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Ce-, Zr-containing oxide layers formed by plasma electrolytic oxidation on titanium as catalysts for oxidative desulfurization

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ABSTRACT

Mixed cerium-zirconium-titanium oxide layers: $CeO_x + TiO_2$, $CeO_x + ZrO_2 + TiO_2$, $ZrO_2 + TiO_2$ - on titanium were formed by plasma electrolytic oxidation technique in the electrolytes with different ratio of $Ce(SO_4)_3$: $Zr(SO_4)_2$ and investigated by the complex of physical-chemical methods. Their activity was studied in the peroxide oxidation of sulfur compounds (thiophene, thioanizole and dibenzothiophene) and the desulfurization of diesel fuel. Element and phase composition of the PEO-coated samples affect their catalytic activity. $ZrO_2 + TiO_2 + CeO_x$ systems with the largest content of zirconium showed the highest catalytic activity in oil desulfurization. Their catalytic activity correlates with the presence of the double oxides $ZrTiO_4$ and Ti_2ZrO_6 in the coating composition. The decrease in the activity of catalysts when they are used in consecutive cycles can be accounted for by the etching of the coatings in the area of the pores. This drawback one can overcome by the addition of an ionic liquid namely 4-(3'-ethylimidazolium)-butanesulfonate, which increases not only the activity, but also the stability of the catalysts. Under these conditions, the structure and activity of the catalyst did not change significantly over several reaction cycles. The combination of PEO treatment and deposition of the ionic liquid allowed one not only to oxidize model substrates, but also carry out the desulfurization of diesel fuel to a residual sulfur content of less than 10 ppm.

1. Introduction

Plasma electrolytic oxidation (PEO) is the electrochemical formation of oxide layers on metals and alloys under electric spark and microarc discharges [1–3]. The method allows one not only to form protective coatings [3–6], but also to obtain catalytically active layers of oxides [7–10]. On one hand, the use of PEO makes it possible to form oxide layers of desired composition by the choice of electrolyte formula. On the other hand, during the PEO, an intermediate layer of oxides of the metal or alloy under treatment is always formed between the substrate metal and the outer functional layer. As a result, in one operation, a coating can be obtained, in which the active phase is located on the outer surface of the oxide carrier on the metal substrate. Such construction advantageously distinguishes these systems from heterogeneous catalysts supported on silica, alumina or carbon materials.

Due to the porous structure, the traditional carriers have a large specific surface area, but often the active phase may be inaccessible to

reagents, since it is deposited in deep narrow pores. Such diffusion limitations are particularly important for liquid-phase processes involving bulk organic molecules. Although the systems based on PEO layers do not have a branched surface such as mineral or carbon carriers, but due to the wide pores and uniform distribution of the active phase on the outer surface, they exhibit appreciable activity in different catalytic processes, including CO oxidation into CO_2 [8,10], afterburning of the diesel exhausts [11] and soot [12], oxidative dehydrogenation of cyclohexane to cyclohexene [7], conversion of naphthalene [13], dehydration of ethanol to ethylene [14], conversion of methane to synthesis gas [15], oxidative desulfurization of thiophene [16], photocatalytic decomposition of organic dyes [17,18].

Oxidation of sulfur-containing compounds of petroleum raw materials, such as aromatic sulfides and thiophene derivatives, is an alternative to an expensive hydrotreatment process, so the search for catalysts for this process is highly relevant [19,20]. Individual and mixed oxides and salts containing ions of transition metals in high oxidation

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states are used as heterogeneous catalysts of desulfurization process [16,19–22]. In our previous paper [16], using the example of WO₃-containing PEO coatings on aluminum and titanium, we showed that the PEO technique allows one to synthesize, in a single stage, multi-component oxide catalysts active in peroxide oxidation of thiophene. The samples containing mixed oxides of W and Mn were most active, which is in full agreement with the literature data [19].

Ce-containing oxide systems are known to be used as catalysts and sorbents in desulfurization of sulfur-containing compounds of petroleum raw materials and products [23,24]. The addition of zirconia to ceria leads to the formation of thermostable catalytically active composites and carriers due to the formation of mixed oxides. The ability of cerium and zirconium to form mixed oxides, active in the oxidation of various substrates and stable in aggressive media [25–29], is especially important for the oxidation of thiophene, since sulfuric acid is one of the products of its conversion [16,30]. As it was previously shown [31], Ce- and/or Zr-containing oxide layers on titanium surface can be obtained by plasma-electrolytic oxidation technique. Catalytic tests of Ce- and/or Zr-containing PEO coatings in CO oxidation and naphthalene conversion have revealed the prospects of their use both as carriers and as catalysts for redox reactions [32,33]. It is of interest to find out how the obtained PEO composites will behave in the desulfurization of various organic sulfur compounds contained in petroleum raw materials and how their surface will change during catalytic tests.

The purpose of this work is to investigate the catalytic activity of titanium-supported Ce-, Zr-containing catalysts obtained by PEO technique in oxidative desulfurization sulfur-containing compounds of petroleum raw materials.

In order to increase the activity of heterogeneous catalysts and stabilize their active centers, one can use ionic liquids (ILs) [34–37]. Ionic liquids supported as nanolayers on porous materials (supported ionic liquid phase, SILP; or solid catalyst with an ionic liquid layer, SCILL) act as a sort of 2D solvents and active site stabilizers. Supported ILs can also selectively adsorb a polar substrate, which accelerates the oxidation. Therefore, one of the objectives of this work is to investigate the effect of the deposition of an ionic liquid on the titanium supported PEO-obtained Ce- and Zr- oxides (their structure, catalytic activity and stability). 4-(3'-ethylimidazolium)-butanesulfonate was chosen as the ionic liquid, because sulfonated ILs are widely used as adsorbents and oxidation catalysts in desulfurization processes [30,38,39].

