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The effect of methyl methacrylate transformations during photocatalysis in the presence of $RbTe_{1.5}W_{0.5}O_6$ on the change of the complex oxide surface

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Abstract. *The features of the surface changes of the* $RbTe_{1.5}W_{0.5}O_6$ *photocatalyst during polymerization processes involving methyl methacrylate (MMA) under irradiation with visible light λ= 400–700 nm at a temperature of 20–25 °C, as well as regeneration conditions for its reuse, have been studied. The realization of a chemical reaction in a mixture of a photocatalyst and a monomer is determined by its kinetic parameters and the concentration of reacting particles. The formation of OH• radicals, which are active in radical polymerization, occurs in this case by both ways: interacting between water molecules adsorbed on the surface, as well as during the recovery of oxygen dissolved in water. Due to the high reactivity of the hydroxyl radical, an active process of radical polymerization of MMA could be expected. However, the formation of polymethyl methacrylate (PMMA) in the reaction takes place with a low conversion – the formation of 5–10% polymer, which is related to changes on the surface of the complex oxide* $RbTe_{1.5}W_{0.5}O_6$ *during the reaction. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) methods have been used to investigate the catalyst surface. The presence of organic and polymer substrates was revealed on the catalyst surface after the reaction. As a result of the catalyst treatment by ultrasound in an aqueous emulsion, polymer macromolecules are not identified on the surface, but chemically adsorbed monomer and oligomers formed under the ultrasound destruction of the polymer are presented. Other methods of cleaning the catalyst surface by washing in different solutions as chloroform and tetrahydrofuran also are not effective and cause the adsorbates transformations on the surface. It leads to decreasing the* $RbTe_{1.5}W_{0.5}O_6$ *catalyst's activity for repeated polymerization. Thus, to successful regeneration of the catalyst's powder not only ultrasound treatment is required, but also heating it at 300–400 °C to remove organic substrates.*

Keywords: *photocatalysis, β-pyrochlore, complex oxide* $RbTe_{1.5}W_{0.5}O_6$*, emulsion polymerization, X-ray photoelectron spectroscopy, scanning electron microscopy*

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CHEMICAL SCIENCES

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Влияние превращений метилметакрилата при фотокатализе в присутствии $RbTe_{1,5}W_{0,5}O_6$ на изменение поверхности сложного оксида

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Аннотация. *Изучены особенности изменения поверхности фотокатализатора $RbTe_{1,5}W_{0,5}O_6$ в полимеризационных процессах с участием метилметакрилата (ММА) при облучении видимым светом λ=400–700 нм и температуре 20–25 °C, а также условия регенерации для его повторного применения. Реализация той или иной химической реакции в смеси фотокатализатора и мономера определяется ее кинетическими параметрами и концентрацией реагирующих частиц. Образование OH• радикалов, активных в радикальной полимеризации, происходит в этом случае как при взаимодействии с адсорбированными на поверхности молекулами воды, так и в объеме раствора, а также при восстановлении растворенного в воде кислорода. В связи с тем, что гидроксильный радикал обладает высокой реакционной способностью, можно было ожидать активный процесс радикальной полимеризации ММА. Однако образование ПММА в рассматриваемой реакции проходит с низкой конверсией – наблюдается образование 5–10% полимера, что связано с изменениями на поверхности сложного оксида $RbTe_{1,5}W_{0,5}O_6$ в процессе реакции. Для исследования поверхности катализатора были использованы методы сканирующей электронной микроскопии (СЭМ) и рентгеновской фотоэлектронной спектроскопии (РФЭС). После реакции на поверхности катализатора было обнаружено присутствие органических и полимерных субстратов. В результате обработки катализатора ультразвуком в водной эмульсии макромолекулы полимера не идентифицируются на поверхности, но представлены химически адсорбированные мономер и олигомеры, образующиеся при разрушении полимера ультразвуком. Другие способы очистки поверхности катализатора путем промывки в различных растворах, таких как хлороформ и тетрагидрофуран, также неэффективны и вызывают превращения адсорбатов на поверхности. Это приводит к снижению активности катализатора $RbTe_{1,5}W_{0,5}O_6$ при повторной полимеризации. Таким образом, для успешной регенерации порошка катализатора требуется не только обработка ультразвуком, но и нагрев его при 300–400 °C для удаления органических субстратов.*

Ключевые слова: *фотокатализ, β-пирохлор, комплексный оксид $RbTe_{1,5}W_{0,5}O_6$, эмульсионная полимеризация, рентгеновская фотоэлектронная спектроскопия, сканирующая электронная микроскопия*

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INTRODUCTION

Photocatalytic reactions under the influence of visible light attract attention due to compliance with the principles of green chemistry and the wide range of possibilities with their use. Different metal oxides, which are capable of catalyzing reactions under visible light irradiation rather than ultraviolet, have recently become the most widespread [1–5].

Photocatalytic oxidation is especially widely known for the decomposition of pollutants with different nature in water and air. It is due to the presence of variety active particles in the reaction volume: charged particles, radicals, singlet oxygen, hydrogen peroxide, capable of destroying organic compounds. Significant progress has been recently reached in this direction [1, 6–17].

It is attractive to use an active hydroxyl radical, also formed under irradiation of metal oxides, to obtain new polymer materials for a number of reasons: the possibility of carrying out the process at room temperature, the absence of fragments of material initiators with organic nature, etc. Photo-catalytic radical polymerization at low temperatures with the active hydroxyl radical participation is the best known for titanium oxide [18, 19]. A number of articles describe similar studies for the production of composites used for 3D printing of biomedicine materials [20], or along with controlled copolymerization by the mechanism of reversible transfer of the addition-fragmentation chain for the synthesis of block copolymers of acrylic monomers with a certain composition [21].

