

Section 5. Chemistry

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THEORETICAL ASPECTS INVESTIGATION OF THE STRUCTURE OF PHOSPHORMOLYBDENUM HETEROPOLY ACID CATALYSTS FOR THE OXIDATION OF METHACROLEIN TO METHACRYLIC ACID

Abstract. The present study investigates of the structure of phosphormolybdenum heteropoly acid catalysts for the oxidation of methacrolein to methacrylic acid. As a result of the studies of the reaction of oxidative transformation of unsaturated C₃-C₄- aldehydes into the corresponding acids, the composition of samples with empirical formula was established: Cs_{0,2-1} W_{0,1-1} Cu_{0,1-0,5} Cr_{0,07-0,4} Zn₂₋₄ P₁ Mo₁₂ V_{0,1-0,5} (NH₄)₁₋₄ O_x

The selected sample for a detailed study of the structure is as follows:

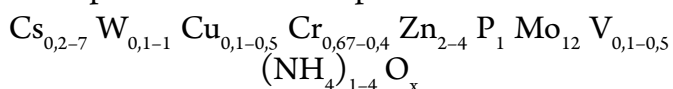
Cs_{0,7} W_{0,2} Cu_{0,1} Cr_{0,4} Zn₃ P₁ Mo₁₂ V_{0,3} (NH₄)₃₋₄ O_{45,5} The first sample was prepared from ammonium salts of P, Mo, and V, and the second was based on phosphormolybdenum heteropoly acid. The same evaporation, drying, and calcination conditions were followed in all cases. The calcined aluminum oxide was used as a reference substance. As the results showed, regardless of the catalyst preparation method, increasing temperature up to 430 °C affects its properties. These changes lead to irreversible activity loss and selectivity by 5–6 times. Presented X-ray pictures of samples that have worked for 75 hours in methacrolein oxidation mode indicate that the properties of the catalysts are unchanged. Diffractometers show that the catalyst samples are not amorphous but crystalline. The paper gives IR spectra of the catalyst samples before and after they reached stable activity. Data for the catalysts modified with cesium compared with the original heteropoly acid are presented. It is indicated that the position and relative intensity of several characteristic reflexes on the X-ray diffraction pattern change. The low catalytic activity of the samples revealed is caused by the presence on the surface of ammonia formed during the synthesis of the catalyst heating removes ammonia. The catalyst activity increases more than threefold,

and the selectivity does not change. Heating of freshly prepared catalyst removes crystallization water ($\sim 170^\circ\text{C}$). A series of experiments were conducted to determine the catalyst's thermal stability limit. Increasing of temperature to 430°C does not affect its properties. It should be noted that the catalyst decomposition temperature is higher than that of phosphormolybdenum acid (370°C , 50° higher). This is achieved by modifying it with various additives. Thanks to the conducted research, it is possible to change the catalyst structures to improve their properties.

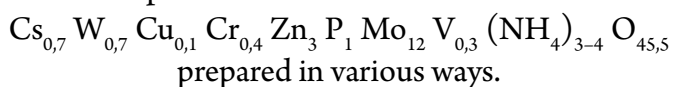
Keywords: phosphormolybdenum, methacrylic acid, methacrolein, molybdenyl, catalysts, conversion, ammonium phosphate, vanadate.

Acrylic and methacrylic acid are industrially produced via the partial oxidation of their corresponding aldehydes, namely acrolein and methacrolein [1–8]. Different catalysts are used for these tasks: mixed-oxides based on Mo, V and W for the acrolein oxidation, and heteropolyacids based on Mo, V and P for the methacrolein oxidation, since the respective other catalyst has a poor performance. To generate a deeper knowledge of the catalytic mechanism, especially of the different properties of the catalysts, the of phosphormolybdenum heteropoly acid catalysts for the oxidation of methacrolein to methacrylic acid [11–20].

The results of tests of a series of modified phosphormolybdenum heteropoly acid catalysts in the reaction of oxidative conversion of unsaturated C_3 - C_4 -aldehydes into corresponding acids allowed establishing the optimal qualitative and quantitative composition of samples that meet the empirical formula:



For the study of the structure, selected samples of the composition:



Sample № 1 was prepared from ammonium salts of P, Mo, and V by precipitation from an aqueous solution. Ammonium paramolybdate, ammonium phosphate and vanadate, nitrates of Zn, Cs, and other metals included in the catalyst were used. The resulting suspension was dried and calcined.