2. Experimental

2.1. Coating formation and characterization

Oxide layers were formed on VT1-0 titanium (99.9% Ti) samples of a size of 20 × 20 × 0.5 mm. Preliminary the samples were stripped with emery buff, removing barbs, and chemically polished in a mixture of concentrated acids (HF: HNO₃ = 1: 3, volume relation) at 70 °C. Then the samples were washed with running and distilled water, and dried by air at 70 °C.

For the preparation of electrolytes, distilled water and commercial reagents of the “chemically pure” grade were used: Ce₂(SO₄)₃ and Zr(SO₄)₂·4H₂O. Two base electrolytes were prepared, each containing 0.049 mol/L of Ce₂(SO₄)₃ or Zr(SO₄)₂·4H₂O. These solutions were mixed at volume ratios *B* = 0:1, 1:3, 1:1, 3:1 and 1:0 to obtain Zr- and/or Ce-containing solutions. The data of each of the electrolytes are presented in Table 1. For their characterization, we used the value δ_{Zr} that is relation of zirconium ions concentration to total concentration of cerium and zirconium ions in solutions.

Electrochemical treatment was carried out in a stainless steel bath with water cooling jacket. The body of the bath served as a counter electrode. The electrolyte was stirred with a mechanical stirrer. A PC-controlled commercial TER-4/460-2 thyristor unit operating in a unipolar mode was used as a current source. Coatings on titanium samples were obtained during *t* = 5–30 min at effective current density *i* = 5 A/

Table 1

The working electrolyte compositions.

№	<i>B</i>	Electrolyte [mol/L]		Zr(IV):Ce(III)	δ_{Zr}
		Zr(SO ₄) ₂	Ce ₂ (SO ₄) ₃		
1	0:1	0	0.049	0:1	0
2	1:3	0.01225	0.03675	1:6	0.14
3	1:1	0.0225	0.0225	1:2	0.33
4	3:1	0.03675	0.01225	3:2	0.6
5	1:0	0.049	0	1:0	1

Notes: *B* is volume ratio of base solutions containing 0 0.049 mol/L Zr(SO₄)₂ and 0.049 mol/L Ce₂(SO₄)₃.

Zr(IV):Ce(III) – molar ration of salt cations in electrolyte.

$\delta_{Zr} = C_{Zr} / (C_{Zr} + C_{Cer})$ the zirconium fraction in electrolyte.

dm². The temperature of the electrolyte did not exceed 20 °C. After PEO treatment, the coated samples were rinsed with distilled water and air-dried at room temperature.

The thickness of coatings was measured using an eddy-current thickness gage VT-201 and was calculated as the average of at least 10 separate thickness measurements on both sides of a flat sample.

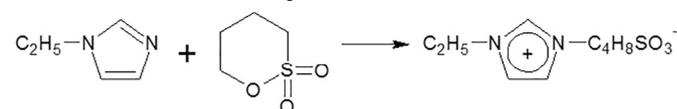
The elemental composition of the coatings (analysis depth ~2–5 μm) was determined by an electron probe X-ray microanalyzer JXA-8100. At least 5 individual areas of a size of 200 × 300 μm (hereinafter referred to as XSA) were scanned for each measurement. The values of the element concentrations were averaged. To create electrically conductive layer, graphite was sputtered on sample surfaces before measurements. SEM images of the coating surfaces were obtained on the same apparatus as well.

In some cases, a Hitachi S5500 high-resolution scanning electron microscope equipped with a Thermo Scientific accessory for energy-dispersive analysis was used to obtain the data on the samples morphology and element composition of individual surface formations. In that case, gold was preliminarily sputtered on the samples for preventing surface charging. The depth of scanning beam penetration was about 1 μm. Note that prior to microscopic investigation, the PEO-coated samples with the deposited ionic liquid (before and after catalytic tests) were dried in nitrogen atmosphere at 150 °C for 4 h.

The X-ray diffraction (XRD) patterns of the coated samples were recorded on a D8 Advance X-ray diffractometer using the Breg-Bretano method with rotation of the sample in CuK_α-radiation. The corresponding analysis was carried out using the EVA retrieval program based on the PDF-2 database.

2.2. The synthesis of the ionic liquid and catalyst treatment

The synthesis of 4-(3'-ethylimidazolium)-butanesulfonate was carried out as described in [40] with slight modifications. 1-Ethylimidazole (9.4 g, 0.1 mol) were mixed with 1,4-butanediol (13.6 g, 0.1 mol) in toluene. The system was purged with argon. The system was refluxed under slight argon purge for 24 h. Afterwards the white precipitate was filtered off. It was washed twice with acetone and dried overnight under vacuum at 80 °C. The purity of the zwitter ion was controlled by NMR (the spectra is absolutely equal to the ones reported in the [40]). The reaction is given below:



To deposit ionic liquid, PEO-coated samples were mixed with IL in a mass ratio 1:1 into room-temperature aqueous solution, and kept for 2 h with stirring. Then the samples with the applied IL were dried under vacuum at 80 °C.

2.3. Catalysis

The oxidation of organosulfur substrates (thiophene, thioanazole, dibenzothiophene) with hydrogen peroxide in isooctane was done as follows: a model mixture (10 mL) and the catalyst (0.1 g), were placed into a thermostated reactor, the solution was heated to 60 °C, and 50% H₂O₂ (0.4 mL) was added. In case when the solid catalyst contained the ionic liquid, its mass was increased to 0.2 g (as the IL-containing catalyst contained 50 wt% of the ionic liquid).

The model mixtures contained 1 wt% of a sulfur-containing compounds: thiophene, methyl phenyl sulfide, dibenzothiophene or 1:1 thiophene - dibenzothiophene mixture.