In previous studies, we have described the synthesis of the MMA polymer and its graft copolymers with natural polymers, collagen and pectin, in an aqueous emulsion in the presence of a complex oxide $RbTe_{1.5}W_{0.5}O_6$ under irradiation with visible light λ=400–700 nm at a temperature of 20–25 °C [22, 23]. The structural and relief organization of the obtained graft copolymers is typical of scaffolds and allows us to consider them as a promising material for medical materials – hydrogel scaffolds with a new set of properties. Such composites based on copolymers of natural and synthetic polymers are well known, especially for tissue engineering [22–31]. The repeated usage of the catalyst deserves special attention in case of developing new methods for obtaining polymer materials. Such studies have been carried out for many catalysts with a practical focus of research. For example, the reuse of catalysts Ag_3PO_4-Guar gum [32], Fe_3O_4/CeO_2/g-C_3N_4 [33], $SiO_2/WO_3–TiO_2$@rGO [34] is possible for several cycles with a slight loss of activity after solvent treatment and heating. Thus, the study of the reuse possibility of the complex oxide $RbTe_{1.5}W_{0.5}O_6$ is relevant due to photocatalytic activity for polymerization processes.

In this paper, different surface purification methods of the $RbTe_{1.5}W_{0.5}O_6$ catalyst after polymerization of MMA have been carried out. In order to analyze the surface behavior of the complex oxide $RbTe_{1.5}W_{0.5}O_6$ in detail during the adsorption of organic substrates and further photocatalytic polymerization in water MMA emulsion under irradiation with visible light λ=400–700 nm at a temperature of 20–25 °C, the methods of XPS and SEM were used, which allows to qualitatively and quantitatively determine the chemical composition of compounds at the near-surface layer from 1–2 nm to several micrometers.

EXPERIMENTAL SECTION

Materials. Commercial organic solvents were used in the study: tetrahydrofuran (99.5%, Component-Reagent, Russia), chloroform (99.85%, Component-Reagent, Russia). MMA (99.8%, Energoeffect, Russia) was used as a monomer. It was previously purified from the stabilizer by washing the monomer with a 10% w/w alkali solution in a ratio of 1:1 at least 4 times, and then it was repeatedly washed with cold water to a neutral pH. Then the monomer was dried using calcium chloride for at least a day. At the end, the MMA was distilled under vacuum (1.33 Pa) at 40 °C. Potassium salts of resin and fatty acids (Ediscan, Orghim, Russia) and dimethacrylic ether of triethylene glycol (TEGDME, Khimtransit, Russia) played the role of emulsion stabilizers.

Preparation of MMA-in-water emulsion. The synthesis of a polycrystalline sample of the $RbTe_{1.5}W_{0.5}O_6$ compound with an average particle size of ~700 nm was carried out by a solid-state reaction, a detailed experimental technique was described earlier in our papers [13, 23, 35]. The emulsion for the reaction was prepared by mixing $RbTe_{1.5}W_{0.5}O_6$ powder, water and monomer with the addition of emulsion stabilizers (mass ratio monomer-water mixture : Ediscan : TEGDME : catalyst = = 100:1:3:1), treating with ultrasound for 5 mi-nutes using the ultrasonic dispergator UZDN-A650. The v/v ratio of water and monomer was 75:25. The reaction was carried out in an argon current, irradiation was carried out using an LED lamp of visible radiation (white, 30 W LED, 6500 K) (Fig. 1).

Photocatalyst treatment after emulsion polymerization reactions. After the end of the reaction, the emulsion was centrifuged for 30 minutes to separate the catalyst. Catalyst powders after parallel polymerization experiments were subjected to different purification methods (purification was not carried out sequentially, and a specific procedure was carried out for each catalyst powder after the polymerization reaction):

1) washing at 50 °C in THF solution for 3 hours;

2) chloroform extraction at 61 °C in the Soxhlet extractor for 15 h;

3) powder treatment with ultrasound for 40 minutes in the presence of water at 20 °C;

4) powder heating at 300–400 °C in the Pt crucible in a muffle oven.

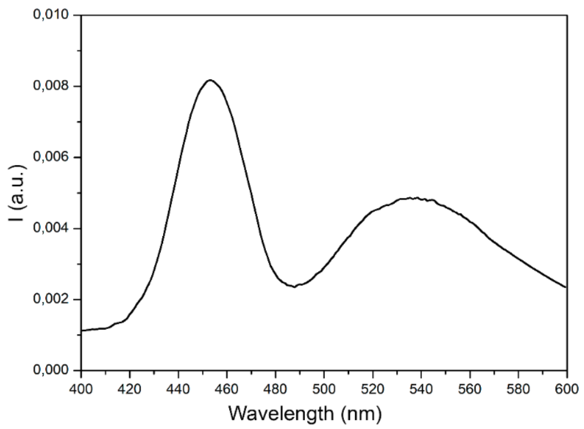


Fig. 1. Lamp spectrum (white, 30 W LED, 6500 K)

Рис. 1. Спектр лампы (белый, 30 Вт LED, 6500 K)

Then all the powders were dried under vacuum (1.33 Pa) at 40 °C to a constant mass.

Characterization. The obtained samples of the catalyst powder were examined by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The study of the surface of photocatalyst powder was performed using a scanning electron microscope JSM-IT300 (Jeolltd, Japan) with an electron probe diameter of 5 nm (operating voltage 20 kV), using a backscattered electron detector in high vacuum mode. Determination of the features of the chemical composition of the surface in the samples was carried out by XPS on an electronic spectrometer “Escalab 250Xi”. A monochromatized line Al Kα=1486.6 eV was used as the radiation source. The spectra were recorded in the mode of constant transmission energy at 100 eV for the survey spectrum and 50 eV for the spectra of regions of elements with a spot size of 650 microns. The depth of the surface analysis is up to 2 nm. The total energy resolution was about 0.3 eV. A neutralizer gas was used to neutralize the surface charge. The pressure in the chamber during the study was no more than 10^{-9} mbar, which guaranteed a clean surface. Correction of the position of the element lines in all cases was carried out along the carbon line C 1s (285 eV). The study of the surface composition by depth was carried out by etching the surface with an ion gun (Ar^+) with an accelerating voltage of 3 kV.

RESULTS AND DISCUSSION

It was previously shown [36] that after the catalyst – oxide $RbTe_{1.5}W_{0.5}O_6$ irradiation with visible light, electron-hole pairs are formed, which can lead to a number of transformations according to schemes 1–7 in Fig. 2.

