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Heterogeneous Catalysts SILP with Phosphotungstic Acid for Oxidative Desulfurization: Effect of Ionic Liquid

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Abstract—SILP (supporting ionic liquid phase) catalysts for peroxide thiophene oxidation were obtained on silica gel, they included imidazole cations with sulfonic acid group and phosphotungstate anions. The composition of the active phase and the surface structure of the catalysts are characterized by a set of modern physicochemical methods, including mass spectrometry using the SALDI technique. It was found that the organic cation structure affects the stability of heteropolyanions, decomposition processes in the SILP and the catalytic properties of the samples. SILP catalysts are effective in desulfurization of the diesel fraction and provide fuel with an S content of less than 10 ppm.

Keywords: thiophene oxidation, hydrogen peroxide, phosphotungstic heteropolyacid, SILP catalysts, diesel desulfurization

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INTRODUCTION

Heteropolyacids (HPAs) and polyoxometallate compounds based on them are widely used in combination with ionic liquids (ILs) to create catalytically active hybrid materials. Due to their high acidity, oxidation potential, and compatibility with green oxidants, such as oxygen and hydrogen peroxide, these kinds of compositions are effectively used in a number of oxidative processes [1], including the desulfurization of petroleum [2–4].

Desulfurization is an important process in the oil refining industry, which is aimed at obtaining fuel that meets modern environmental standards (total sulfur content of less than 10 ppm) [5]. The problem of petroleum processing is directly related to the removal of heteroatomic compounds that have a negative impact on the environment, corrode equipment, and etch expensive catalysts. The traditional method of fuel purification from sulfur-containing compounds, i.e., hydrodesulfurization (HDS), requires high temperature, pressure, and high hydrogen consumption [6]. The HDS process is effective for removal of thiols, sulfides, and thiophene, but to remove heterocyclic compounds, for example, dibenzothiophene and its alkyl derivatives, it is necessary to use more severe conditions for its implementation, which often leads to an increase in the cost of the final product [7]. Therefore, adsorption [8, 9], extraction [10, 11], and oxidative desulfurization (ODS) [2, 4] are used in addition to hydrodesulfurization. Among the listed methods, ODS is most promising due to mild conditions and the possibility of implementation on the traditional oil refining equipment [12].

In the process of oxidative desulfurization, polar sulfones and sulfoxides are usually formed, which are then removed by adsorption or extraction methods [3, 13]. The catalyst of the process is a key component of any oxidizing system. As a rule, compositions containing oxides in individual and mixed forms, as well as salts of transition metals are used [2, 12, 14, 15]. Particular attention is paid to heterogeneous catalysts based on HPAs and polyoxometallate compounds deposited on porous materials with a large specific surface area, which have a high catalytic activity in the oxidation of organosulfur compounds [2, 4, 16]. However, the low stability of anions due to the strong inter-

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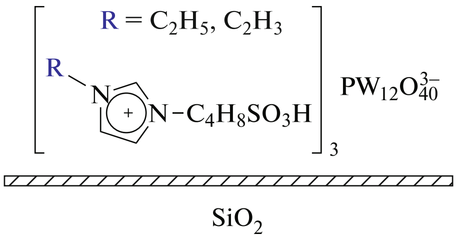
Abbreviations: HPA, heteropolyacid; IL, ionic liquid; ODS, oxidative desulfurization; ZI, Zwitterionic compound; PTA, phosphotungstic heteropolyacid; SALDI, surface-assisted laser desorption/ionization; NMR, nuclear magnetic resonance; TPD NH_3, temperature programmed desorption of ammonia; SEM, scanning electron microscopy; SEI, secondary electron imaging; GLC, gas–liquid chromatography; DMF, dimethylformamide; BJH, Barrett–Joyner–Halenda method; BET, Brunauer–Emmett–Teller method.

action between the heteropolyacid and the surface of mineral carriers is an urgent problem that arises when creating such systems [17–19].

It is known that ILs are widely used as homogeneous desulfurization catalysts [20, 21] and extractants [10, 22]. Nevertheless, their high cost limits the possibility of large-scale use; therefore, a method for their immobilization on the surface was proposed to reduce the consumption of ionic liquids [4, 23, 24]. The SILP catalyst is a layer of an ionic liquid deposited on the surface of porous materials by physical adsorption [25]; in this case, both the IL itself (cation and/or anion) and additional metal-containing components located in the IL layer can exhibit catalytic activity. As a result, the obtained hybrid compositions have the advantages of both homogeneous (high activity and selectivity under mild conditions) and heterogeneous systems (stability and ease of separation of products) [26]. As a result, heterogeneous systems of the SILP type are widely used in a number of catalytic processes, including oxidative desulfurization [4, 24, 27–29].

In our previous study [4], we proposed an efficient method for the synthesis of heterogeneous catalysts based on phosphotungstic or phosphomolybdic acids and 4-(3'-ethylimidazolium)-butanesulfonate. The aim of this work was to establish the effect of the structure of the imidazole cation on the stability of phosphotungstate anions on the surface of silica gel and the activity of the obtained hybrid materials of the SILP type in the oxidation of thiophene with hydrogen peroxide. This compound was chosen as a model substrate because of its highest resistance to oxidation among other sulfur-containing heterocycles [30]. Samples of SILP catalysts were synthesized from imidazolium butanesulfonate with ethyl or vinyl substituents and phosphotungstic acid (Scheme 1). The choice of reagents was based on the published data, according to which vinyl ILs, in comparison with ethyl ILs, are capable of forming intra- and intermolecular hydrogen bonds [31]. We assumed that such an additional interaction would help stabilize both the IL and anions on the silica gel surface. Moreover, we tested, for comparison, a sample synthesized under similar conditions from phosphotungstic acid and silica gel without using organic additives.