One of the approaches for increasing the efficiency of catalysis is the portionwise addition of hydrogen peroxide, which reduces its inappropriate consumption. This approach is known from the literature [41,42] and has been used in our previous study with a broad range of catalysts for peroxide oxidation of sulfur compounds [16,43]. This technique relies on the fact that the reaction order of hydrogen peroxide decomposition in the presence of heterogeneous catalysts based on transition metals depends on the initial concentration of H₂O₂ and changes from first to second upon the increasing of H₂O₂ concentration [44,45]. Meanwhile, the order of heterogeneously catalyzed thiophene oxidation reaction with respect to hydrogen peroxide is close to zero [46]. Thus, for reducing the rate of peroxide decomposition and more efficient its utilization in the model reaction, one must conduct the reaction at a low peroxide concentration, which can be attained by addition of the peroxide in small portions.

In the case of portionwise addition of the oxidant, 0.2 mL portions of hydrogen peroxide were poured into the reactor with a 2-hour interval. The content was thoroughly stirred with an overhead mechanical stirrer at 60 °C for 4 h, with samples for analysis being taken at intervals.

Quantitative analysis of the liquid phase of the reaction mixture was performed by gas liquid chromatography on a Kristall 4000 instrument equipped with a Zebtron ZB-1 capillary column of a length of 30 m (100% dimethylpolysiloxane as the liquid phase) and a flame ionization detector. The contents of thiophene, dibenzothiophene, methyl phenyl sulfide, and oxidation products were determined with linear temperature programming in the 90–220 °C range by the internal reference method.

The desulfurization of diesel fuel was carried out as follows: the fuel (10 mL) with sulfur content of 1080 ppm and the catalyst (0.02 g) were placed into a thermostated reactor, and heated up to 60 °C; then 50% H₂O₂ (0.2 mL) was added to the mixture. After 4 h, oxidation products were removed by DMF extraction and the second portion of H₂O₂ (0.2 mL) was added to the reaction solution, then the mixture was stirred another for 4 h. After the reaction, the catalyst was washed with isooctane. For comparison, the process was carried out in one stage with 0.4 mL of H₂O₂. In some experiments, PEO samples (0.02 g) with the ionic liquid (0.1 g) were added to the mixture.

The total sulfur content was determined by X-ray fluorescence spectrometry using ASE-2 sulfur analyser.

3. Results and discussion

3.1. Effect of electrolyte formula

Table 2 presents data on the effect of the working electrolyte formula on the thickness, elemental composition of the coatings formed within 5 min, as well as the catalytic activity of these composites in thiophene oxidation (identified with the conversion of thiophene). Fig. 1 shows the X-ray diffraction patterns of PEO-coated samples. As follows from the presented data, in the electrolyte containing only Ce₂(SO₄)₃ ($\delta_{Zr} = 0$), coatings predominantly contain TiO₂ doped with cerium, the content of which is 2.4 at.%. In the electrolyte with Zr(SO₄)₂ ($\delta_{Zr} = 1$), coatings containing both TiO₂ and appreciable amounts of ZrO₂ are formed, as well as double oxides of ZrTiO₄ and

Table 2

Effect of the electrolyte formula δ_{Zr} on the thickness h and element composition of the coatings as well as thiophene conversion X .

δ_{Zr}	h , μm	C, at. %				X, %	
		Ce	Zr	Ti	O	0.4 mL H ₂ O ₂	0.2 + 0.2 mL H ₂ O ₂
0	4.6 ± 1.0	2.4	0	30.8	66.4	26	31
0.14	4.5 ± 1.0	2.9	6.1	26.2	64.8	28	34
0.33	5.2 ± 1.0	2.5	9.2	22.6	65.7	30	36
0.6	4.5 ± 1.0	2.6	13.7	19.0	65.7	38	43
1	8.0 ± 1.5	0	17.8	13.4	68.4	34	38

Notes: The coatings were formed within 5 min.

Ti₂ZrO₆ (sriilankite). Coatings formed in a mixed electrolyte with $\delta_{Zr} = 0.6$ contain predominantly double oxides and titania, while coatings obtained in an electrolyte with $\delta_{Zr} = 0.14$ contain only traces of double oxides and TiO₂ in rutile modification. Reflexes of titanium on X-ray diffraction patterns are associated with the X-ray irradiation of the substrate metal.

According to [47], in the acid electrolyte with Zr(SO₄)₂ (pH ~ 2), the incorporation of zirconium into the coatings is most likely due to the formation of [ZrO(SO₄)₂]²⁻ complex anion, its migration to the anode surface and further participation in the process of coating growth initiated by electric discharges during PEO. Hydrolysis of Ce₂(SO₄)₃ (pH ~ 4) apparently proceeds according to a different mechanism. The insignificant incorporation of cerium into the anodic oxide layers formed by electrical discharges in the electrolyte with Ce₂(SO₄)₃ indirectly indicates that cerium in the electrolytes used is in the form of hydrated or complex cation.

For the sake of clarity, the data given in Table 2 are shown in Fig. 2. The transition from an electrolyte with Ce₂(SO₄)₃ ($\delta_{Zr} = 0$) to an electrolyte with Zr(SO₄)₂ ($\delta_{Zr} = 1$) results in increasing zirconium concentration and decreasing titanium concentration at approximately constant cerium concentration in the coating composition, Fig. 2a. The variation of the elemental composition of the system was always performed in such a way that the sum of the concentrations (at.%) (Ti + Zr + Ce) was always constant, and the ratio of oxygen to this sum is close to two. This fact indirectly indicates the presence of TiO₂, ZrO₂ and CeO₂ in the analyzed layer.

