidenced by the microelectronic photographs of the 1% Mo(VI)-catalyst presented in Figure 5%W(VI)/zeolite at appropriate microscope resolutions – ×1000, ×5000 and ×30000.



(a) (b)

(c)

Fig. 5. Microelectronic photos of the 1%Mo(VI)-1%W(VI)/ zeolite catalyst: a) ×1000; b) ×5000; c) ×30000

As is known, the higher the acidity of aluminosilicates, the greater the probability of formation of low-boiling liquid products, including alkanes, isoalkanes, and aromatic hydrocarbons [50-53]. A significant contribution can also be made by Brønsted centers located close to each other on the catalyst surface, where water is adsorbed and hydrogen bonds are formed at centers with increased adsorption energy. This can lead to an in-crease in the polarization of the water molecule due to interfacial charge transfer. In this case, a proton can break away from the zeolite framework with the formation of a hydroxonium ion, which determines the structural stability of the crystalline body. Thus, the activity and selectivity of reactions catalyzed by zeolite can be affected by increased polarization and delocalization of protons [38].

The results of this study show that preliminary acid-free activation with ammonium chloride and further modification of the zeolite with Mo(VI) and W(VI) salts can significantly affect its surface morphology and adsorption capacity, and, therefore, the resulting catalysts can selectively affect the yield and composition of liquid fractions at thermocatalytic hydrogenation processing of waste plastics.

The resulting catalyst 1%Mo(VI)-1%W(VI)/zeolite was tested in the reaction of thermocatalytic hydrogenation processing of waste polymers based on polyethylene and polypropylene. The process was carried out at a temperature of 450 °C and a pressure of 0.5 MPa.

When the zeolite was heated, partial dehydroxylation occurred with the formation of Lewis acid sites, as well as the reduction of molybdenum and tungsten, which had a significant effect on the course of the process, determined the adsorption activity of the catalyst, as well as its efficiency and selectivity during the transformation [54-65].

The ratio of the initial polymeric raw material and the paste-forming agent was 1:1 (total 14 g), and the sample of the catalyst was 1% of the total mass of the reagents. The reaction time was 30 min. The total yield of liquid distillates obtained by distillation after the process of thermocatalytic hydrogenation was 66.70 wt.%. By fractional distillation of liquid distillate, a gasoline fraction (boiling point up to 180 °C), diesel fraction (boiling point from 180 to 250 °C), gas oil (boiling point from 250 to 320 °C) were obtained, and a predominantly C_1-C_2 containing gas was also obtained. The resulting distillates were studied by gas-liquid chromato-mass spectrometry. Chromatograms are presented in Figures 6 to 8.

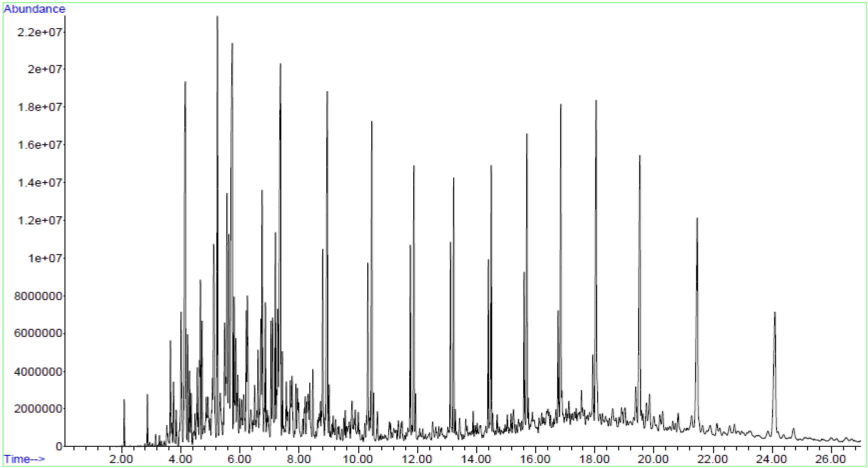


Fig. 6. Chromatogram of mass spectrometric analysis of the gasoline fraction in the presence of 1%Mo(VI)-1%W(VI)/ zeolite catalyst (up to 180 °C)