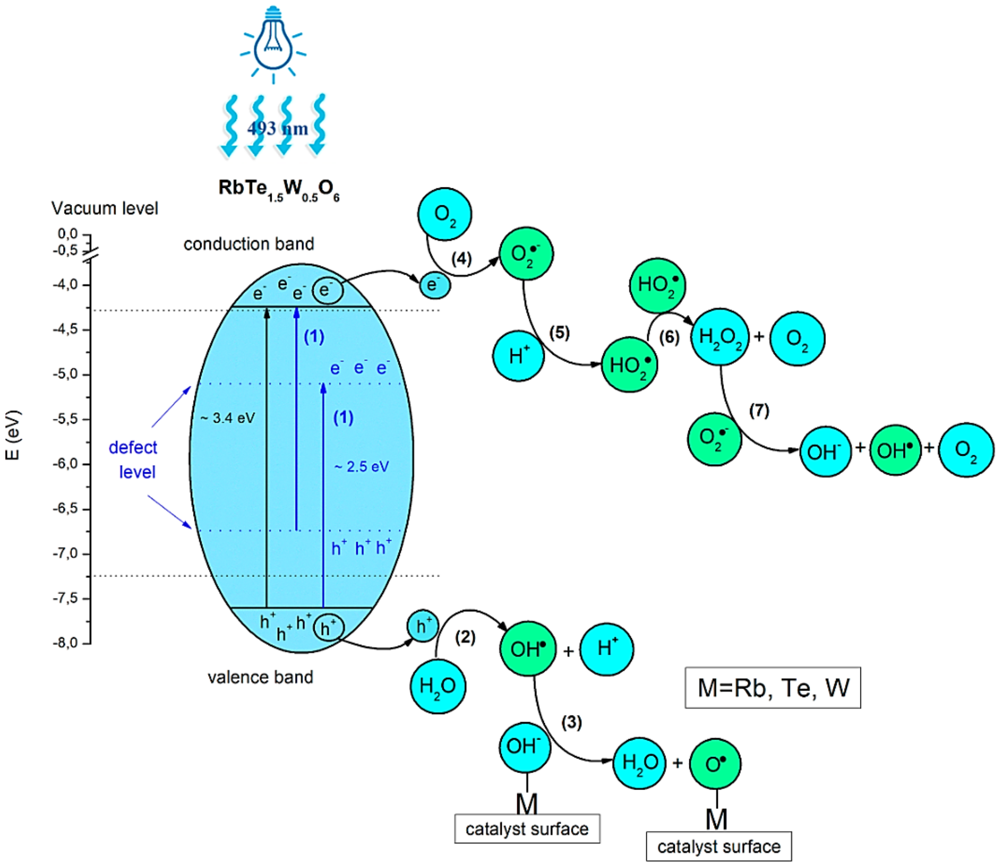


Fig. 2. Scheme of formation of electron-hole pairs during photocatalysis

Рис. 2. Схема образования электронно-дырочных пар при фотокатализе

Reactions (1–7) indicate that several chemical transformations can actually occur simultaneously in the reaction mixture of a photocatalyst and a monomer. The realization of a chemical reaction is determined by its kinetic parameters and the concentration of reacting particles. The formation of OH• radicals, which are active in radical polymerization, occurs in this case by both ways: interacting between water molecules adsorbed on the surface (scheme 2, 3), as well as during the recovery of oxygen dissolved in water (scheme 6, 7). Due to the high reactivity of the hydroxyl radical, an active process of radical polymerization of MMA could be expected. However, as was shown in the work [22], the formation of polymethyl methacrylate (PMMA) in the reaction takes place with a low conversion - the formation of 5–10% polymer with molecular weight (MW) and polydispersity coefficient (PDI) 140–145 kDa and 2.2, respectively, are observed. In addition, the product of oxidative dimerization of MMA (OMMA) and its oligomer were also isolated in small amounts and polymer on the catalyst's surface. If a natural polymer (collagen, pectin) is presented in the reaction mixture, a graft copolymer is formed [22, 23]. Schematically, reactions in a mixture of a catalyst with a monomer, including in the presence of a natural polymer, are shown in Fig. 3.

Thus, it was necessary to conduct a detailed study of the catalyst powder surface and test it after the photocatalytic polymerization reaction for reuse. To achieve this goal, PMMA was synthesized from an MMA emulsion using a photocatalyst. To study the features of the processes occurring on the surface, the catalyst powder after the reaction was subjected to various purification methods.

Analysis of the catalyst powder after the MMA polymerization reaction by SEM showed the presence on the surface of a significant number of polymer fibers with a length of up to 200–700 microns, as well as smaller organic particles with a size of 5–10 microns (Fig. 4), as previously in works [22, 23].

Study of the catalyst powder surface by SEM after washing in THF and chloroform, as in the previous experiments [22, 23], showed the presence of polymer and organic fibers (Fig. 4, b, c). However, after purification in water by ultrasound and subsequent drying in vacuum, polymer fibers on the $RbTe_{1.5}W_{0.5}O_6$ oxide surface are not identified by the SEM method (Fig. 4, d) as well as after further heating at 300–400 °C.

However, the catalyst powder after ultrasonic purification in water without additional calcination showed a significant drop in its effectiveness in the synthesis of a polymer based on MMA. Such powder leads to PMMA formation with a conversion of less than 5% (when using fresh powder, up to ~10% of the polymer can be isolated from the reaction mixture) [22]. It is obvious that the change in the efficiency of the photocatalyst is associated with a change in the $RbTe_{1.5}W_{0.5}O_6$ oxide surface, which are not identified by the SEM method.