The data presented show that all the coatings tested (TiO₂ + CeO_x, ZrO₂ + TiO₂ + CeO_x, ZrO₂ + TiO₂) display catalytic activity in the desulfurization of thiophene. Increasing zirconium concentration in the coatings and, accordingly, a change in the Zr/Ti ratio in favor of zirconium, results in increasing their activity in thiophene conversion. ZrO₂ + TiO₂ + CeO_x coatings with the largest content of zirconium demonstrate the maximum catalytic activity. Perhaps this is due to the presence of a sufficient number of double oxides of ZrTiO₄ and Ti₂ZrO₆, in such coatings, Fig. 1.

3.2. Effect of PEO treatment duration

The effect of PEO processing time on the composition, structure, and catalytic activity of the coatings was studied in an electrolyte with $\delta_{Zr} = 0.6$, at which the samples showed the highest activity in thiophene desulfurization. The data obtained are presented in Table 3.

According to Table 3, the effectiveness of the coatings for the thiophene desulfurization passes through a maximum: the highest conversion of thiophene is characteristic for coatings formed within 10 min. Meanwhile, for the systems under study, the overall element composition of the outer coating layer, analyzed by XSA (analysis depth is ~2–5 μm , averaging over scanning areas of 200 × 300 μm), practically does not depend on the formation time. We cannot relate the change in the catalytic properties of coatings to changes in their overall element composition.

The effect of the processing time is apparently related to a change in

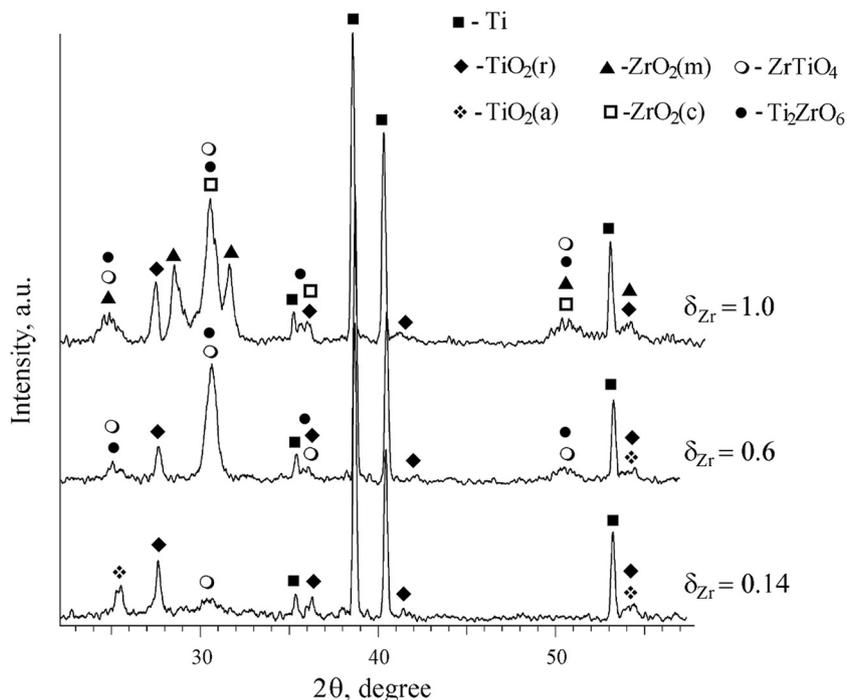


Fig. 1. X-ray patterns of the coatings formed for 5 min in electrolytes with different δ_{Zr} .

the structure and composition of the surface of PEO coatings that is in contact with the thiophene solution. An increase in the duration of PEO treatment in galvanostatic conditions leads to a change in the mechanism of coating growth due to the transition from the stage of spark discharges to the stage of microarc ones. Fig. 3a shows the behavior of the voltage across the electrodes U as a function of the coating formation time $U = f(t)$. According to the inflection points, the stages of spark (I) and microarc (II) discharges are identified on the curve. From the comparison of the data in Fig. 3a, b, it can be seen that the most catalytically active coatings are formed at the beginning of the microarc stage realization. The micro-arc electric discharges, which are more powerful than spark ones, in general, result in the formation of a more defect surface with large relief fragments. On the other hand, the phase composition of the coatings changes due to the thermal action of microarc discharges. In addition, due to diffusion thermally stimulated by

Table 3

Effect of PEO processing time t on the thickness h , element composition of the coatings and thiophene conversion X .

t , min	h , μm	C, at. %				X, %	
		Ce	Zr	Ti	O	0.4 mL H_2O_2	0.2 + 0.2 mL H_2O_2
5	4.5 ± 1.0	2.6	13.7	19.0	65.7	38	43
10	7.7 ± 1.8	2.8	14.0	16.8	66.4	44	67
15	8.8 ± 1.5	3.0	14.4	16.7	65.9	40	45
20	10.3 ± 1.5	2.4	14.0	16.4	66.8	30	35
30	11.9 ± 1.5	2.7	14.5	19.3	66.8	25	29

Notes: PEO coatings are fabricated in electrolyte with $\delta_{Zr} = 0.6$.