Scheme 1. Structure of synthesized SILP composites.

The use of thiophene as a model substrate is of interest for the following two reasons: first, it has a low electron density on the sulfur atom and, consequently, is most difficult to oxidize among the organosulfur compounds of the thiophene series [2, 32]; second, the oxidation of thiophene can lead to the formation of sulfate anion, styrene, carboxylic acids, and carbon dioxide [2, 33–35]. The latter products, especially sulfuric acid, can adversely affect the catalyst and reduce its stability. Therefore, the catalysts were tested under intentionally severe conditions. In addition to the model process, all the heterogeneous catalyst compositions were tested in the process of oxidative desulfurization of petroleum diesel provided by OAO Var'eganneft'.

A side reaction of decomposition of hydrogen peroxide under the action of metal-containing catalysts is among the factors preventing deep oxidation of the substrate. To increase the efficiency of oxidizer use, we applied the approach of fractional loading of hydrogen peroxide. This method is based on the fact that the kinetic reaction order of catalytic decomposition of H_2O_2 depends, according to the published results of studies [36, 37], on its initial concentration, while the order of the main reaction with respect to the oxidant remains unchanged. Therefore, to increase the efficiency of use, hydrogen peroxide must be added in small portions, i.e., its initial concentration should be lowered, thereby slowing down the side decomposition reaction. This approach is well known [38, 39] and has been successfully implemented in our previous studies [4, 40–42].

The performed studies made it possible to carry out a comparative analysis of SILP catalysts and an analogous heterogeneous catalyst sample without ionic liquid, as well as to evaluate the effect of the structure of the imidazole-containing cation on the stability of heteropolyanions, the textural characteristics of the samples, their acidity and activity in oxidation of the model substrate, and the process of ODS of petroleum diesel.

EXPERIMENTAL

Reagents and Auxiliary Materials

We used the following reagents manufactured by Sigma Aldrich: thiophene (99%), hydrogen peroxide (50%), 1,4-butane sultone (99%), 1-ethylimidazole (95%), 1-vinylimidazole (95%), and phosphotungstic acid (99%). Solvents were obtained from commercial sources without further purification. The support for the preparation of catalysts was a Perlkat 97-0 silica gel from BASF.

Preparation of Catalysts

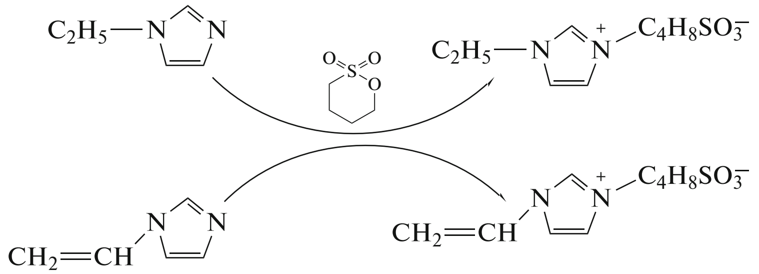
Synthesis of Zwitterionic Compounds

Zwitterionic compounds (ZIs) were synthesized according to the procedure (Scheme 2) previously described in [4]. An imidazole derivative (9.4 g of vinylimidazole or 9.6 g of ethyl imidazole) was dissolved in acetonitrile (100 mL) and mixed with 15 g of

1,4-butane sultone (imidazole : sultone molar ratio 1 : 1.1). The mixture was purged with argon and then boiled under reflux with vigorous stirring for 24 h. The precipitate formed was filtered off, washed thrice with acetone, and dried under a vacuum at 100°C for 16 h. The structure of the obtained zwitterions was confirmed by NMR spectroscopy on a JNM ECX instrument (JEOL, Japan) at a frequency of 400 MHz. The data for two ZI samples are given below:

4-(3'-ethylimidazolium)-butanesulfonate: ^{1}H NMR (400 MHz, $\mathrm{D_2O}$) 1.51 (3H, t, *J* = 7.2 Hz, $\mathrm{NCH_2C}\mathit{H}_3$), 1.83–1.72 (2H, m, $\mathrm{NCH_2CH_2C}\mathit{H}_2\mathrm{{-}CH_2SO_3}$), 2.11–2.03 (2H, m, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2SO_3}$), 2.93 (2H, t, *J* = 7.1 Hz, $\mathrm{NCH_2CH_2CH_2C}\mathit{H}_2\mathrm{SO_3}$), 4.32–4.24 (4H, m, $\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2CH_2SO_3}$), 7.81 (2H, s, $\mathrm{NCHNC}\mathit{H}\mathrm{C}\mathit{H}$–), 9.03 (1H, s, $\mathrm{NC}\mathit{H}\mathrm{NCHCH}$); ^{13}C NMR ($\mathrm{D_2O}$) 14.3 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 23.5 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2SO_3}$), 29.7 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2SO_3}$), 45.7 ($\mathrm{NCH_2CH_2CH_2}\mathit{C}\mathrm{H_2SO_3}$), 51.3 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2CH_2SO_3}$, $\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 51.6 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2CH_2SO_3}$, $\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 124.9 ($\mathrm{NCHN}\mathit{C}\mathrm{H}\mathit{C}\mathrm{H}$), 125.3 ($\mathrm{NCHN}\mathit{C}\mathrm{H}\mathit{C}\mathrm{H}$), 134.6 ($\mathrm{N}\mathit{C}\mathrm{HNCHCH}$);

