Effect of the Composition of Oxide Layers Formed by Plasma Electrolytic Oxidation on the Mechanism of Peroxide Oxidative Desulfurization

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Abstract—The peroxide oxidation of thiophene, thioanisole, and dibenzothiophene in the presence of Ce, Zr, Ce + Zr, W, and W + Zn oxide layers formed by plasma electrolytic oxidation on the titanium surface was studied. The composition of the resulting composites was found to affect the activity and conversion of the organosulfur substrates. It was shown by the radical inhibition method that the composites differed in the mechanism of their catalytic action.

Formation of active composite of a given structure on the surface of solid supports is one of the key problems in creating heterogeneous catalysts. It is important to develop new methods for the synthesis of mono- and bimetallic surface structures possessing both the catalytic activity and high chemical and thermal stability. For this purpose, it is promising to use plasma electrolytic oxidation (PEO). This techniques affords oxide layers of given compositions under electric spark and microarc discharge conditions on the surface of metals and alloys [1, 2]. The PEO systems have no large specific surface area, but due to their wide pores and uniform distribution of active particles, these are effective catalysts for some processes such as CO oxidation [3], oxidative dehydrogenation of cyclohexane to cyclohexene [4], conversion of ethanol into ethylene [5], steam reforming of naphthalene [6], conversion of methane into synthesis gas [7], and oxidation of organosulfur compounds [8, 9].

Over the past two decades, permissible sulfur concentration in motor fuels decreased from 2000 to 10 ppm in view of the existing restrictions aimed at environmental protection, which makes desulfurization basically important in crude oil processing [10]. The conventional hydrotreating technology is ineffective in respect of heterocyclic compounds [11]. Therefore, hydrogen-free processes are used in addition to it, for example, oxidative desulfurization—an approach aimed at increasing the polarity of sulfur-containing substances with their subsequent removal by adsorption or extraction [12]. Individual and mixed oxides containing transition metal ions in high oxidation states are used as the heterogeneous catalysts of this process [8–17].

The difference in the catalyst efficiency may be due to the different mechanisms of oxidative desulfurization, which depend on the catalyst composition [9, 17–19]. As is known, the oxidation of sulfur-containing compounds catalyzed by polyoxometallates (POMs) proceeds via nucleophilic substitution in the V, W, and Mo peroxo complexes formed during the interaction of POMs with H_2O_2 [14, 20–22]. On the other hand, metal (Cu, Fe, Ce, and Ce + Zr) oxides can interact with hydrogen peroxide by the radical mechanism without formation of peroxo complexes [23–28]. The rates of the reactions of hydroxyl radicals with the majority of organic compounds and of their recombination are limited only by the frequency of collisions with other particles; the stationary concentration necessary for detection by electron paramagnetic resonance is thus never achieved. Therefore, to study the radical mechanisms, it is possible to use the inhibition method [29], which is based on the use of substances that selectively react with one type of radical.

The goal of this study was to examine whether the hydroxyl radicals and superoxide ions are involved in the oxidation of organosulfur compounds using PEO composites as an example. The catalysts used involved

Abbreviations: PEO, plasma electrolytic oxidation.

Table 1. Conditions of formation and element and phase compositions of the mono- and bimetallic PEO coatings