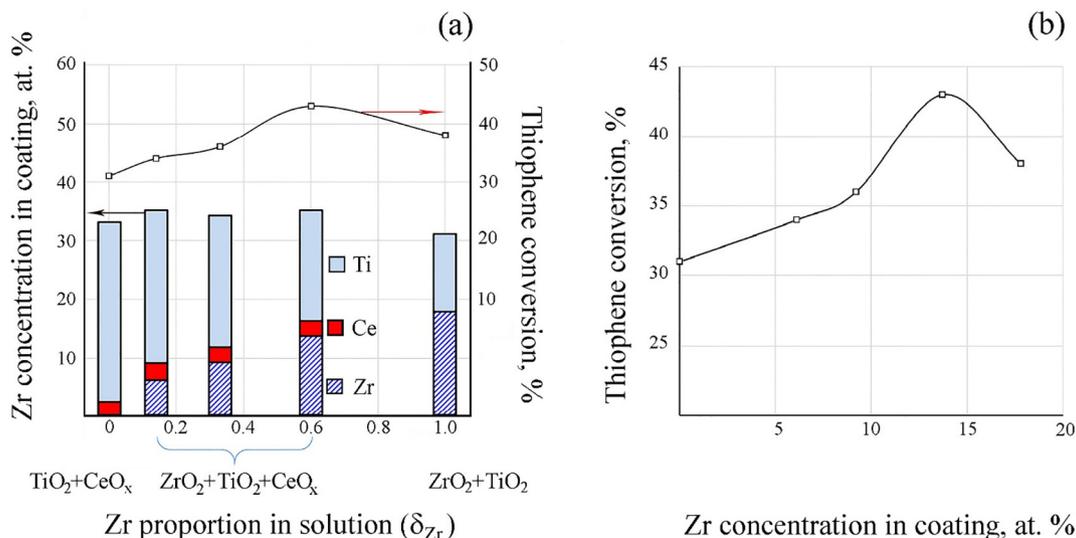


Fig. 2. Effect of the electrolyte formula (δ_{Zr}) on the elemental composition of the coatings (a) and the effect of the zirconium concentration in coatings on thiophene conversion (b).

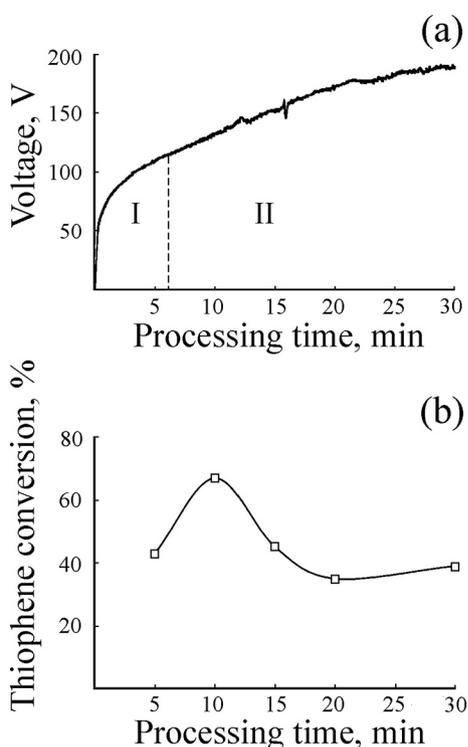


Fig. 3. Dependence of the voltage on the electrodes on PEO processing time (a) and the thiophene conversion for the coatings formed at different durations of PEO treatment (b) in the electrolyte with $\delta_{Zr} = 0.6$.

electric breakdowns, the distribution of elements in the surface layer can change, while maintaining a constant overall element composition.

Fig. 4 shows SEM images of the surface of coatings formed during 5, 10 and 15 min. At $500\times$ magnification, all coatings look dense and uniform. As the formation time increases, the surface of the coating becomes more developed, its roughness increases, and its real surface area increases. One can assume that the higher activity of the coatings formed during 10 min, compared with coatings formed within 5 min, is due, among other reasons, to their difference in surface architecture.

XRD patterns in Fig. 5 demonstrate the influence of the processing time on the phase composition of the coatings formed in the electrolyte with $\delta_{Zr} = 0.6$. It can be noted that an increase in the formation time from 5 to 15 min results in the growth of the reflections corresponding to the double oxides $ZrTiO_4$ and Ti_2ZrO_6 . With a further increase in the formation time, the corresponding peaks change insignificantly. The increased activity of the coatings formed within 10 min correlates with the increase in the content of these phases in the coatings.

Thus, $ZrO_2 + TiO_2 + CeO_x/Ti$ samples with the largest zirconium content are the most active of the studied ones. The optimal time for their plasma electrolytic formation is about 10 min. Such catalysts contain double oxides of $ZrTiO_4$ and Ti_2ZrO_6 and have developed

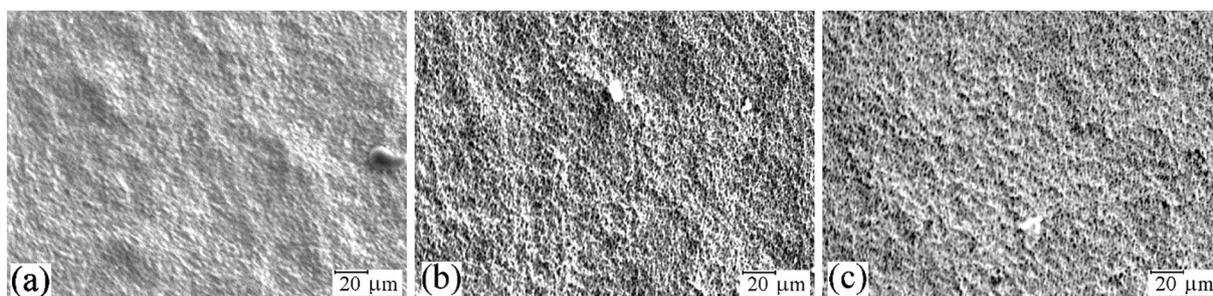


Fig. 4. SEM images of surface of the coatings formed within 5, 10 and 15 min in electrolyte with $\delta_{Zr} = 0.6$.

surface.