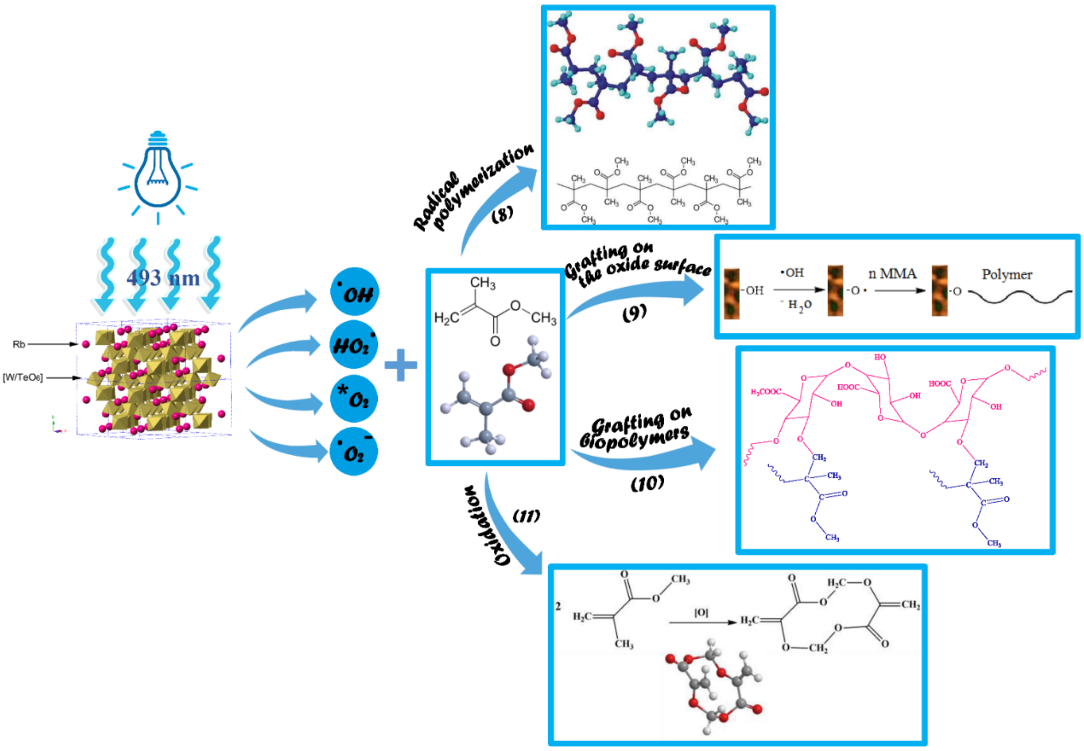


Fig. 3. Schemes of various directions of interaction of formed radicals with the substrate

Рис. 3. Схемы различных направлений взаимодействия образованных радикалов с субстратом

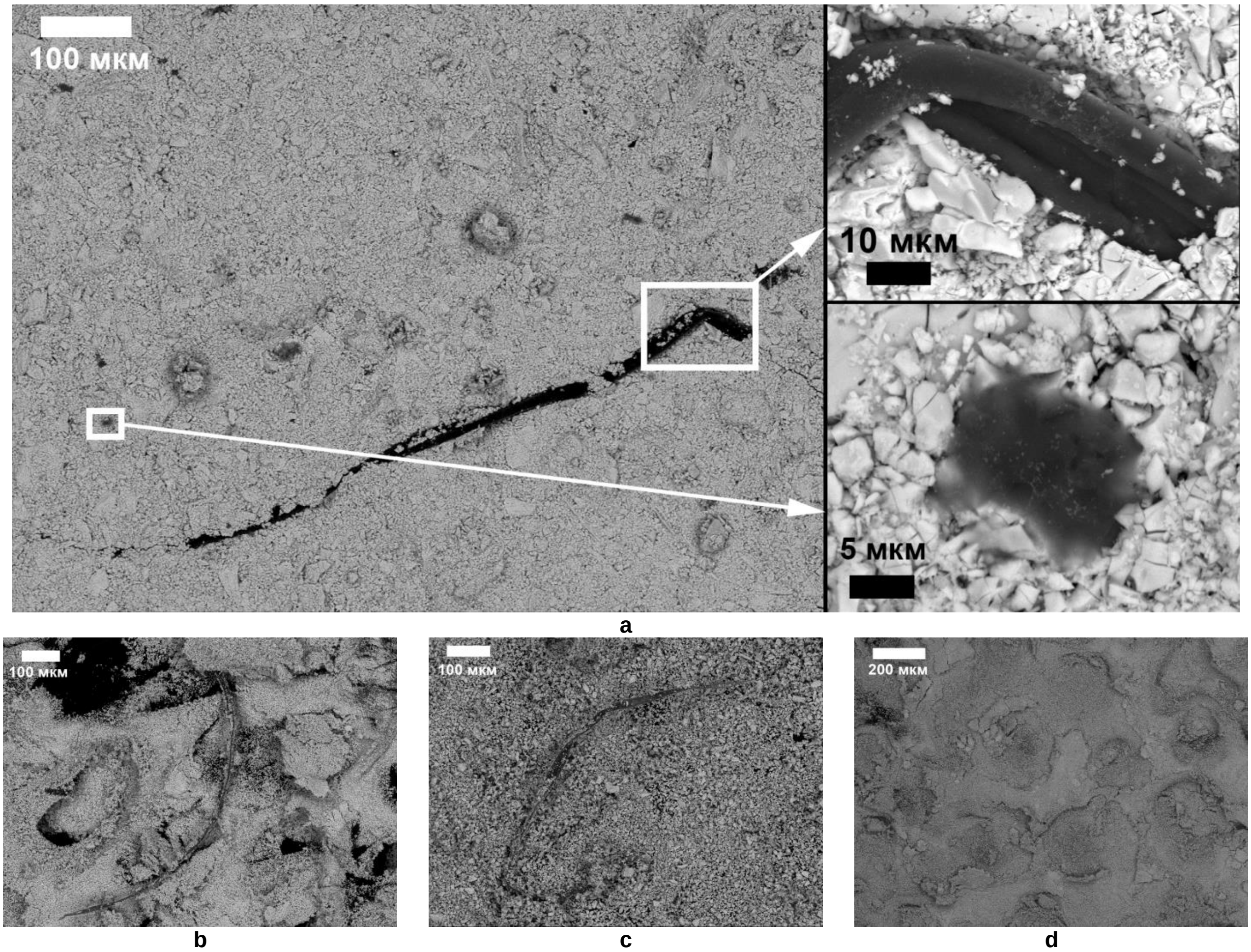


Fig. 4. Polymer macromolecules on the surface of the $RbTe_{1.5}W_{0.5}O_6$ catalyst powder after the polymerization reaction of MMA (a); the $RbTe_{1.5}W_{0.5}O_6$ catalyst powder surface after washing of PMMA in a THF solution (b), $CHCl_3$ (c) and water in UZDN-A650 (d)