Notation for PEO coating	Conditions of formation		Characteristics of composite		
	conditions	electrolyte	phase composition	element composition, at %	structure of layers on Ti
W	$i = 0.2$ A/cm^2 $t = 10$ min	0.1 M Na$_2$WO$_4$ + 0.84 M CH$_3$COOH + 0.01 M NaOH	WO$_3$ TiO$_2$ (anatase) Na$_{0.28}$WO$_3$	15.8 W 7.4 Ti 74.0 O 0.9 Na	WO$_3$/TiO$_2$
W + Zn	$i = 0.2$ A/cm^2 $t = 10$ min	0.1 M Na$_2$WO$_4$ + 0.1 M CH$_3$COOH + 0.04 M Zn(CH$_3$COO)$_2$	WO$_3$ TiO$_2$ (anatase) ZnWO$_4$	5.2 Zn 17.7 W 6.4 Ti 65.6 O 4.6 C	ZnO$_x$, WO$_3$/TiO$_2$
Ce + Zr	$i = 0.05$ A/cm^2 $t = 10$ min	0.012 M Ce$_2$(SO$_4$)$_3$ + 0.03 M Zr(SO$_4$)$_2$	TiO$_2$ (anatase, rutile) ZrTiO$_4$ Ti$_2$ZrO$_6$	3.0 Ce 14.4 Zr 16.7 Ti 65.9 O	CeO$_x$, ZrO$_2$/TiO$_2$
Zr	$i = 0.05$ A/cm^2 $t = 5$ min	0.05 M Zr(SO$_4$)$_2$	ZrO$_2$ (monoclinic + cubic) TiO$_2$ (rutile)	17.8 Zr 13.4 Ti 68.8 O	ZrO$_2$/TiO$_2$
Ce	$i = 0.05$ A/cm^2 $t = 5$ min	0.05 M Ce$_2$(SO$_4$)$_3$	TiO$_2$ (anatase, rutile)	2.4 Ce 30.8 Ti 66.8 O	CeO$_x$/TiO$_2$

the W- and W–Zn-containing PEO composites, which catalyze the reactions occurring by the nucleophilic substitution mechanism, and the Ce- and/or Zr-containing PEO composites, which catalyze the reactions by the radical mechanism without formation of peroxo complexes. The widely used benzoquinone [27, 28, 30, 31] and isopropanol [27, 32–34] were chosen as the radical inhibitors. Thus, the goal of this study is to establish the effect of the composition of bimetallic PEO catalysts on the mechanism of peroxide oxidation of organosulfur compounds (thiophene, dibenzothiophene, and thioanisole). The use of surfaces of different oxide compositions formed by PEO and the study of oxidations with their use may be useful in creating highly efficient catalytic systems.

EXPERIMENTAL

Reagents

For the catalytic tests, we used thiophene (99%), dibenzothiophene (99%), thioanisole (99%), isooctane (99%), hydrogen peroxide (50%), isopropanol (99%), and benzoquinone (99%) (all of Sigma Aldrich). The electrolytes for PEO were prepared from distilled water and the following reagents: Na$_2$WO$_4$ · 2H$_2$O (analytical grade), glacial CH$_3$COOH (reagent grade), NaOH (analytical grade), Zn(CH$_3$COO)$_2$ ·

2H$_2$O (analytical grade), Ce$_2$(SO$_4$)$_3$ (reagent grade), and Zr(SO$_4$)$_2$ · 4H$_2$O (reagent grade). The composition of the electrolytes used and notation for the samples obtained in them are presented in Table 1.

Synthesis of Composites

The synthesis of the composites by PEO was described in detail in our previous works [8, 9, 35]. The oxide layers were formed on VT1-0 titanium alloy samples with dimensions of 20 × 20 × 0.5 mm. The alloy contained (wt %) 99.2–99.7 Ti, ≤0.2 O, and ≤0.1 Si. An insignificant admixture of Fe (≤0.25 wt %) and Al (≤0.7 wt %) was also admissible. The samples were preliminarily subjected to mechanical treatment for removing any burrs. Then they were chemically polished in an acid mixture (HF : HNO$_3$ = 1 : 3) and washed first with running water and then with distilled water; then they were dried in air. The samples were electrochemically processed in a stainless steel bath with a water cooling jacket. The bath case served as a counter electrode. The electrolyte was mixed with a mechanical stirrer. The current source was a computer-controlled thyristor unit TER4-100/460 (Russia), operating in a unipolar mode. The coatings on the titanium samples were obtained within 5–10 min at an effective anode current density of 0.05–

0.2 A/cm^2. The electrolyte temperature was up to 20°C. The PEO-coated samples were washed with distilled water and dried in air. Dense films 5−8 μm thick formed on titanium in all cases.

Determination of the Coating Composition

The phase composition of the coatings was determined from the X-ray diffraction patterns obtained on DRON-2 (Burevestnik, Russia) and Bruker D8 ADVANCE (Bruker, Germany) X-ray diffractometers (CuK_α radiation) by the standard procedure. The compounds were identified automatically using the EVA search program with the PDF-2 database.