4-(3'-vinylimidazolium)-butanesulfonate: ^{1}H NMR (400 MHz, $\mathrm{D_2O}$) 1.58–1.67 (2H, m, $\mathrm{NCH_2CH_2C}\mathit{H}_2\mathrm{{-}CH_2SO_3}$), 1.87–1.96 (2H, m, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2CH_2SO_3}$), 2.91 (2H, t, *J* = 7.6 Hz, $\mathrm{NCH_2CH_2CH_2C}\mathit{H}_2\mathrm{SO_3}$), 4.16 (2H, t, *J* = 8.4 Hz, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2CH_2SO_3}$), 5.26–5.30, (1H, dd, N–CH=C*H*H), 5.63–5.69, (1H, dd, N–CH=CH*H*), 6.96–7.04 (1H, dd, N–C*H*=$\mathrm{CH_2}$), 7.47 (1H, m, NCHNC*H*CH), 7.65 (1H, m, NCHNCHC*H*), 8.94 (1H, s, NC*H*NCHCH); ^{13}C NMR ($\mathrm{D_2O}$) 21.0 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2SO_3}$), 28.0 ($\mathrm{NCH_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2CH_2SO_3}$), 49.3 ($\mathrm{NCH_2CH_2CH_2}\mathit{C}\mathrm{H_2SO_3}$), 50.1 ($\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2CH_2SO_3}$), 109.4 (N–CH=$\mathit{C}\mathrm{H_2}$) 119.6 (NCHN*C*H*C*H), 122.9 (NCHN*C*H*C*H), 128.3 (N*C*HNCHCH), 134.5 (N–*C*H=$\mathrm{CH_2}$).



Scheme 2. Synthesis of zwitterionic compounds.

Synthesis of ILs and preparation of SILP samples

To protonate the sulfonate group, 0.7 g of a zwitterionic compound (4-(3'-ethylimidazolium)-butanesulfonate or 4-(3'-vinylimidazolium)-butanesulfonate was added to a concentrated aqueous solution of 2.9 g of phosphotungstic heteropolyacid (PTA) (ZI : PTA molar ratio 3 : 1). The mixture was vigorously stirred for 6 h at room temperature; the obtained ILs in the form of white crystalline substances were dried in air.

A silica gel was kept in an aqueous solution of IL (support : IL mass ratio 10 : 1) at room temperature for 12 h. Next, the solution layer was decanted, and the catalytic samples were dried under a vacuum at 60°C until obtaining a constant weight.

Thus, the samples designated as vin-W and et-W were obtained from 4-(3'-vinylimidazolium)-butanesulfonate and 4-(3'-ethylimidazolium)-butanesulfonate, respectively (Scheme 1).

Synthesis of catalyst without ionic liquid

The catalyst sample designated as W was prepared by depositing a phosphotungstic heteropolyacid on silica gel from an aqueous alcohol solution (silica gel : acid mass ratio 10 : 1) [17]; the process lasted for 12 h, and then the resulting granules were dried under a vacuum as described above.

Characterization of Catalysts

The obtained ionic liquids were identified by IR spectroscopy in KBr pellets on an Infralum FT-801 FT-IR spectrophotometer (SIMEKS, Russia) operated in the range of 4000–400 $\mathrm{cm^{-1}}$.

To determine the composition of heteropolyanions on the surface of the support, the mass spectrometry method with surface-assisted laser desorption/ionization (SALDI) was used. The mass spectra of the samples were recorded in the RN Pep Mix operation mode on an Ultraflex instrument (Bruker, Germany) equipped with a nitrogen laser (wavelength 337 nm, energy 110 μJ) and a time-of-flight mass analyzer. The spectra were recorded using a reflectron operating in the mode of detection of negatively charged ions. Cluster ions were identified from isotopic distribution using the IsoPro simulator software.

Elemental analysis was performed using a CE1106 automatic CHN analyzer (Carlo Erba Instruments, Italy).

Data on the acidic properties of the catalyst composites was obtained by the method of temperature programmed desorption of ammonia (TPD NH_3) on a USGA-101 sorption analyzer (Unisit, Russia). The sample was preheated in an inert atmosphere at 150°C and then cooled to room temperature. Ammonia adsorption was carried out at 60°C for 30 min; NH_3 was diluted with nitrogen in a ratio of 1 : 1. Physically sorbed ammonia was blown off in a flow of dried helium at 100°C for 1 h. Temperature programmed desorption experiments were carried out in the temperature range from 60 to 400°C in a flow of dried helium (flow rate 30 mL/min). The heating rate was 8°C/min.

The acidic properties of aqueous solutions of ZIs were determined using an HI 8314 portable pH meter (Hanna Instruments, Germany).

The surface topography was investigated by scanning electron microscopy (SEM) using a JSM-6000 NeoScope electron microscope (JEOL, Japan) with an EX-230 integrated X-ray analyzer for energy dispersive analysis (EDA) of the particle size distribution. Microscopy studies were performed in the high-vacuum mode with an accelerating voltage of 15 kV. The secondary electron imaging (SEI) mode was used in signal detection.