3.3. Sulfur compounds oxidation

The $ZrO_2 + TiO_2 + CeO_x/Ti$ catalyst prepared over a 10 min period in an electrolyte with $\delta_{Zr} = 0.6$ and possessing enhanced activity towards thiophene oxidation was tested in the oxidation of other organosulfur compounds, such as, thioanizole and dibenzothiophene. The results of experiments with H_2O_2 addition as one portion or in portions are summarized in Table 4 (2 and 3 columns).

As can be seen from Table 4, the conversion of thioanizole is more vigorous, with complete conversion being achieved 1.5 h after the onset of the reaction. Thiophene is oxidized somewhat more slowly, with the conversion increasing 1.5-fold in the case of portionwise addition of the peroxide. Dibenzothiophene is not oxidized in noticeable amounts in the absence of thiophene, irrespective of whether peroxide was added as one portion or in portions. This result was unexpected, as substituted thiophenes are known to be oxidized much faster than thiophene [48]. However, as noted above, oxidation of thiophene gives sulfuric acid as one of the products. It is known from the literature that acids accelerate the peroxide oxidation of sulfur compounds [19,21,49]. We suggested that co-oxidation of the two substrates, thiophene and dibenzothiophene, would promote conversion of the latter and the acid formed in situ would possibly accelerate the oxidation. Therefore, we tested the catalyst in the system containing a binary mixture of thiophene and dibenzothiophene in 1:1 weight ratio. The dibenzothiophene conversion increased to 35% when the two substrates were co-oxidized and to 51% when portionwise addition was also used. The oxidation of dibenzothiophene gave the corresponding sulfone as the major product, as was confirmed by chromatography.

Thus, titanium-supported Ce-, Zr-containing catalysts, formed by PEO technique, catalyze the desulfurization of various sulfur-containing compounds of petroleum raw materials and products.

3.4. Behavior of the catalyst with and without ionic liquid

As it has been stated in the introduction, ionic liquids can be used to increase the activity of catalysts and stabilize their active centers [34–37].

Fig. 6 shows the kinetic curves for the conversion of sulfur-containing substrates when hydrogen peroxide was added in one portion at the absence and in the presence of IL. It can be seen that the reaction rates markedly increased (by a factor of 1.5 thioanizole and by a factor of 2 for thiophene) upon the addition of the IL. It is noteworthy that the IL itself catalyzes the reaction, but thiophene conversion without a metal-containing catalyst does not exceed 35% even when 0.5 g of IL was used. Thus, the simultaneous use of Ce-, Zr-containing catalyst and ionic liquid leads to an increase in the efficiency of oxidative desulfurization.

Even more impressive results were attained when both approaches, portionwise addition of the oxidant and the presence of IL, were used simultaneously. As can be seen from the Table 4 (4 and 5 columns), the

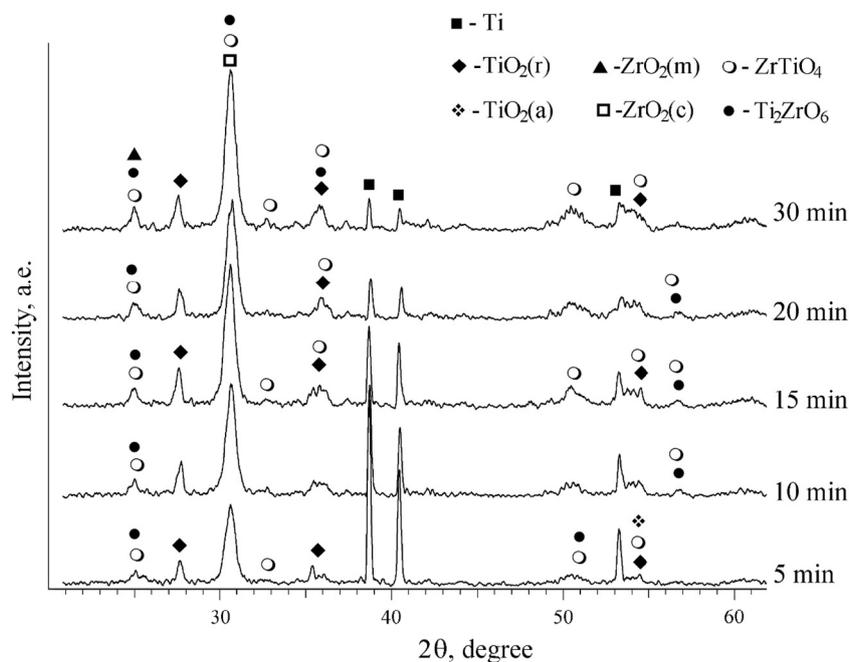


Fig. 5. XRD patterns of the samples with PEO coatings formed in the electrolyte with $\delta_{Zr} = 0.6$ during different formation time.

Table 4

Conversion of sulfur-containing compounds (%) at various loads of H_2O_2 , 4 h.

Substrate, wt%	PEO sample		PEO sample with IL	
	0.4 mL H_2O_2	0.2 mL + 0.2 mL H_2O_2 in 2 h	0.4 mL H_2O_2	0.2 mL + 0.2 mL H_2O_2 in 2 h
Thioanisole, 1%	100	100	100	100
Thiophene, 1%	44	67	77	89
Thiophene, 0.5%	45	61	68	83
Dibenzothiophene, 0.5%	35	48	56	65

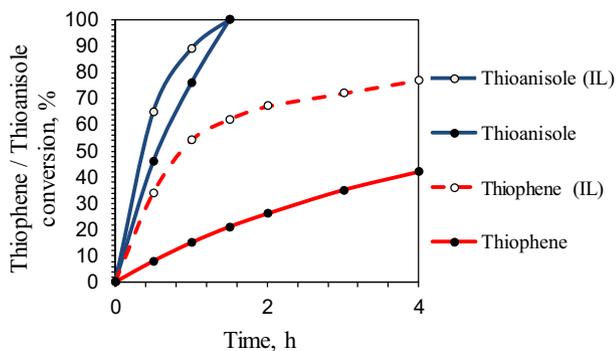


Fig. 6. The influence of the IL on the kinetics of desulfurization. Reaction conditions: 10 mL of model mixture, 0.2 g of catalyst with IL, 0.4 mL of H_2O_2 , 60 °C, 4 h.

combination of the approaches (portionwise addition of hydrogen peroxide and IL) considerably enhances the reaction intensity and may bring the thiophene conversion up to 90%, and the dibenzothiophene conversion in the presence of thiophene may reach 65%.