The total elemental composition of the PEO coatings (analysis depth ~2−5 μm) was determined on a JXA-8100 electronic X-ray microanalyzer (JEOL, Japan) while scanning at least five separate sites with dimensions of 200 × 300 μm (Table 1). The element concentrations were averaged. Fragments of plates 0.5−1 mm wide were used in the catalytic experiments.

Catalytic Tests

For catalytic tests, a model mixture (10 mL, 1 wt % isooctane solution of thiophene, dibenzothiophene, or thioanisole), catalyst (0.1 g), and oxidizing agent 50% hydrogen peroxide solution (0.4 mL) were placed in a jacketed reactor connected to a thermostat. The contents of the reactor were thoroughly mixed using an overhead mechanical stirrer and thermostatted at 60°C, intermittently taking samples for analysis. Preliminary experiments showed that the initial alloy had no activity: the conversion of the substrates did not exceed 5%. All experiments were performed at a stirrer rate of at least 500 rpm, at which the reagent conversion does not depend on the intensity of mixing.

For reactions with radical inhibitors, isopropanol or benzoquinone was added to the reaction mixture in an equimolar ratio with the substrates (thiophene and thioanisole). Then the reaction was performed by the procedure described above.

Analysis of Reaction Mixtures

The organic phase of the reaction mixture was quantitatively analyzed by gas-liquid chromatography on a Crystal 4000 instrument (Meta-Chrom, Russia) equipped with a Zebron ZB-1 capillary column with a length of 30 m (liquid phase: 100% dimethyl polysiloxane) and a flame ionization detector. The thiophene, dibenzothiophene, and thioanisole contents were determined in the linear programming mode at 90−220°C using the internal standard method.

The organic compounds in the reaction mixture were identified by ^{1}H and ^{13}C NMR spectroscopy (Bruker Avance-600 instrument, 600 MHz, room temperature) and gas chromato-mass spectrometry

(GC/MS) (THERMO TRACE DSQ II instrument, Thermo Fisher Scientific, United States).

RESULTS AND DISCUSSION

To compare the activities of the mono- and bimetallic composites obtained by PEO (Table 1), catalytic tests were performed on peroxide oxidation of thiophene, which is most stable to oxidation [36]. In addition to low reactivity, interest in the oxidation of thiophene was dictated by the wide range of possible products: according to the published data, the process can occur with formation of the sulfate anion, hydrocarbons (e.g., styrene), carboxylic (benzoic, formic) acids, or carbon dioxide (at higher degrees of oxidation) [37−40]. In the present study, thiophene oxidation did not proceed according to ^{1}H and ^{13}C NMR spectroscopy and GC/MS data. It was found by the barium sulfate method that the sulfate anion was the product of the oxidation of sulfur in thiophene. Thus, deep oxidation of thiophene with destruction of the aromatic structure occurred, and this product formed on all the catalysts under study.