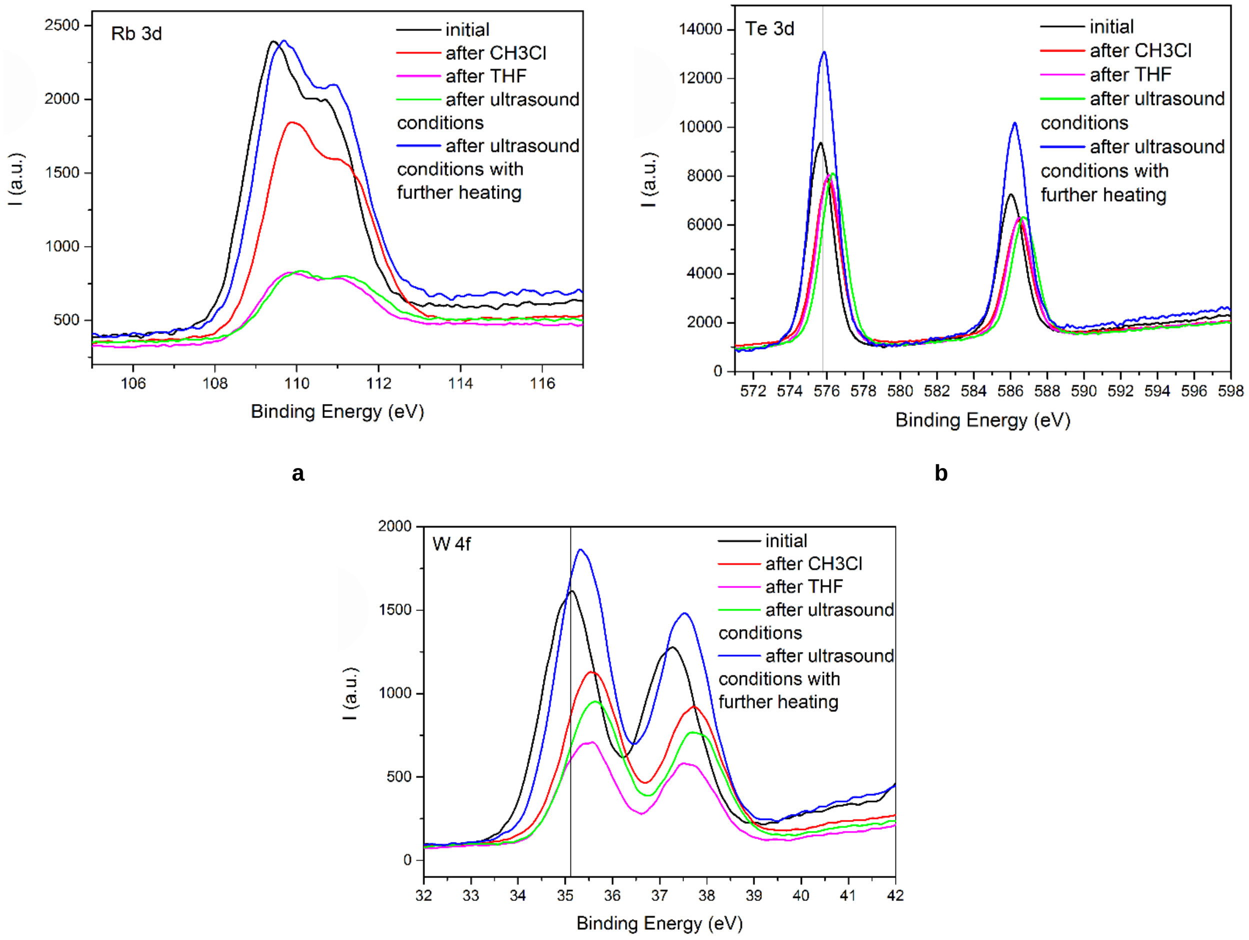
Рис. 4. Макромолекулы полимера на поверхности порошка катализатора $RbTe_{1,5}W_{0,5}O_6$ после проведения реакции полимеризации метилметакрилата (a); поверхность порошка катализатора $RbTe_{1,5}W_{0,5}O_6$ после отмывания полиметилметакрилата в растворе тетграгидрофурана (b), $CHCl_3$ (c) и воды в УЗДН-А650 (d)

A more in-depth study of the $RbTe_{1.5}W_{0.5}O_6$ oxide surface after the 1st, 2d and 3d purification methods by the XPS method showed that a shift of the photoelectronic lines of Rb, Te, W metals towards high binding energies respect to $RbTe_{1.5}W_{0.5}O_6$ initial sample is observed [13, 35]. The shift shows Rb, Te, W atoms on the surface are predominantly connected to oxygen that is, all the atoms on the surface after the polymerization process and purification are in an oxidized state “M-O-” (Fig. 5). Simultaneously, ultrasound purification with further calcination at 300–400 °C leads to almost full recovering the positions of the metals photoelectron lines on the surface.

The behavior of the surface carbon also should be noted. Photoelectronic lines C 1s and O 1s for the initial catalyst powder show the presence of a characteristic insignificant amount of adsorbed organic pollutants and CO_2 on the surface (Fig. 6, a, b), while there are significant changes of C1s and O1s for samples after the 1st, 2d and 3d treatment methods. Only ultrasonic treatment with next heating allows to reach quite close the initial decompositions of the C 1s and O 1s lines. Moreover, as it has been confirmed earlier [35], the ratio of Rb:Te:W atoms on the surface strongly impacts on the photocatalytic activity of the powder. Using XPS method, it has been obtained that the Rb:Te:W ratio is significantly depended on purification procedure, and it becomes close to the initial only after chloroform solution treatment and ultrasound conditions with further heating.