Another important result of using IL is the increased stability of the catalyst (Fig. 7). Experiments without IL have shown that the conversion of thiophene is reduced by 10–15% after 5 cycles of catalytic tests. As can be seen from Fig. 7, with the portionwise addition of the oxidant and the use of IL, the thiophene conversion remains invariable in five successive cycles.

Fig. 8 shows the surface morphology of titanium-supported Ce-, Zr-

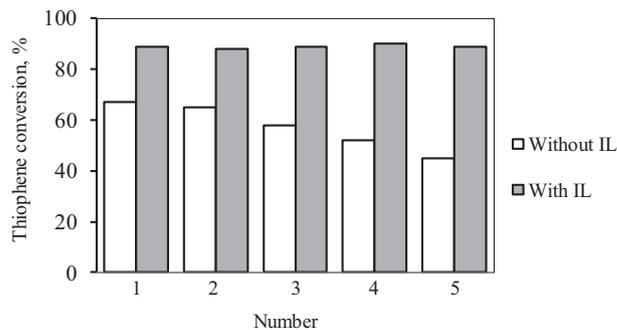


Fig. 7. The conversion of thiophene in five consecutive reaction cycles. Reaction conditions: 10 mL of model mixture, 0.2 g of catalyst with IL, H_2O_2 fractional loading.

containing catalyst with and without ionic liquid before and after 5 cycles of catalytic oxidative desulfurization of thiophene. In all cases, the elemental composition of the coatings, averaged over large areas of $60 \times 80 \mu m$ in size determined with an attachment for energy dispersive analysis is close to the microprobe analysis data given in Table 2.

After applying the ionic liquid and drying the samples in a stream of nitrogen at 150 °C for 4 h, particles are present in some pores of the sample, Fig. 8b. Obviously, filling the pores is associated with the ingress and concentration of the ionic liquid in them.

For the samples subjected to five catalytic test cycles, the main differences in the surface morphology of PEO coatings with and without

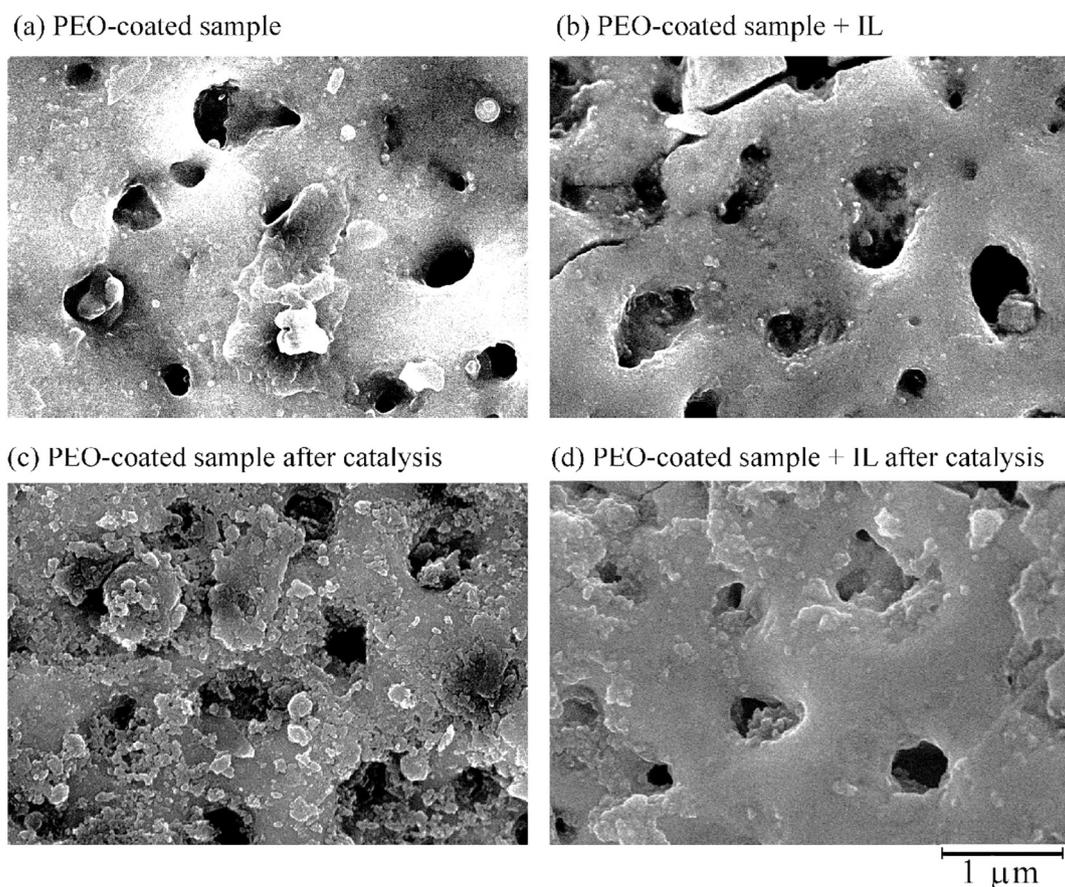


Fig. 8. SEM images of initial PEO-coated samples (a) before and (c) after catalytic tests; SEM images of PEO-coated samples with applied ionic liquid (b) before and (d) after catalytic tests. PEO coatings on titanium have been formed within 10 min in electrolyte with $\delta_{Zr} = 0.6$. All images have the same magnification of $30,000\times$.

ionic liquid are the changes in the pores and their surroundings, Fig. 8c, d. In both cases, numerous particles (flakes) are visible on the surface. The compositions of such scales are given below.