The low conversion of thiophene (Fig. 1), even at long reaction times, is the consequence of the side reaction of hydrogen peroxide decomposition. In the oxidation of thiophene, monometallic PEO systems with cerium or zirconium are more active than the tungsten oxide catalyst. On the other hand, the use of the Ce + Zr and W + Zn bimetallic samples increases the conversion by 5−30% for some reasons. The introduction of zinc makes it possible to control the electron density on the tungsten ions and increases the electrophilicity of the active site—the peroxo complex, which is directly involved in the process mechanism
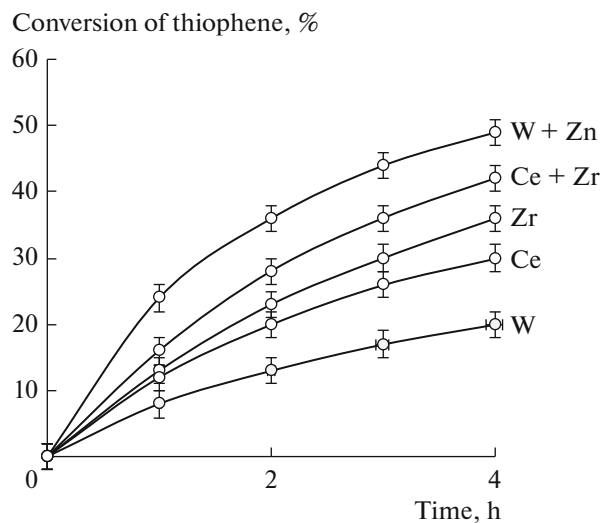
Fig. 1. Kinetic curves of thiophene oxidation on mono- (W, Ce, or Zr) and bimetallic (W + Zn and Ce + Zr) PEO catalysts. Reaction conditions: 60°C, 0.1 g of catalyst, 0.4 mL of H$_2$O$_2$, reaction time 4 h.
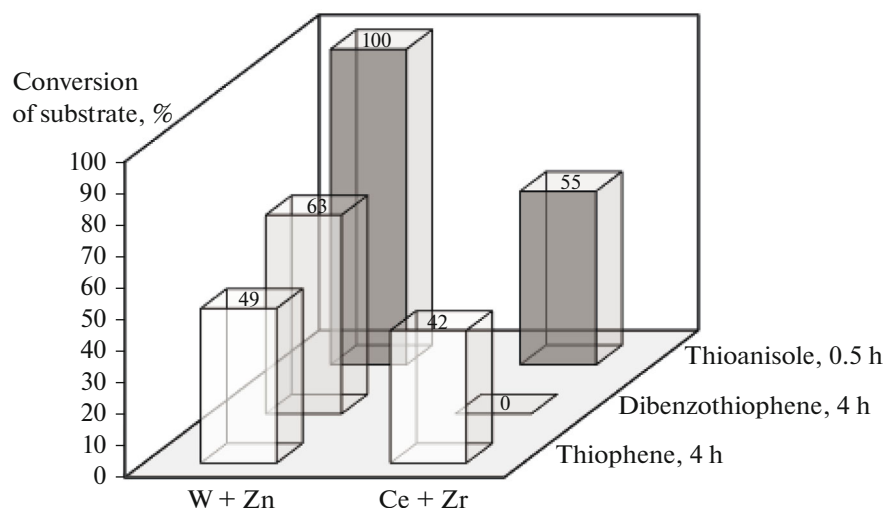
Fig. 2. Conversion of organosulfur substrates on bimetallic PEO catalysts. Reaction conditions: 60°C, 0.1 g of catalyst, 0.4 mL of H₂O₂, reaction time with thioanisole 0.5 h, with thiophene and dibenzothiophene 4 h.

[41]. Modification of cerium-containing oxide composites with zirconium leads to an increase in the mobility of active oxygen [42], which affects the catalytic activity in redox reactions proceeding by the radical mechanism.

For comparison, the maximum conversion of thiophene on the typical oxidation catalysts is usually 30–70% [43–46]. Among the tested samples in our study, the maximum conversion (49%) was achieved using the W + Zn catalyst.