Sample № 2 was synthesized from phosphorus molybdenum heteropoly acid (water solution $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O}$), of ammonium carbonate, and nitrates of al-

kali and other metals; vanadium ions were introduced by dissolving metallic vanadium in the heteropoly acid. This was followed by drying and calcination.

In all cases, evaporation and drying of the suspension were performed at $t=125^\circ\text{C}$. The following burning regime was observed: $200^\circ\text{C} - 4\text{ h}$, $260^\circ\text{C} - 2\text{ h}$, $310^\circ\text{C} - 1\text{ h}$, $330^\circ\text{C} - 1\text{ h}$. X-ray studies of the phase composition of the samples were performed by the Debye-Scherrer method on the diffractometer DRON-3 with filtered Cu-K-radiation.

IR spectra were recorded on a spectrophotometer UR-20 at room temperature.

Thermograms of freshly prepared and run catalysts were taken on the derivatograph of Hungarian firm MOM-500. The calcined aluminum oxide was used as a reference substance. The samples were taken in the temperature interval of 20 – 1000°C at the speed of 2.5; 5, and 10°C per minute. The temperature curves (DTA), sample mass (TG), and mass change rate (DTG) were recorded on the thermograms.

Figure 1 shows radiographs of samples freshly prepared and run for 75 h in the methacrolein oxidation mode. The structure of the catalysts remains unchanged during long-term operation. X-ray patterns of the samples correspond to tabulated data for the ammonium salt of 12-molybdenum phosphoric acid [1] with the main values of interplanar distances (d) equal to 8.40; 5.93; 4.16; 3.72; 3.40; 2.93; 2.5; 2.3; 2.07; 1.65. Diffractograms show that the catalyst samples are not amorphous but crystalline. The diffraction peaks belong to the same basic phase of composition: $(\text{NH}_4)_3\text{PO} \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$. The values of interplanar distances and intensities are taken from the reference book [9–11].