The tungsten content on the catalyst surface was determined photometrically using pyrocatechol, which forms a stable complex compound with tungstate in the presence of sodium sulfite and sodium hydroxide [43]. Electronic spectra were recorded on a UV-2101PC instrument (Shimadzu, Japan) by measuring the optical density at 350 nm.

Adsorption measurements were carried out on an ASAP 20000N automatic sorption analyzer (Micromeritics, United States). Before measurements, the samples were exposed to vacuum pressure at 150°C for 2 h.

Catalytic Experiments and Analysis of Products

To prepare a model mixture, the calculated amount of thiophene was dissolved in isooctane to obtain a concentration of 1 wt % of the substrate.

Experiments on thiophene oxidation were carried out in a thermostatically controlled glass reactor with a jacket. A model mixture (10 mL), 50% hydrogen peroxide (0.4 mL), and a catalyst (0.1 g) were placed in the reactor at room temperature, and then the mixture was heated to 60°C and stirred for 4 h. For catalysts based on heteropolyacids, the optimal temperature of the process (60°C) has been determined in our previous studies [4, 40, 42]. Under conditions of fractional loading of H_2O_2, the oxidizing agent was added in 0.2-mL increments every two hours. Gas–liquid chromatography (GLC) was used for the quantitative analysis of the organic phase; samples (0.5 μL) were taken with a time interval of 1 h; dodecane served as an internal standard. The chromatographic analysis was performed on a Kristall 2000 instrument (Khromatek, Russia) equipped with a Zebron ZB-1 capillary column with dimensions of 30 m × 0.32 mm × 0.5 μm (Phenomenex, United States). The products of the process were identified using the ^1H and ^{13}C NMR spectroscopy methods. The NMR spectra were recorded on an Avance-600 instrument (Bruker, Germany, 600 MHz) at room temperature. To reuse the catalysts, the reaction mixture was decanted and the catalyst samples were washed with isooctane.

For oxidative desulfurization, diesel fuel produced by OAO Var'eganneft' (20 mL, total sulfur content 1080 ppm), catalyst (0.04 g), and H_2O_2 (0.4 mL, 50%) were thermostated for 4 h in a glass reactor (60°C) under vigorous stirring. The mixture was cooled to room temperature and washed with 5 mL of dimethylformamide (DMF) in a separatory funnel. Dimethylformamide was chosen because it is the most effective extractant for the removal of oxidation products of organosulfur components of diesel fuel [18]. Preliminary experiments on fuel treatment with DMF without oxidation showed that the extraction of sulfur did not exceed 20%. Next, the fuel sample was placed into the reactor, and a fresh portion of the oxidizer (0.4 mL) and the catalyst, which was used in the previous stage and washed with isooctane, were added. The mixture was stirred for another 4 h at 60°C, and the procedure of extraction of oxidation products was repeated. For comparison, the same process was carried out in one step with hydrogen peroxide (0.8 mL). The residual sulfur content was determined on an ASE-2 X-ray fluorescence spectrometer (Burevestnik, Russia) with a measurement error of ± 0.5%.

RESULTS AND DISCUSSION

Characterization of Catalysts

The IR spectra of individual ILs prepared using two ZIs and phosphotungstic acid in KBr pellets are shown in Fig. 1. Assignment of bands and identification of compounds were carried out using the published data [44, 45].

As seen from Fig. 1, both spectra contain bands in the range of 3200–2800 cm^{-1}, which correspond to stretching vibrations of the C–H bonds in the aromatic heterocycle and in the alkyl and vinyl fragments. The bands in the region of 1600–1500 cm^{-1} characterize the stretching vibrations of the imidazolium ring. A relatively strong band at 1650 cm^{-1} in the spectrum of vin-W can correspond to ν(C=C) vibrations in the vinyl fragment. In addition, the bands in the region of 1173–1165 cm^{-1} in the spectra of both samples can be attributed to δ(H–C–C) and δ(H–C–N) bending vibrations in the heterocycles and to stretching vibrations of the S–O and S=O bonds in the sulfo groups (1160–1170 and 1350–1380 cm^{-1}, respectively). The bands of stretching vibrations in heteropolyanion PW_{12} are observed in the range of 1100–800 cm^{-1}. The P–O bond is characterized by absorption bands at 1080 and 500 cm^{-1}, which can be attributed to stretching and bending vibrations, respectively. The bonds of W with the O atoms of the WO_6 group, as well as the W–O–W bridging bonds linking WO_6 octahedra that have a common angle or a common face, are characterized by absorption bands at 975, 895, and 806 cm^{-1}, respectively. Thus, the IR spectroscopy data confirm the presence of ionic liquids, relevant imidazoliosulfonates, and Keggin-type heteropolyanions in the analyzed samples.

Physicochemical parameters of the obtained solid samples and catalyst support are given in Table 1. A substantial decrease in the specific surface area and volume of pores of the support was achieved as a result of the synthesis of SILP catalysts; according to the SEM data, the formation of dense layers of ILs uniformly distributed over the silica gel surface is observed (Fig. 2). On the contrary, modification of the surface with HPA without ILs (catalyst W) does not lead to a noticeable change in the specific surface area and volume of pores. We believe that this can be explained by decomposition of PTA (Table 2) with the formation of low-molecular-weight tungstates and WO_3 and W_2O_6 tungsten oxides, which have molecules with sizes much smaller than the size of heteropolyacid molecules and do not have a substantial effect on the textural characteristics of the support. Nevertheless, the surface of this sample and the surface of et-W have a similar rough loose structure, in contrast to the structure of catalyst vin-W, the SEM images of which clearly show the formation of large IL agglomerates (Figs. 2 and 3). Such a difference in the behavior of ILs on the surface may be due to the tendency of vinyl derivatives to form hydrogen bonds between cations and anions both within and between molecules [31].