The W + Zn and Ce + Zr catalysts, which have increased activity compared to their monometallic analogs, were tested in the oxidation of thioanisole and dibenzothiophene (Fig. 2). Dibenzothiophene and thioanisole were chosen as model substrates as typical representatives of sulfides and sulfur-containing heterocycles of diesel fuel [47, 48]. According to Fig. 2, the oxidation of thioanisole proceeds much faster than that of thiophene. In the presence of the W + Zn catalyst, the complete conversion of thioanisole occurs in 0.5 h after the start of the reaction; in the presence of the Ce + Zr catalyst, the maximum conversion can be achieved after 1.5 h. In the oxidation of dibenzothiophene, the bimetallic cerium–zirconium catalyst was ineffective. This result was unexpected because, as is known, substituted thiophenes are oxidized much faster than unsubstituted ones [14, 20–22, 49, 50]. On the other hand, for the catalyst based on W and Zn oxides, its activity in respect of organosulfur substrates decreases in the series: thioanisole > dibenzothiophene > thiophene. The nature of this dependence was described in the literature [49, 50]; it was associated with differences in electron density on the sulfur atom. The peroxide oxidation of thioanisole and dibenzothiophene proceeds according to Scheme 1 [14, 20–22].
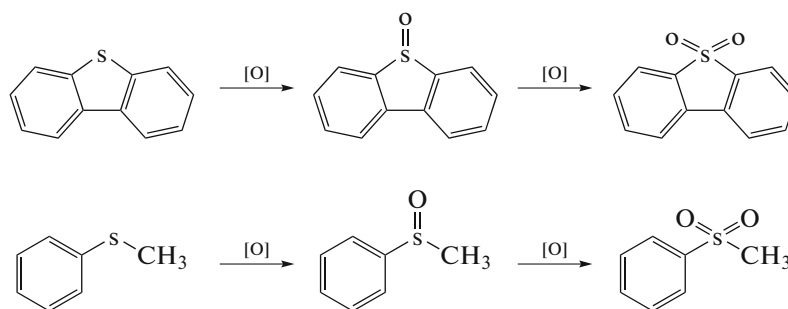
Scheme 1. Oxidation of dibenzothiophene and thioanisole.

It was found, using ¹H and ¹³C NMR spectroscopy, that thioanisole and dibenzothiophene were oxidized to the corresponding sulfones in the reactions on the W + Zn catalyst. In contrast, when the Ce + Zr catalyst was used, thioanisole sulfoxide was found in the reaction mixture in addition to sulfone. Thus, the conversion rates of the intermediates of the reaction on the bimetallic composites under study differ, which is

(a)

Conversion of thioanisole, %

(b)

Conversion of thiophene, %
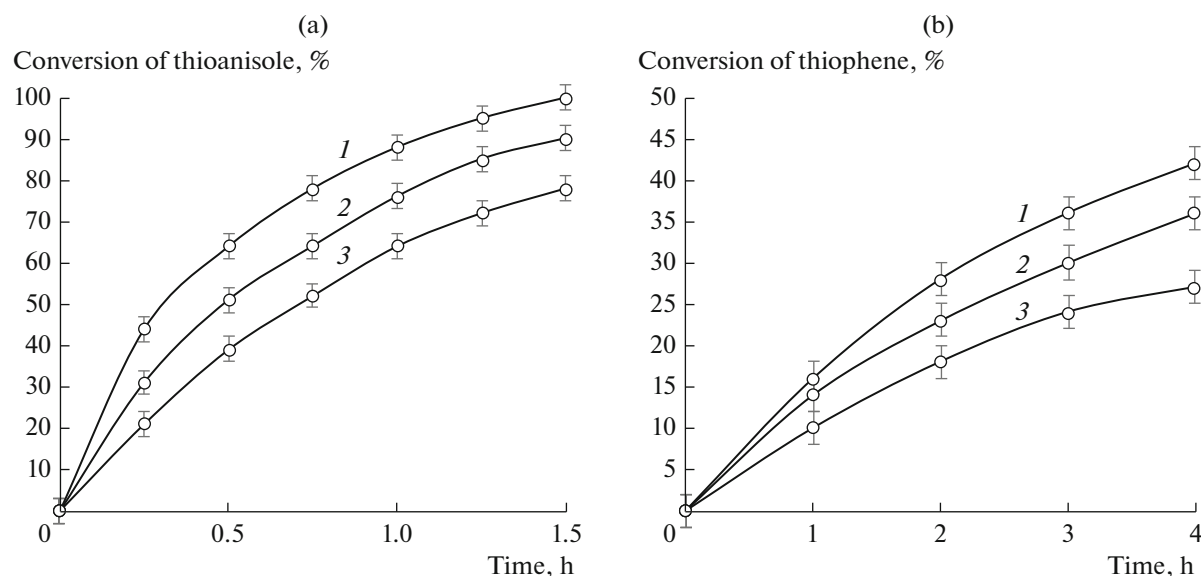
Fig. 3. Effect of radical inhibitors on the oxidation of (a) thioanisole and (b) thiophene: (*1*) no inhibitor; (*2*) isopropanol; and (*3*) benzoquinone. Reaction conditions: 60°C, 0.1 g of the Ce + Zr catalyst, 0.4 mL of H_2O_2, [substrate] : [inhibitor] = 1.

probably due to differences in the mechanism of oxidation.