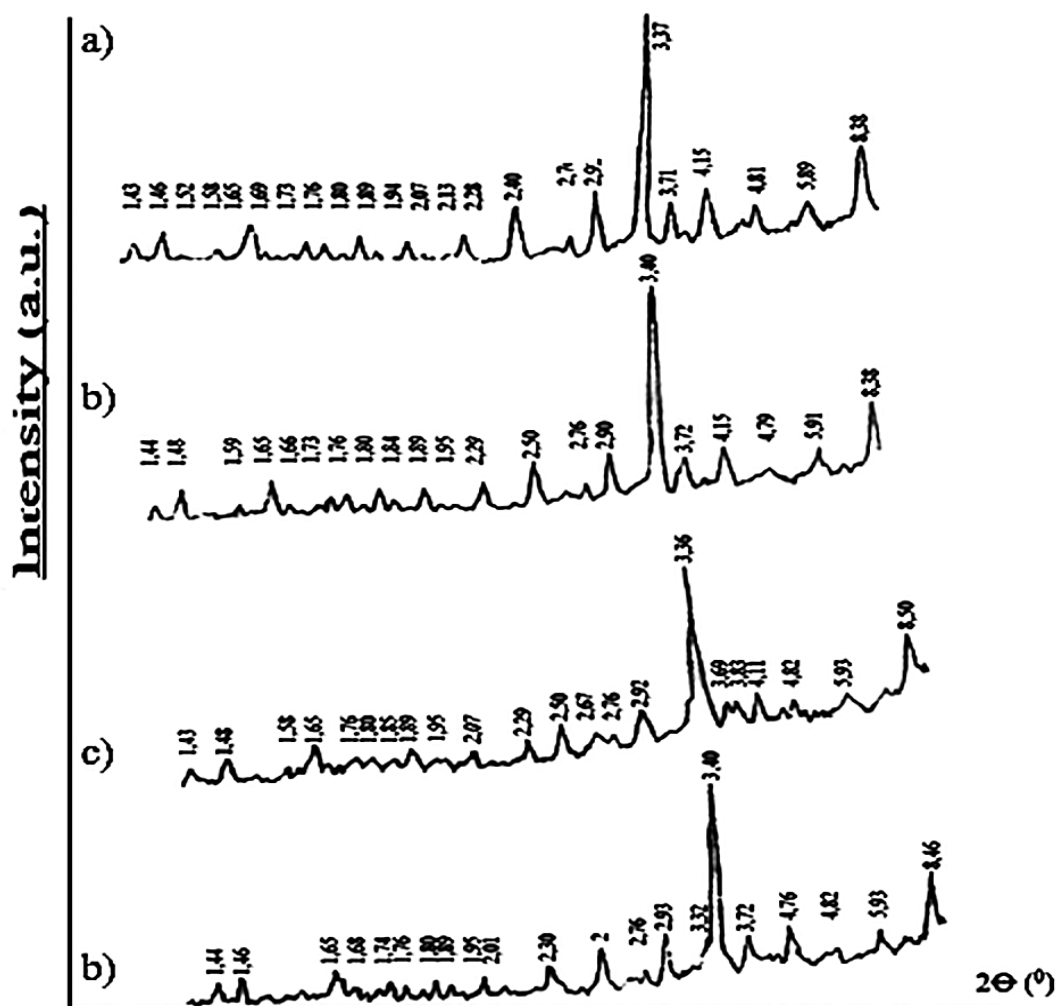


Figure 1. X-ray diffraction patterns of catalyst samples: a, c) freshly prepared; b, d) worked for 75 hours

According to XRD data, for catalysts modified with cesium, in comparison with the original GDC, the position and relative intensity of several characteristic reflexes on the X-ray diffraction patterns change. Practically, intensive lines corresponding to interplanar distances of 9.90; 4.36, and 1.97 Å in GDC disappear, new ones appear – 8.41 and 2.93 Å, maxima of the most intensive band are shifted from 3.21 to 3.40 Å.

Fig. 2 shows infrared spectra of catalyst samples before and after they reached stable activity. As is known [3; 4], for the initial HPA. The leading absorption bands with maxima at 1065, 965, 870 (w), and 790 (w) cm characterize vibrations of P-O-Mo, Mo = O, and Mo-O-Mo bonds typical for heteropolyanion

$[\text{PMo}_{12}\text{O}_{40}]^{-3}$. In addition to the usual main absorption bands describing the Keggin cell, there are bands at 1420 cm^{-1} related to ammonium ions in the spectra.

When cesium ions are introduced into the catalyst, the maximum absorption band of the molybdenum group (Mo = O) shifts to 970 cm^{-1} (the M = O bond increases, and coordination octahedron symmetry changes); the position of the optimal bands remains unchanged. In addition to the 960, 870, 990, and 1060 cm^{-1} absorption bands, 1420 cm^{-1} absorption bands characteristic of NH_4^+ ions comprising the heteropoly acid salt or NH_3 molecules chemisorbed on the Brønsted acid centers or coordinately bound to the catalyst surface are observed. However, the intensity of these absorption bands after a 35-hour

“development” of the catalyst becomes somewhat lower than in the freshly prepared sample. The firmly bound ammonia on the catalytic surface formed during catalyst synthesis and adsorbed on its Brandsted and Luis acid centers causes the low catalytic activity of freshly prepared samples. Additional heating of the catalyst in the reaction mixture removes ammonia. In

this case, the activity of the catalyst increases more than threefold, and the selectivity remains constant throughout the activation process and further operation. Experiments on ammonia poisoning of the catalyst synthesized from phosphormolybdenum HPA showed that adsorption of NH_3 in 1% of the surface filling leads to its complete deactivation.