According to the study results obtained by mass spectrometry in the SALDI mode, the catalysts differ in the composition of ions, the structure of which changes depending on the type of the IL used (Table 2).

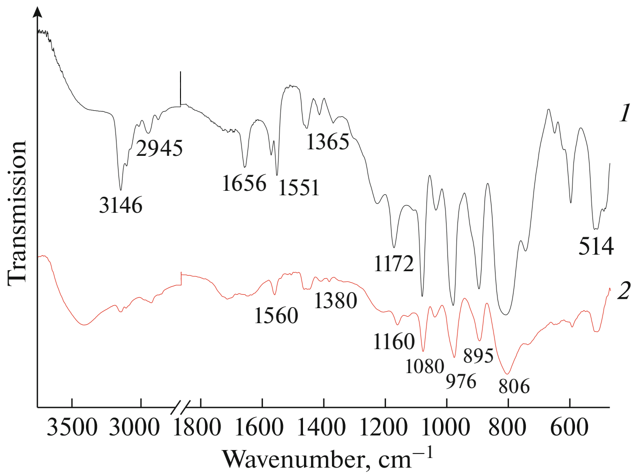


Fig. 1. IR spectra of ILs based on $H_3PW_{12}O_{40}$ with (*1*) 4-(3'-vinylimidazolium)-butanesulfonate and (*2*) 4-(3'-ethylimidazolium)-butanesulfonate.

As a result of the synthesis of catalyst W (without an ionic liquid), the heteropolyacid is completely decomposed with the formation of low-molecular-weight tungsten oxides (Table 2). On the other hand, the mass spectra of SILP samples (et-W and vin-W) contain peaks that correspond to the following fragments of PTA: PWO_6^-, $PW_2O_5^-$, $PW_3O_{12}^-$, $PW_4O_{14}^-$, $PW_5O_{15}^-$, $PW_6O_{17}^-$, $PW_7O_{19}^-$, and $PW_{12}O_{40}^-$. Despite similar procedures used in the syntheses of catalysts (et-W, vin-W, and W), the heteropolyacid structure can be damaged by strong interaction between the heteropolyanions and the surface of the support [4, 19, 46]. In addition, the stability of PTA on silica depends, according to [17, 47], on its loading and a stable phase is formed only at loads above 20 wt %, while the content of the active phase on the catalyst surface in our study did not exceed 10 wt % (Table 1). Sample et-W based on 4-(3'-ethylimidazolium)-butanesulfonate contains a wide range of heteropolyanions with preferential preservation of the structure of the initial phosphotungstic acid precursor. However, HPAs on the surface of sample vin-W are partially decomposed with the formation of high-molecular-weight polytungstates (Table 2). This difference in stability is determined, in our opinion, by the acidity of the medium used in the synthesis of ILs and solid catalysts. According to the measurement results, the acidity of an aqueous solution of 4-(3'-ethylimidazolium)-butanesulfonate is higher than that of 4-(3'-vinylimidazolium)-butanesulfonate, which can be explained by the low solubility of the latter due to the presence of strong intermolecular interactions. Taking into account that the syntheses of ILs were carried out in water and HPA is stable in aqueous solutions only in an acidic medium in a narrow pH range [1, 17, 48], the role of ZIs consists in

Table 1. Textural characteristics of the catalyst support and samples, and the content of tungsten and nitrogen in them according to the elemental analysis data

Samples	S_{sp}, m^2/g	D_{pore}, nm	V_{pore}, cm^3/g	*W*, wt %	*N*, wt %
W	297	9	0.69	9	0
vin-W	150	11	0.39	6.5	0.78
et-W	104	10	0.32	2.8	0.45
Silica gel	300	10	0.75	0	0

Specific surface area S_{sp} was determined by the BET method, and pore diameter D_{pore} and pore volume V_{pore} were determined by the BJH method.

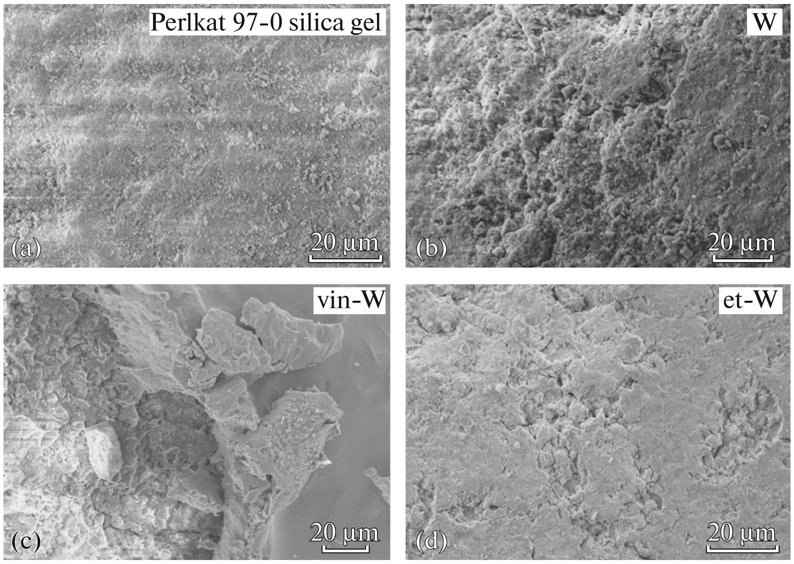


Fig. 2. SEM of (a) Perlkat 97-0 silica gel and catalysts (b) W, (c) vin-W, and (d) et-W.