To understand the nature of catalyst activity with respect to various organosulfur substrates, the oxidation in the presence of radical inhibitors was studied. Isopropanol was used as an acceptor of $OH^{\bullet}$ [27, 32–34], and benzoquinone was used as an acceptor of $O_2^{\bullet-}$ [27, 28, 30, 31].

According to Fig. 3, the addition of radical inhibitors slows down the oxidation of thiophene and thio-

anisole in the presence of the Ce + Zr bimetallic catalyst. Benzoquinone had a more pronounced inhibitory effect, which is consistent with the data of [51]. Based on our results, it can be assumed that the hydroxyl radical and superoxide ion can form as a result of reactions similar to the Fenton−Haber−Weiss reactions. Similar results for catalytic systems based on cerium/zirconium oxides in various processes were described in [23−25], where the processes occurred by the radical mechanism in accordance with Scheme 2.
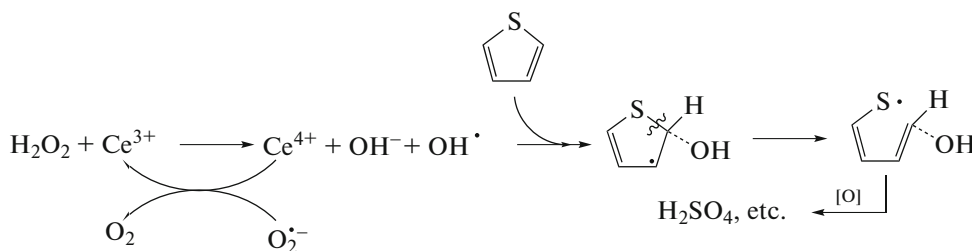

Scheme 2. Oxidation of thiophene by the Fenton−Haber−Weiss mechanism.

According to Scheme 2, the superoxide ion formed in the reaction system participates in the catalytic cycle, reducing Ce^{4+}, and the hydroxyl radical is attached to the thiophene molecule, causing its further transformations. The reaction with thioanisole possibly occurs in a similar way. An alternative way is elimination of a hydrogen atom by both radical particles. According to the calculations performed in the literature, the interaction of radicals with the thiophene molecule during the oxidation proceeds at the carbon atom adjacent to the sulfur atom [52]. In the case of

dibenzothiophene, probably there are steric hindrances for this interaction. This leads to inhibition of the radical process, which was just observed in the case of the Ce + Zr catalyst (Fig. 2).