Decomposition of photoelectronic lines of carbon C 1s and oxygen O 1s showed that chemically adsorbed MMA and its oligomers are present on the surface of the powder sample washed in an ultrasonic bath: contributions of the C–C (285 eV), C–C=O (285.75 eV), C–O (286.7 eV), O–C=O (289.1 eV) bonds are correlated as 2.4:1:0.7:0.4 (Fig. 6, c, d; Tab. 1). A slight change in the peaks ratio compared to pure PMMA (2:1:1:1) in the line C 1s occurs due to the influence of the metals of the $RbTe_{1.5}W_{0.5}O_6$ compound on the distribution of electron density along the bonds, formed between Rb, Te, W and carbon of the MMA molecules though oxygen. Besides the chemical bonds of MMA, there is a small excess of C=O – ether group bonds on the photocatalyst surface, as well as potassium (doublet), which got to the surface of the catalyst from the emulsifier, and C–F bonds associated with the storage of samples in plastic bags, are observed at the level of impurities. Thus, although the powder treatment in an ultrasonic dispergator leads to the destruction of large catalyst-bound macromolecules observed by SEM, the monomer and oligomers formed during the destruction of macromolecules by ultrasound form chemical bonds with the catalyst and remain on its surface. Thus, while SEM does not identify polymer macromolecules, XPS shows the catalyst surface is not free.

After prolonged chloroform extraction, part of the MMA and OMMA macromolecules formed in the reaction mixture (Fig. 3), passes into solution. Previously it was noted [6] that MMA and OMMA polymers were also identified in chloroform after washing the photocatalyst powder by ^{13}C NMR spectroscopy and MALDI methods (Fig. 4). However, a significant part of macromolecules remains on the surface of the catalyst, and it is detected by the SEM method (Fig. 4, c). Despite this, the analysis of the photocatalyst powder washed in chloroform at boiling point (61 °C) immediately after the synthesis of the polymer by the XPS method shows the absence of PMMA and MMA molecules on the surface. In this case, decomposition of the photoelectronic carbon line 1s gives a distribution of bond contribution intensities that does not correspond to PMMA. There is a significant increase in the contribution of the C=O bonds of the ether group and C–O–R and the appearance of CO_3^{2-} groups on the powder surface (Fig. 6, e, f; Tab. 1), which can be attributed to the oxidation products of polymer molecules and monomers. That is, although large macromolecules remain bound to the photocatalyst powder after treatment with chloroform, the surface layer of the adsorbed MMA is noticeably oxidized.



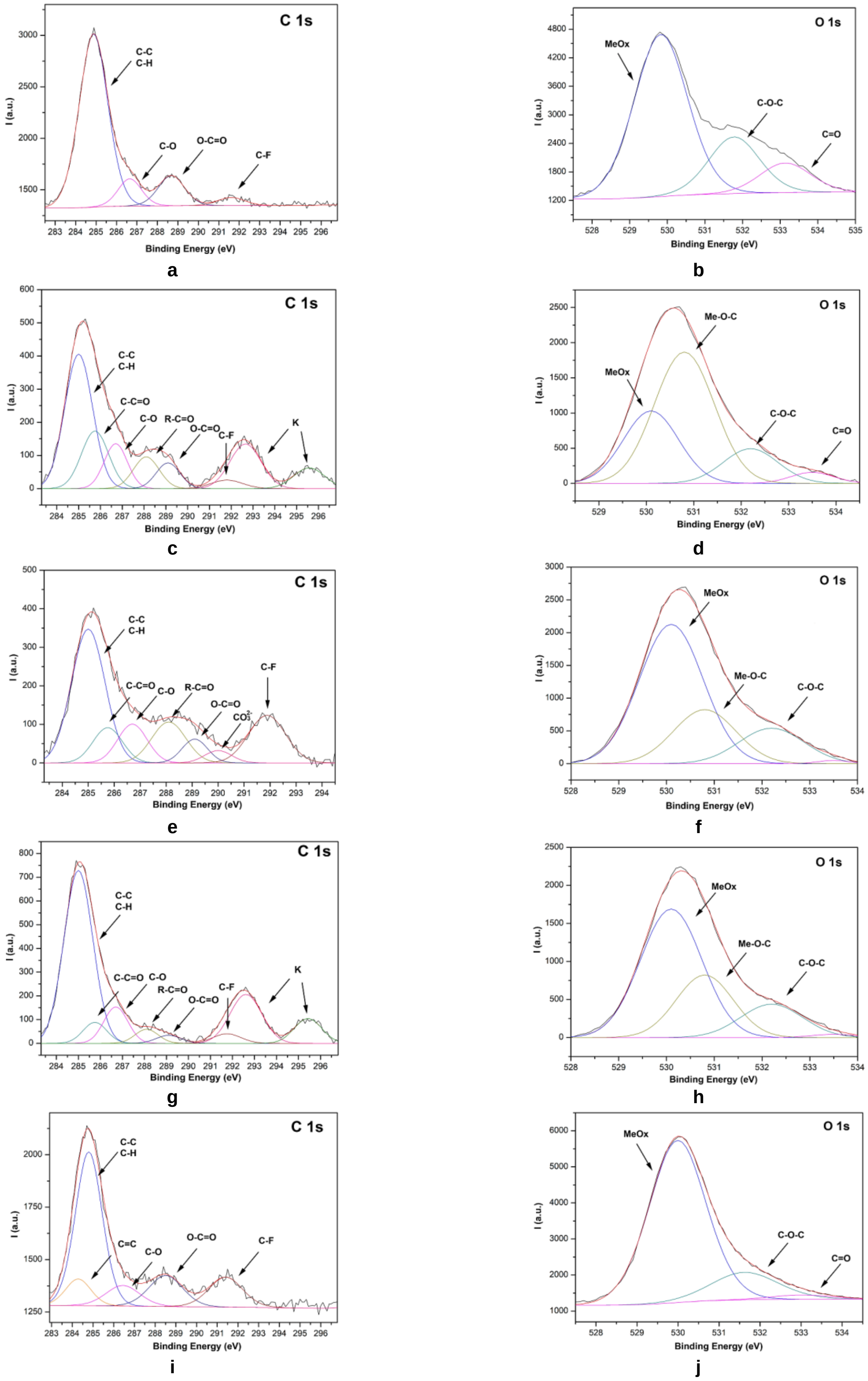
a

b

c

Fig. 5. Rb 3d (a), Te 3d (b) and W 4f (c) lines for samples of initial catalyst, after ultrasonic treatment, after washing in $CHCl_3$, in THF and after heating at 300–400 °C