Table 2. Composition of ions on the surface of the catalysts according to the results of analysis by the SALDI method in the mode of detection of negative ions*

Catalyst	Ions	*m*/*z*	Absolute intensity, arb. u.
W	WO_3	232	86
	W_2O_6	464	54
et-W	PWO_6	311	15
	PW_2O_5	479	62
	PW_3O_{12}	775	102
	PW_4O_{14}	991	46
	PW_5O_{15}	1191	23
	PW_6O_{17}	1407	8
	$PW_{12}O_{40}$	2879	12
vin-W	PWO_6	311	510
	W_2O_6	464	5410
	PW_2O_5	479	870
	W_3O_9	696	5720
	W_4O_{12}	928	5700
	W_5O_{15}	1160	2830
	W_6O_{18}	1392	2440
	PW_6O_{17}	1407	115
	PW_7O_{19}	1623	118
	$PW_{12}O_{40}$	2879	130

* The mass spectra of PTA heteropolyacid are published in our previous study [42].

regulating the acidity in the process of prepration of metal-containing ILs. In addition, HPAs could also decompose at the stage of immobilization of ILs on silica gel; however, the nature of interaction of protonated ILs and metal-containing anions with the surface of silica (Scheme 1) is apparently different from the interaction of free PCA with silica, which leads to an increase in the stability of heteropolyanions in the following sequence of samples: et-W > vin-W > W.

The sample acidity parameters measured by the TPD NH_3 method are given in Table 3.

As a result of the formation of the active phase layer, the total acidity increases; moreover, et-W is distinguished by a significant number of acid sites, which is apparently associated with their availability due to the uniform distribution of the ionic liquid over the surface (according to the SEM data). It also follows from Table 3 that a temperature range up to 190°C can be distinguished for catalysts, in which ammonia desorbs from weak Brønsted acid sites composed, probably, of hydroxylated tungsten oxides. Desorption of NH_3 in the range of 190–250°C can be associated with stronger Brønsted acid sites, which are related to acidic fragments of HPAs or sulfo ($-SO_3H$) groups of ILs. For catalysts W and et-W, the presence of Lewis acid sites (T_{des} above 250°C) can also be noted, which is possibly caused by the partial decomposition of HPA anions during the analysis. The absence of these sites in catalyst vin-W may be due to the island planting of this IL, which leads to a greater stability of metal-containing fragments and their lower accessibility for the adsorbate. As will be shown below, et-W turned out to be the most active catalyst, since acid sites play, as is known, an important role in the activation of both organosulfur compounds and hydrogen peroxide. We believe that it is the strong Brønsted acid sites that make the main contribution to the catalytic properties of this sample.

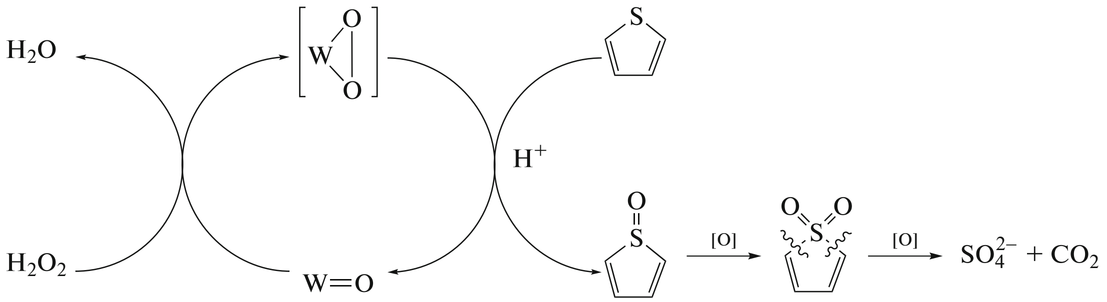
The isotherms of nitrogen adsorption on the catalysts are shown in Fig. 4. The isotherms are of type IV with an H1 hysteresis loop, which indicates a mesoporous surface structure. In addition, a sharp kink at a sufficiently high relative pressure ($P/P_0 > 0.6$) indicates capillary condensation in uniform cylindrical pores.

Catalytic Properties of the Composites

The catalytic properties of the samples were determined in the reactions of peroxide oxidation of thiophene and ODS of petroleum diesel provided by OAO Var'erganneft'.

In Fig. 5 shows the results of testing catalysts W, et-W and vin-W in the oxidation of a model mixture containing 1 wt % thiophene, which is an organosulfur compound that is most difficult to oxidize [2, 32]. An obvious advantage can be seen in et-W, for which the high conversion rate of the substrate correlates with the number of strong Brønsted acid sites and the stability of heteropolyanions.