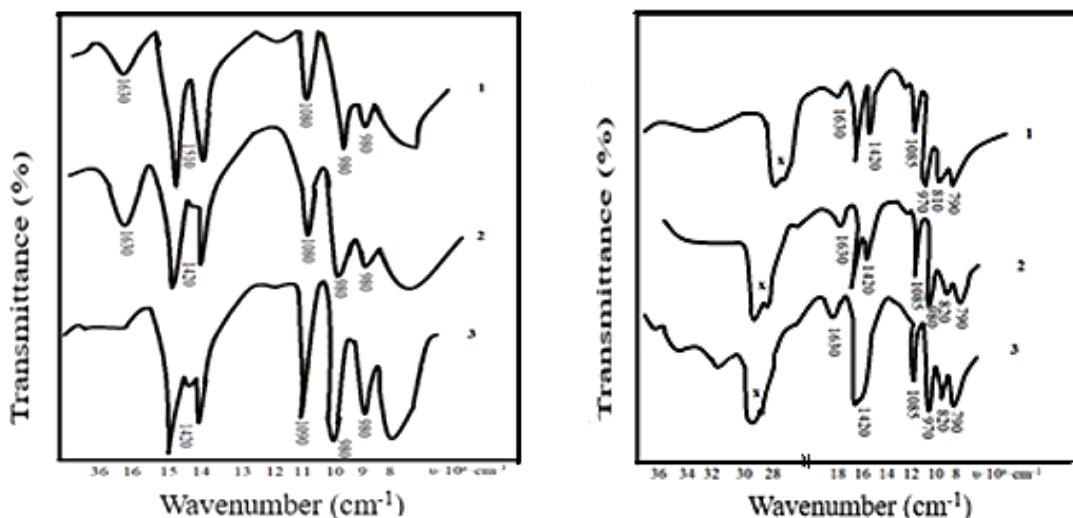


Figure 2. IR spectra of catalyst samples: 1 – Freshly prepared; 2 – Worked for 75 hours; 3 – Working for 170 hours; * – absorption bands of vaseline oil

Thermographic studies were performed for fresh samples, as well as samples that had been in operation for 75 and 175 hours. Due to the simi-

ilarity of results, derivatograms of only samples of catalyst from phosphorus molybdenum HPA are shown in (fig. 3).

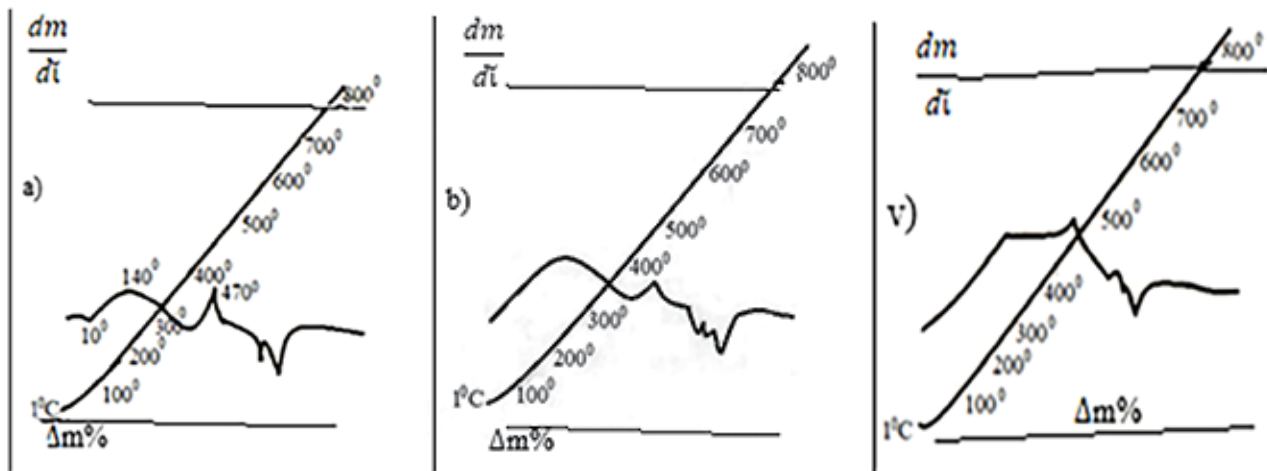


Figure 3. Derivatograms of catalyst sample; a) freshly prepared; b) worked for 75 hours; v) worked for 170 hours

When the freshly prepared catalyst is heated to 200 °C, the removal of crystallization water occurs,

as evidenced by the endothermic effect in the region of 100–200 °C (170 °C). The decomposition of the

catalyst begins at $t > 430^\circ\text{C}$, and an exo-effect is observed at 479°C , which corresponds to a clear step of weight loss on the TG curve. This is followed by a series of endo-effects at 560°C and 600°C , which presumably can be attributed to phase transitions of the melting type. At this temperature segment of the TG-curve, there is no mass loss.

In the derivatogram of the catalyst that worked for 75 h, the endo-effect of moisture loss at 170°C is absent. The intensity of the exoeffect decreased at 470°C . A series of subsequent endo-effects repeated with the same intensity, but the endo-effect at 560°C shifted to 580°C .

The sample that had been in operation for a longer time (170 h) was characterized by the disappearance of the exoeffect at 470°C on the derivatogram with a corresponding step loss on the TG curve. The series of endo-effects related to melting is repeated at the same temperatures and with approximately the same intensity as for the catalyst that has worked for 75 h.

To find out the limit of thermal stability of the catalyst in the reaction medium, a series of experiments with increasing the temperature in the reactor to specified values, at which the sample was kept for

1 h, after which the temperature was reduced to the reference and the activity, was reduced. As the results showed, regardless of the method of preparation of the catalyst, increasing its temperature to 430°C did not affect its properties, the activity in the oxidation of methacrolein at this temperature after each successive increase in its temperature remained the same. Higher temperature (430°C) causes irreversible loss of activity and selectivity (4 and 5–6 times, respectively).