Рис. 5. Линии Rb 3d (a), Te 3d (b) and W 4f (c) для образцов катализатора после ультразвуковой обработки, после промывания в $CHCl_3$, в тетрагидрофуране и после нагревания при 300–400 °C



a b c d e f g h i j

Fig. 6. C 1s and O 1s photoelectronic lines for samples of initial catalyst (a, b); after ultrasonic treatment (c, d); after washing in $CHCl_3$ (e, f); in THF (g, h) and after heating at 300–400 °C (i, j)

Рис. 6. Фотоэлектронные линии C 1s и O 1s для образцов исходного катализатора (a, b); после ультразвуковой обработки (c, d); после промывки в $CHCl_3$ (e, f); в тетрагидрофуране (g, h) и после нагревания при 300–400 °C (i, j)

Table 1. The contributions of bonds to the carbon photoelectron line C 1s for the studied samples of $RbTe_{1.5}W_{0.5}O_6$ powder in atomic %

Таблица 1. Вклады связей в фотоэлектронную линию углерода C 1s для исследованных образцов порошка $RbTe_{1,5}W_{0,5}O_6$ в атомных %

Type of chemical bond	E, eV	Initial powder	Powder after ultrasonic treatment	Powder after $CHCl_3$	Powder after THF	Powder after firing 300–400 °C
C–C, C–H	285	77.5%	48.19%	49.88%	72.48	63%
C–C=O	285.75	12.5%	20.08%	11.48%	7.22	16%
C–O	286.7	10%	13.34%	12.68%	12.67	10.7
O–C=O	289.1	–	7.90	6.70	2.86	–
C=O	288.1	–	10.49	15.55	4.77	–
CO_3^{2-}	290	–	–	3.71	–	–
C=C	284.2	–	–	–	–	10.3

After washing the powder with a THF solution, polymer molecules (Fig. 4, b) are also visible on the SEM images [6], however, they are not identified on the catalyst's surface by the XPS method. Potassium from the emulsifier is also detected on the surface (Fig. 6, g, h; Tab. 1). The proportion of C–C and C–H bonds on the photocatalyst's surface increases significantly compared to the other two samples. Probably, in this case, the excess of THF substitutes adsorbed MMA on the catalyst surface with the opening of the ring according to the scheme in Fig. 7 proposed in the work [37].

The study of the composition of the catalyst samples by depth during ion profiling shows that after 2–4 nm adsorbed monomers and oligomers in the line C 1s are absent. There are also no contributions of C–O and C=O bonds in the O 1s photoelectronic line. It suggests that MMA molecules and oligomers are adsorbed only on the thin layer of the catalyst's surface with thickness no more than 1–2 nm.

In general, the following features of changes on the $RbTe_{1.5}W_{0.5}O_6$ complex oxide surface after catalysis of methyl methacrylate polymerization should be distinguished. From the previous study of the surface and the photocatalytic properties of $RbTe_{1.5}W_{0.5}O_6$, it is known that the compound's surface is enriched with Rb atoms, due to their migration from the volume to the surface through the channels of the crystal lattice [32]. It leads to the appearance of a small positive charge on the surface of the powder particles, which in an aqueous solution well adsorbs water and OH^-. Thus, the $RbTe_{1.5}W_{0.5}O_6$ surface in solution has a partially negative charge, which is confirmed by the increased adsorption of cationic dyes by the catalyst surface [35]. The surface may have the form shown in Fig. 8. In addition, Te and W atoms are presented on the surface, which are also capable of adsorbing water to form –(Te/W)-OH and –(Te/W)-O-, however, their contribution to the surface state is less due to the smaller number of atoms on the surface than Rb.