It is known from the literature about the effect of the Brønsted acidity on the activity of heterogeneous catalysts in the oxidation of organosulfur compounds; in particular, neutralization of acidic protons gives rise to a decrease in the rate of the oxidation reaction until its complete cessation [49]. As was shown in [50], acid groups can also serve as adsorption sites for thiophene and its derivatives. In general, a catalyst or an adsorbent with acidic (electrophilic) characteristics is more reactive with respect to sulfur compounds that are present in petroleum owing to their high nucleophilicity [12], and the addition of acids to the reaction mixture promotes the deeper oxidation of organosulfur compounds in homogeneous and biphasic systems [51, 52]. The model of double activation of thiophene on a catalyst containing a Brønsted ionic liquid and ammonium tungstate was proposed in [53]; the aromaticity of the substrate was violated due to the formation of a hydrogen bond with an IL. In our study, no organic products of thiophene oxidation were found according to the ^{1}H and ^{13}C NMR spectroscopy results and the data of chromatographic analysis. The appearance of sulfate anions in the aqueous phase of the reaction solution was established using the barium-sulfate method. Thus, the aromatic structure of thiophene is destroyed as a result of the process with the formation of SO_4^{2-} and, possibly, CO_2. It is well known from the published data that the oxidation mechanism involves peroxo complexes formed as a result of the reaction of hydrogen peroxide with heteropolyanions [2, 16, 54]. During the ODS process, nucleophilic attack by the organosulfur substrate on the peroxo complex occurs (Scheme 3), giving rise to the formation of unstable sulfoxide and thiophene sulfone, which are then converted into sulfate anions and various oxygenates, such as styrene, benzoic acid, or CO_2 [33–35, 53].



Scheme 3. Formation of peroxo complexes and their role in the mechanism of thiophene oxidation.

Despite the high activity of catalyst et-W (thiophene conversion 45%), the side reaction of hydrogen peroxide decomposition under the action of metal-containing catalysts is a factor that prevents the deep oxidation of the substrate in its presence. The consumption of hydrogen peroxide can be particularly reduced by regulating the acidity of the reaction medium through the number of Brønsted acid sites [55]. The fractional loading of the oxidizing agent is another method for decreasing peroxide decomposition [38, 39]; therefore, H_2O_2 was added in two portions in this study. As seen from Fig. 6, this technique increases the degree of conversion of thiophene, which reaches 58% when the most active sample is tested. In addition, it should be noted that the SILP catalyst retains its activity for five operating cycles (Fig. 6).

Table 3. Acidity of catalysts and silica gel according to data of TPD NH_3

Sample	Amount of desorbed ammonia, μmol NH_3/g catalyst			
	<190°C	190–250°C	>250°C	total
W	47	10	17	74
vin-W	25	31	6	62
et-W	22	53	79	154
Silica gel	7	6	7	20