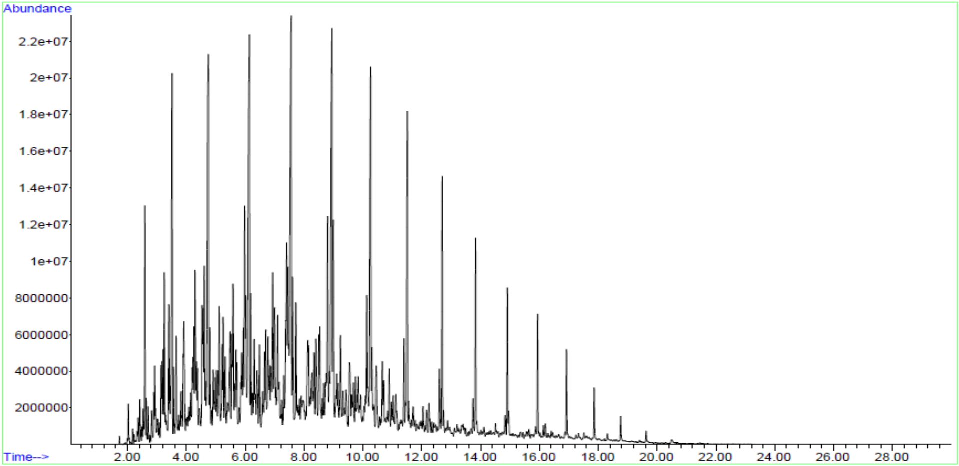


Fig. 7. Chromatogram of mass spectrometric analysis of kerosene fraction in the presence of 1%Mo(VI)-1%W(VI)/ zeolite catalyst (180-250 °C)

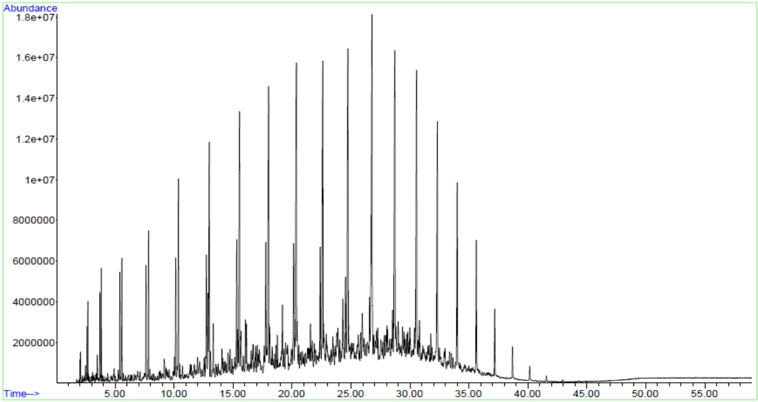


Fig. 8. Chromatogram of mass spectrometric analysis of gas oil fractions in the presence of 1%Mo(VI)-1%W(VI) zeolite catalyst (250-320 °C)

The individual and group hydrocarbon compositions of the resulting distillates were determined by gas-liquid chromatography-mass spectrometry (Table 3).

Table 3
Chemical composition of liquid fractions in the presence of 1%Mo(VI)-1%W(VI)/zeolite catalyst

Liquid fraction, ºC	Group compositions of hydrocarbons, %					
	Alkanes	Alkenes	Isoalkanes	Cycloalkanes	Cycloalkenes	Aromatic hydrocarbons
0-180	40.92	13.62	10.62	12.03	1.07	13.76
180-250	33.9	8.9	5.93	8.03	0.24	15.95
250-320	58.88	14.82	1.91	2.81	0.22	8.71

Thus, the predominant content of alkanes, cycloalkanes, alkenes, aromatic hydrocarbons and isoalkanes in the gasoline fraction is shown. Alkanes, alkenes and aromatic hydrocarbons in the diesel fraction; alkanes, alkenes and aromatic hydrocarbons in the gas oil fraction was found. This indicates that the main contribution to the transformations to alkanes, alkenes, and aromatic hydrocarbons is obviously made by mesoporous inclusions in the cavities of the zeolite under study. Isomerization is possible due to the active sites of metals localized in accessible areas of the adsorption surface of the catalyst.

4. Conclusions

The paper shows that the preliminary acid-free activation with ammonium chloride of heulandite -clinoptilolite zeolite of the Taizhuzgen deposit, and its further modification with Mo(VI) and W(VI) salts can significantly affect the morphology of its surface, adsorption capacity and, consequently, selectivity when used in the process of thermocatalytic hydrogenation processing of plastic waste. By the SEM method, it was found that during acid-free treatment with ammonium chloride by boiling for 6 hours in a water bath in zeolite, there is a slight decrease in the aluminium content with a constant silicon content and a visually distinguishable compaction of zeolite with the formation of smoothed fine-dispersed areas, which may indicate a decrease in the number of mesopores localized in its internal channels and an increase in the number of micropores, and also, a decrease in acidity inside the pores due to compression and destruction of mesopores. It is also suggested that further treatment of activated zeolite with a solution of molybdenum (VI) and tungsten (VI) salts may lead to the formation of an unordered structure with a large spread of micro-, meso- and macropores, with a predominant content of mesopores. The chemical composition of mesoporous catalyst samples was determined by X-ray fluorescence spectroscopy. The resulting catalyst 1%Mo(VI)-1%W(VI)/zeolite was first tested in the reaction of thermocatalytic hydrogenation processing of a mixture of polyethylene and polypropylene waste in the presence of a paste-forming agent. According to gas-liquid chromatography-mass spectrometry, in the composition of the obtained liquid product, predominant cracking of polymers with the formation of alkenes and their subsequent hydrogenation to alkanes, slight isomerization with the formation of isoalkanes, slight dehydrogenation and cyclization, as well as aromatization of the initial polymer raw material were noted. These results echo well-known developments in the use of mesoporous zeolite composites as catalysts for the processing of plastic waste.

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