The addition of benzoquinone and isopropanol to the system with the catalyst based on tungsten and zinc oxides did not lead to a significant change in activity (Fig. 4). Therefore, hydroxyl radicals and superoxide ions are not involved in the oxidation. In this case, the mechanism involves the peroxo complexes resulting from the interactions of hydrogen peroxide and tung-
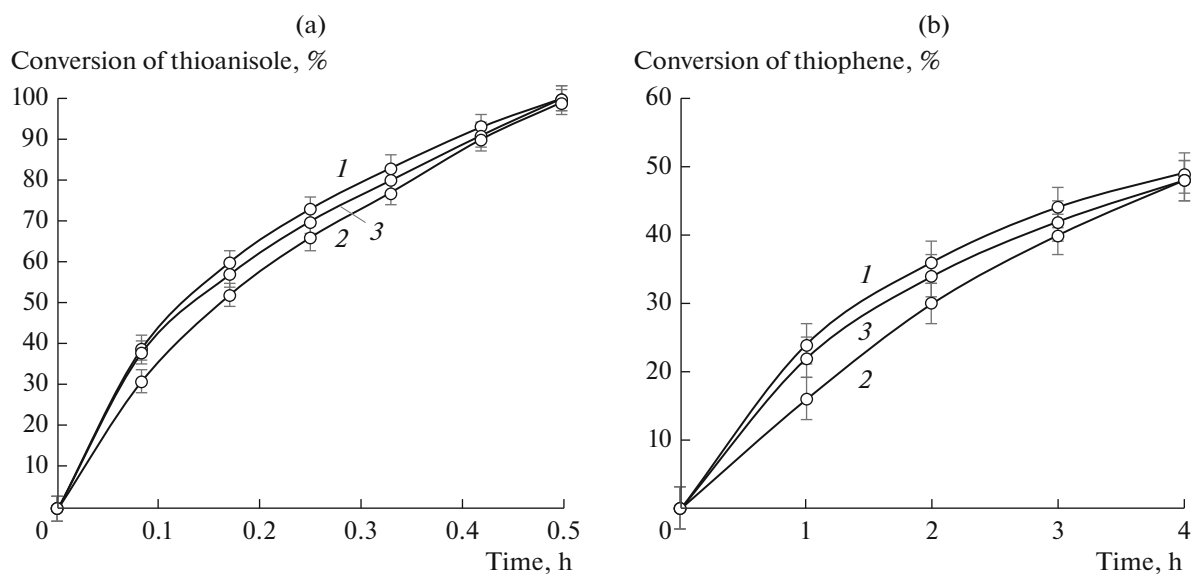
Fig. 4. Effect of radical inhibitors on the oxidation of (a) thioanisole and (b) thiophene: (*1*) no inhibitor; (*2*) isopropanol; and (*3*) benzoquinone. Reaction conditions: 60°C, 0.1 g of the W + Zn catalyst, 0.4 mL of H_2O_2, [substrate] : [inhibitor] = 1.

state derivatives. Then a nucleophilic attack of the organosulfur substrate at the peroxo complex possess-ing high activity occurs (Scheme 3), resulting in the for-mation of mainly sulfone products [14, 20, 21, 26, 41].
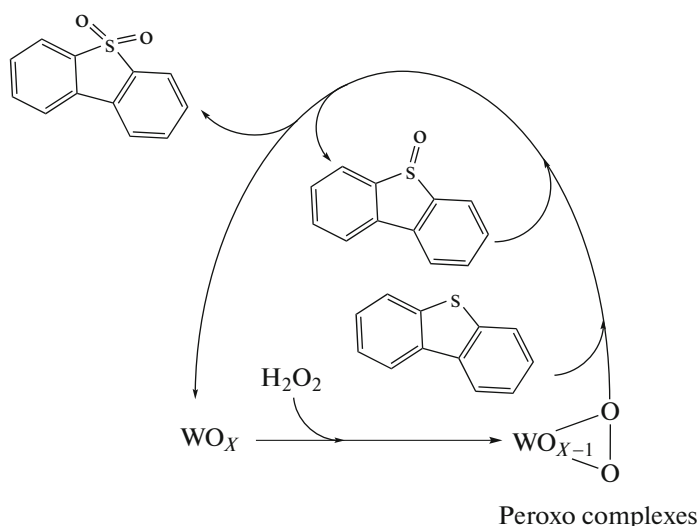
Scheme 3. Formation of peroxo complexes and their participation in the oxidation of dibenzothiophene.

The activity of bimetallic composites with respect to dibenzothiophene can be explained by various mechanisms of catalysis; the radical oxidation involv-ing cerium and zirconium oxides proceeds much more slowly than the nucleophilic substitution via the for-mation of peroxo complexes in the case of zinc–tung-sten systems.

CONCLUSIONS

Thus, the mono- and bimetallic PEO systems are active in the oxidation of organosulfur substrates, and mixed oxide catalysts are more effective than their monometallic analogs. Among the tested samples, the maximum conversion was achieved using the catalyst based on tungsten and zinc oxides. The results of

experiments on radical inhibition with the Ce + Zr catalyst indicate that the reaction involves superoxide ions, i.e., that the radical process occurs. In contrast, the inhibitors do not affect the conversion of thiophene and thioanisole with the W + Zn catalyst, indicating that the mechanism is nucleophilic substitution. The difference in the mechanisms of catalysis leads to a change in the activity series of the substrates.

FUNDING

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