Flakes for the samples without IL, at.%: 18.2C; 55.7 O; 18.7 Ti; 5.7 Zr; 1.7 Ce.

Flakes for the samples with IL, at.%: 17.2C; 46.5 O; 26.6 Ti; 7.3 Zr; 2.4 Ce.

In both cases, the flakes contain Ti, Zr, Ce, O. The formation of the flakes, as is clearly seen in Fig. 8c, can be related to the partial etching of the coating array in the pore area. As noted above, the oxidation of thiophene produces sulfuric acid [16,30]. One can assume that the appearance of the flakes is the result of acid etching of the coating material, mainly in the pore area. Apparently, a gradual decrease in the activity of catalysts without ionic liquid during repeated tests is associated with this process. After the deposition of the ionic liquid, the changes in surface morphology upon the catalysis are much smaller, Fig. 8d. That is, the ionic liquid stabilizes the catalyst under the test conditions in terms of both the structure of the catalyst surface (Fig. 8d) and its catalytic activity (Fig. 7).

3.5. Desulfurization of fuel

As shown above, titanium-supported Ce- and Zr-containing PEO catalysts with and without ionic liquid are active in the oxidation of a number of sulfur-containing compounds present in petroleum raw materials. It was of interest to investigate their catalytic activity in oxidative desulfurization of diesel fuel that is a product of oil refining. Fig. 9 shows the results of testing the catalyst $ZrO_2 + TiO_2 + CeO_x/Ti$ with and without ionic liquid in the reaction of desulfurization of diesel fuel with single and fractional loading of oxidizer (hydrogen peroxide).

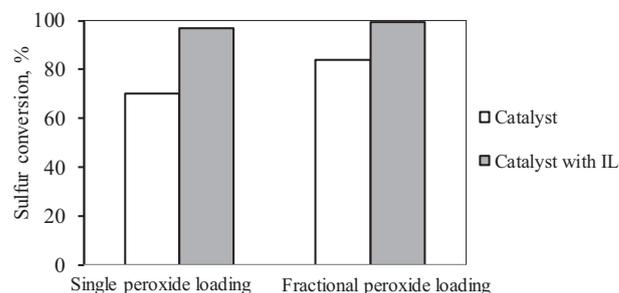


Fig. 9. Desulfurization of fuel: single loading (0.4 mL H_2O_2 , 4 h) and fractional loading (0.2 mL + 0.2 mL H_2O_2 , 4 h) processes, 0.02 g of catalyst, 0.1 g of IL, $60^\circ C$, 10 mL of diesel fuel.

It can be seen that using ionic liquid and fractional peroxide loading allows reducing the sulfur content up to 7 ppm, that meets modern environmental requirements.

4. Conclusion

- Oxide layers $TiO_2 + CeO_x$, $ZrO_2 + TiO_2 + CeO_x$, $ZrO_2 + TiO_2$ were formed on titanium by the plasma electrolytic oxidation in electrolytes containing $Zr(SO_4)_2$ and $Ce_2(SO_4)_3$ with different ratio of Zr^{4+}/Ce^{3+} . Their composition, structure and catalytic activity in oxidative desulfurization of a number of sulfur-containing compounds present in petroleum raw material were studied.
- Oxide layers containing, along with titanium and oxygen, either 18 at.% Zr or 2–3 at.% Ce with variable zirconium content up to 14 at.% were obtained. All oxide systems exhibit catalytic activity in

the thiophene oxidation with hydrogen peroxide. The $ZrO_2 + TiO_2 + CeO_x$ layers with the largest zirconium content, in which composition double oxides $ZrTiO_4$ and Ti_2ZrO_6 are found, demonstrate the maximum catalytic activity. The most active layers are formed in the field of transition from the spark stage of PEO to microarc one.

- $ZrO_2 + TiO_2 + CeO_x/Ti$ catalyst displaying the increased activity was tested in the oxidation of methylphenyl sulfide and dibenzothiophene. The conversion of methylphenyl sulfide occurs very intensive, while dibenzothiophene is not oxidized in the absence of thiophene. So the conjugated oxidation of dibenzothiophene and thiophene was detected. Fractional addition of hydrogen peroxide in the presence of the $ZrO_2 + TiO_2 + CeO_x/Ti$ catalyst makes it possible to increase the conversion of organosulfur compound by 10–50%.
- It was established that the activity of Ce-, Zr-containing PEO catalysts is reduced by 10–15% after 5 cycles of catalytic tests in oxidation of thiophene. This is due to the etching of the surface in the area of pores as a result of producing sulfuric acid during this reaction.
- It has been shown for the first time that the combined use of heterogeneous PEO catalyst and ionic liquid, is 4-(3'-ethylimidazolium)-butanesulfonate, increases the rate of organosulfur compounds oxidation and the stability of the catalyst, protecting it from etching. The conversion of thiophene remained unchanged in five consecutive cycles of catalytic tests.
- The proposed catalyst with ionic liquid has allowed removing sulfur from diesel fuel to the residual content 7 ppm that meets the modern environmental requirements.
- Thus, the combination of Ce-, Zr-containing oxide layers, formed on titanium substrate by PEO technique, and an ionic liquid makes it possible to obtain effective catalysts for the oxidation of various S-containing compounds present in petroleum raw materials and products.

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