To clarify this phenomenon, radiographic, infrared spectroscopic and thermographic analyses of samples before and after their heating were carried out.

On the X-ray film of the sample heated under reaction conditions at 405°C and losing its activity, a sharp decrease in the intensity of reflexes characteristic of the ammonium salt of 12-Mo-P-acid and the appearance of new reflection maxima close to the structure of rhombic MoO_3 , possibly somewhat distorted (Fig. 4).

The loss of activity of the catalyst worked under reaction conditions at $t > 430^\circ\text{C}$ is associated with the destruction of the active phase of the heteropolymer catalyst (Keggin cell) and the formation of inactive MoO_3 .

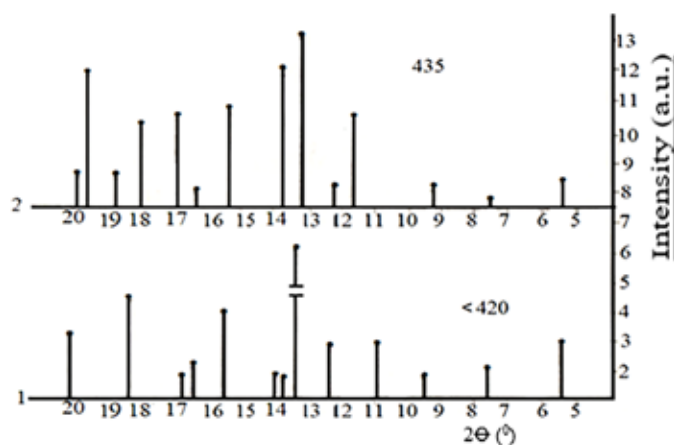
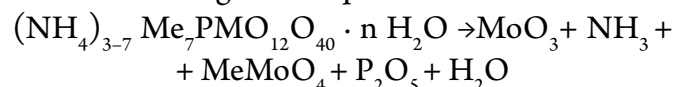


Figure 4. X-ray diffraction of the catalyst sample: 1 – after heating at $t = 420^\circ\text{C}$; 2 – after heating at $t = 435^\circ\text{C}$; * – reflection indices for HPS; * – for MoC_3

The process of decomposition of HPC obviously occurs according to the equation:



It should be noted that the decomposition temperature of the studied catalyst is higher (~ by 60°C) than that of phosphormolybdenum acid (370°C), which is used as an industrial catalyst for methacrolein oxi-

dation. It can be assumed that an increase in thermal stability of investigated samples is achieved due to the modification of $H_3PMo_{12}O_{40}$ by different additives.

In, it was shown that NH_3 from the gas phase is strongly adsorbed on the HPA-catalysts, blocking the conversion centers of methacrolein, whereas NH_4^+ -groups in the catalyst structure has little effect on its activity. It can be assumed that the activation of the catalyst that has worked for 35–40 h is associated

with the removal of such firmly adsorbed ammonia and the release of the active centers of the ammonia surface. This leads to a significant increase in the activity of the catalyst (conversion of methacrolein increases more than 2-fold). At the same time, there is only a slight decrease in its ammonium content. This opens the possibility of purposefully changing the structure of the catalyst in one way or another to improve its catalytic properties.

References:

1. Staroverova I. N., Kuttyrev M. Yu., Khvtisiashvili L. G. Antioxidant Activity of Methano- and Cyclopentofullerenes. *Kinetics and catalysis*, – M., – Vol. 27. – No. 3. 1986. – P. 691–697. (in Russian).
2. Sergienko V. S., Detusheva L. G., Yurchenko E. N., Poray-Koshits M. A. Effect of Fullerene Containing a Maleopimarimide Substituent on the Kinetics of Liquid-Phase Radical Chain Oxidation of Ethylbenzene. *Journal of Structural Chemistry*. – V. 22. – No. 6. 1981. – P. 38–42. (in Russian)
3. Tillaeva S. F., Sattorov M. O. Study of the quality of oil products modified for catalysts, “Science and Education”, – Bukhara. 2022. – No. 3. – P. 123–130. (in Uzbekistan).
4. Mirzaliev S. S., Yaminov F. F. Influence of modifying factors on the environment and active centers of catalysts, Engineering and Technical Institute. – Bukhara. 2016. – P. 38–45. (in Uzbekistan).
5. Staroverova I. N., Kuttyrev M. Yu. IY All-Union conference on the mechanism of catalytic reactions. Conversion of volatile organic compounds on platinum and metal oxide catalysts. – M., – No. 2. 1986. – P. 43–46. (in Russian).
6. Sennerich M., Weidler P. Hexagonal Mo/V/W mixed oxide as a catalyst for the partial oxidation of methacrolein to methacrylic acid. *Catal. Commun.* 2020. – 141 p. URL: <https://doi.org/10.1016/j.catcom.2020.106016>
7. Krauw K. Entwicklung und Einsatz einer DRIFTS-Meßzelle zur In-Situ-Spektroskopie Heterogen Katalysierter Gasphasenoxidationen; Technische Universität Darmstadt: Darmstadt. 2000. – P. 235–249. (in Germany).
8. Xue J., Yin H., Li H., Zhang D., Jiang T., Yu L., Shen Y. Oxidation of cyclopentene catalyzed by tungsten-substituted molybdophosphoric acids. *Korean Journal of Chemical Engineering*. – V. 26. – No. 3. 2009. – P. 654–659. (in Korean).
9. Védrine J. C. Metal Oxides in Heterogeneous Oxidation Catalysis: State of the Art and Challenges for a More Sustainable World. *ChemSusChem* No. 12. 2019. – P. 577–588. DOI: 10.1002/cssc.201801974.
10. Darabi M. J., Dubois J. L., Cavani F., Rostamizadeh M., Patience G. S. Catalysis for the synthesis of methacrylic acid and methyl methacrylate. *Chemical Society Reviews*. 2018. – P. 7703–7738. URL: <https://doi.org/10.1039/D2CS00779G>
11. Nagai K., Ui T. Trends and Future of Monomer–MMA Technologies. *Sumitomo Chem.* – No. 2. 2004. – P. 4–13. (in Japan).
12. Belousova A. S., Esipovicha A. L., Otopkova K. V. Investigation of the process of vapor-phase dehydration of glycerol to acrolein in the presence of polyoxometallates *Kinetics and catalysis*. – V. 61. – No. 4. 2021. – P. 541–548. URL: <https://doi.org/10.1002/jctb.4273>

13. Lowell S., Shields J. E., Thomas M. A., Thommes M. Characterization of Porous Materials and Powders: Surface Area, Pore Size and Density. Netherlands: Springer, 2020.– 350 p. DOI:10.1007/978-1-4020-2303-3
14. Danov S. M., Esipovich A. L., Belousov A. S., Rogozhin A. E. Effect of Diethylene Glycol on the Formation of the Oxide Precursor of the Nickel–Molybdenum Hydrotreating Catalyst. Russian Journal Applied Chemistry.– V. 87. 2019.– P. 461–469. (in Russian).
15. Belousov A. S., Rogozhin A. E. Investigation of the process of vapor-phase dehydration of glycerol to acrolein in the presence of polyoxometallates. Kinetics and catalysis.– Vol. 61.– No. 4. 2020.– P. 541–548. DOI: 10.31857/S0453881120030077
16. Thanasilp S., Schwank J. W., Meeyoo V., Pengpanich S., Hunsom M. Comparison of citric acid and glycol effects on the state of active phase species and catalytic properties of CoPMo/Al₂O₃ hydrotreating catalysts. Journal of Molecular Catalysis A- Chem.– V. 380. 2018.– P. 67–68. DOI: 10.1016/j.mcat.2018.05.020
17. Liu R., Wang T., Liu C., Jin Y. Biomass valorisation over polyoxometalate-based catalysts Chin. J. Catal.– V. 34. 2021.– P. 2174. DOI: 10.1039/D0GC03190 A
18. Abdullayeva M. Y., Habibov I. A. Improvement of the electrical properties of synthetic liquid dielectric for pulse capacitors. EUREKA, Physics and Engineering this link is disabled. 2020.– P. 13–18.
19. Guseynova E. B., Mustafayeva R. E. Modification and study by the method of planning an experiment of a tin-antimony catalyst for the gas-phase oxidation of isobutylene to methacrolein. Natural and mathematical sciences in the modern world. Novosibirsk 2015.– P. 73–83. (in Russian).
20. Dong D. Q., Yang S. H., Wu P., Wang J. Z., Min L. H., et al. Copper-Catalyzed Difluoroalkylation Reaction. Molecules – 27. 2022.– P. 84–61. URL: <https://doi.org/10.3390/molecules27238461>