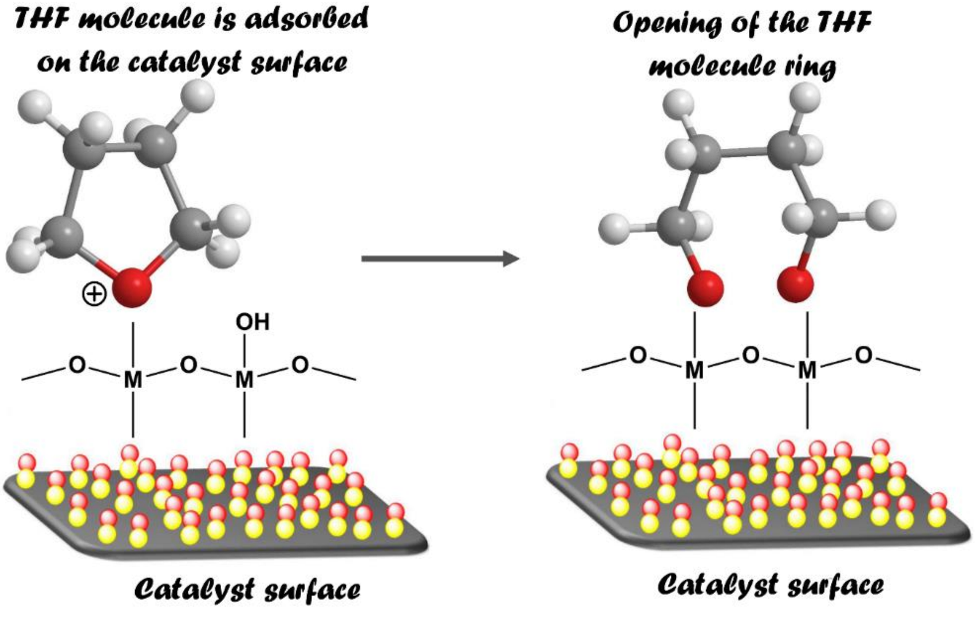


Fig. 7. Mechanism of adsorption of the THF molecule on the catalyst surface

Рис. 7. Механизм адсорбции молекулы тетрагидрофурана на поверхность катализатора

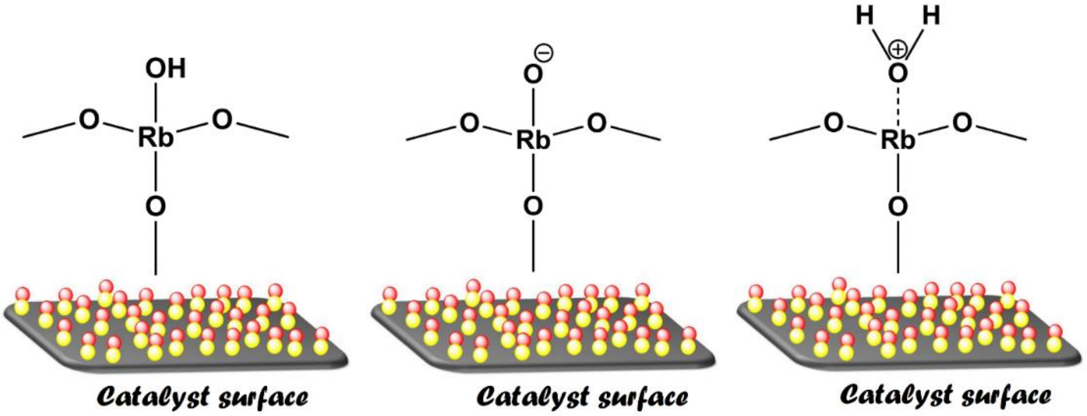


Fig. 8. Types of adsorbed particles on the catalyst's surface in an aqueous solution

Рис. 8. Типы адсорбированных частиц на поверхности катализатора в водном растворе

After the polymerization reaction, metal atoms on the $RbTe_{1.5}W_{0.5}O_6$ surface are in an oxidized state. It means that the active centers -M-O•, where the radical polymerization process starts, are occupied. After the powder is treated with ultrasound, polymer macromolecules are destroyed, while oligomers can still occupy active centers -M-O•. The atomic concentration of Rb (3d), Te (3d) and W (4f) is corresponds to 19.2, 62 and 18.8%, respectively, while initial powder possess containing 49.8, 35.5 and 14.7% for Rb (3d), Te (3d) and W (4f) in atom%, respectively. Thus, it is clearly seen, the Rb-sites on the surface is not recovered (Fig. 5). In addition, due to multiple bonds in the monomer and polymer, organic substrates interact with the complex oxide $RbTe_{1.5}W_{0.5}O_6$ with the formation of coordination complexes [38–40], which prevent the release of hydroxyl radicals into the volume of the monomer solution. These features in the reaction mixture explain the small yield of PMMA (5–10%) in solution after the reaction [12]. Probably, with the formation and growth of a MMA and OMMA oligomers chain on the catalyst surface, the process of interaction between electron-hole pairs and solvent-water becomes sterically difficult, and reactions (2), (4–7) (Fig. 2) practically stop. On the other hand, growth of the electron migration path along the chain of PMMA molecules from the catalyst to the radical center in solution increases the probability of recombination of the electron-hole pair. It leads to a sharp decrease of the number of active particles and formed radicals, and, consequently, to a slowdown and stop of the polymerization reaction on the surface and in solution.

Moreover, for the regeneration of the $RbTe_{1.5}W_{0.5}O_6$ photocatalyst, the treatment by using organic solvents of PMMA is not sufficient for reuse too. After washing the powder in TG solution, the atomic concentration of Rb (3d), Te (3d) and W (4f) on the surface becomes 19.3, 62 and 14.8%, respectively, which is also distinguished in comparison to initial one and characterized by loss of Rb (Fig. 5). In case of using chloroform as solvent, the surface atomic concentrations of Rb (3d), Te (3d) and W (4f) seems to be almost recovered and corresponds to 40.7, 42.7 and 16.6%, respectively (Fig. 5). Despite the fact, strong oxidation of the surface is still observed and influences the photocatalytic activity.

Thus, for the regeneration of the $RbTe_{1.5}W_{0.5}O_6$ photocatalyst, the treatment of its aqueous solution with ultrasound or using PMMA organic solvents is not sufficient for reuse. It was clearly shown by XPS studies, as well as a decrease in the effectiveness of MMA polymerization processes and MMA grafting on collagen and pectin.

To remove organic molecules from the catalyst's surface, it was fired at a temperature of 300–400 °C after ultrasonic treatment. After such treatment of the catalyst, the polymerization process of MMA leads to the isolation of its polymer with a conversion rate of ~5%, which is slightly less, than for the fresh catalyst. It is due to the recovery of the chemical state of metals and their quantitative distribution on the surface to close the original (Rb (3d), Te (3d) and W (4f) is 42.9, 42.8 and 14.3% in atom%, respectively). The surface is also cleaned of organic compounds – reagents and products of the polymerization process, which can be confirmed by the decomposition of the C 1s and O 1s photoelectronic lines for the heated sample (Fig. 6, i, j) to a state close to the original, except for the presence of a small number of bonds C = C (~284.2 eV).

CONCLUSIONS

Different ways of surface purification of the $RbTe_{1.5}W_{0.5}O_6$ catalyst after MMA polymerization in an aqueous emulsion under irradiation with visible light λ=400–700 nm at a temperature of 20–25 °C for further reuse have been carried out. Analysis of the catalyst surface by SEM and XPS methods showed that the treatment of the catalyst under ultrasonic conditions in an aqueous emulsion allows the destruction of polymer macromolecules, but the monomer and oligomers formed under the action of ultrasound due to the destruction of the polymer remain on the surface of the catalyst, forming chemical bonds with it. It was also found that prolonged treatment of the catalyst powder with chloroform at its boiling point in the Soxhlet extractor, as well as mixing it in THF, leads to partial removal of organic substrates – oxidative products and solvents. These processes lead to inactivation of the $RbTe_{1.5}W_{0.5}O_6$ catalyst during polymerization. To reach the efficient regeneration of the powder, not only ultrasound treatment is required, but also its heating at 300–400 °C to fully clean the surface of organic substrates and recover the Rb:Te:W ratio.

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