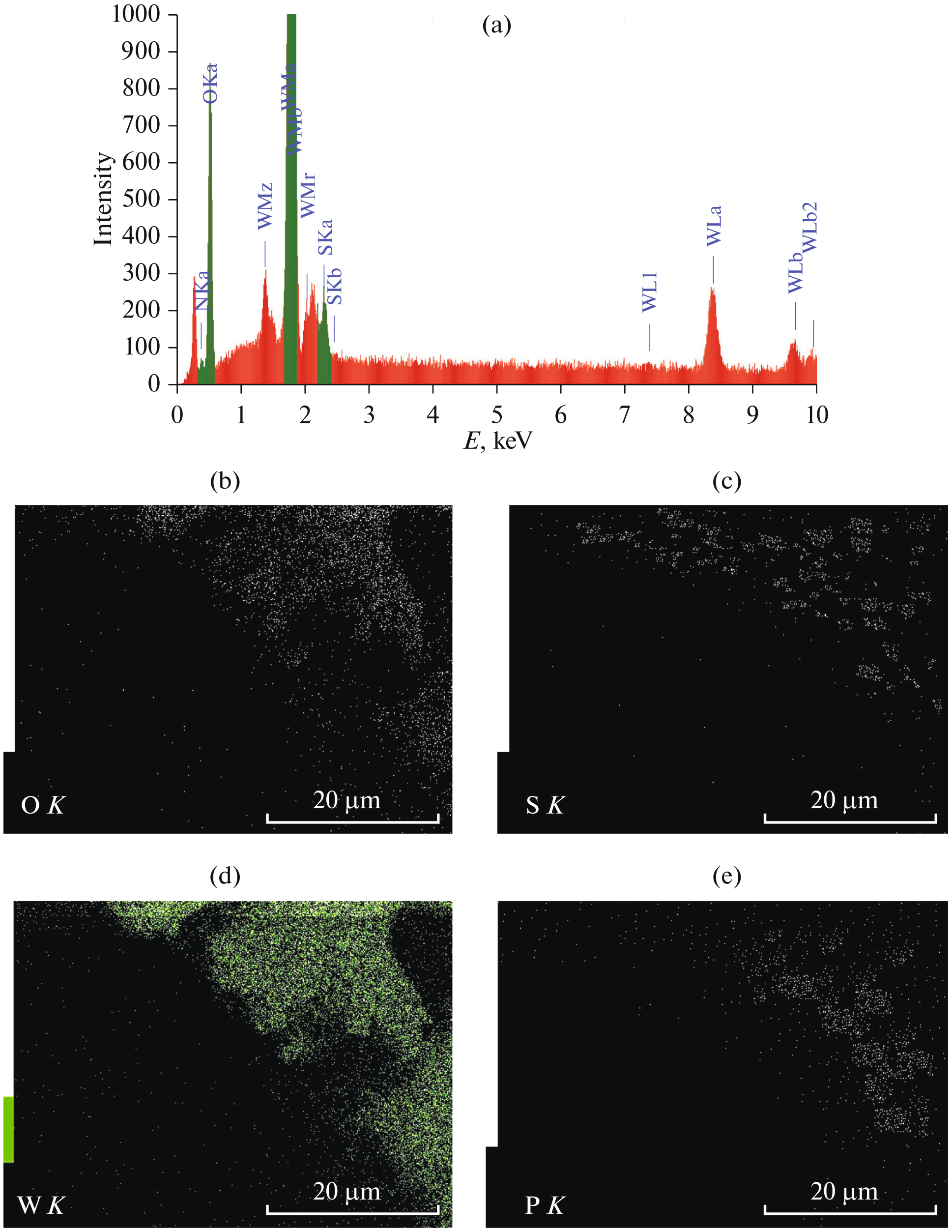


Fig. 3. (a) SEM–EDA spectrum and (b–e) distribution of elements on the surface of catalyst vin-W.

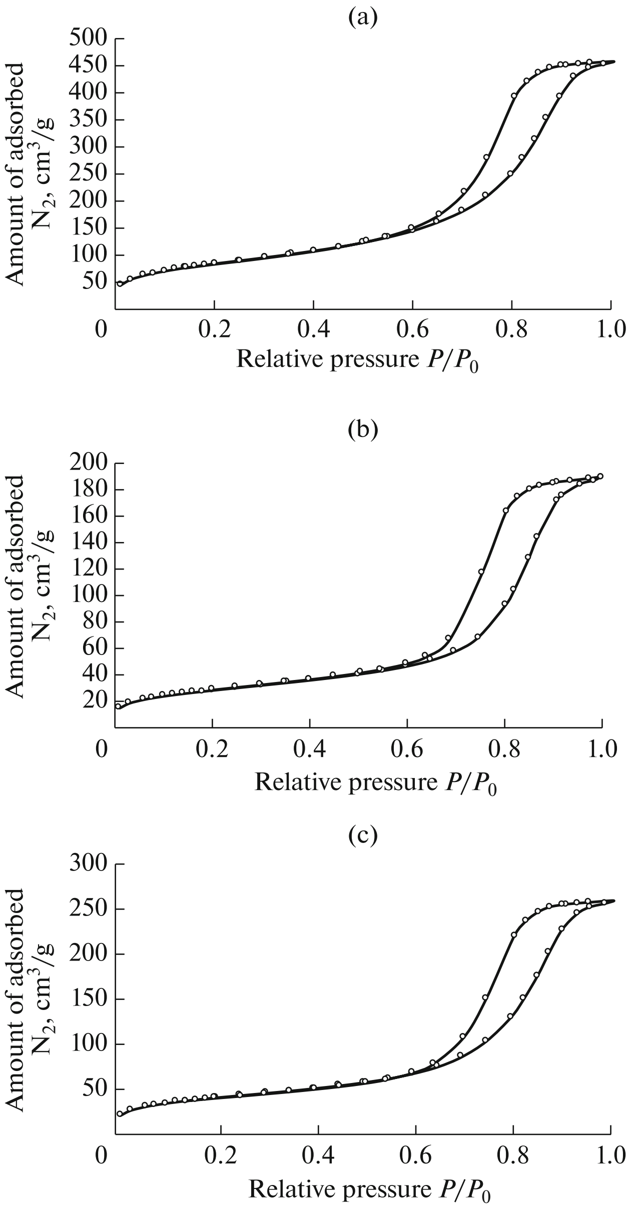


Fig. 4. Nitrogen adsorption–desorption isotherms for the samples of (a) W, (b) et-W, and (c) vin-W.

The results of ODS of petroleum diesel (initial sulfur content 1080 ppm) are shown in Fig. 7. All catalysts showed high efficiency when the fractional loading of hydrogen peroxide was used; however, only SILP samples et-W and vin-W made it possible to obtain diesel fuel with a sulfur content of 3 and 7 ppm, respectively. In comparison with a number of other known methods for conducting ODS [3, 56–60], the proposed method allows one to obtain diesel fuel that meets international environmental standards (total sulfur content less than 10 ppm).

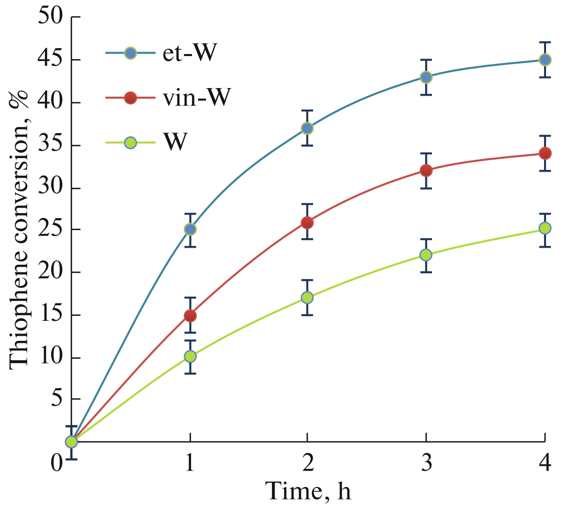


Fig. 5. Curves for the conversion of thiophene. Reaction conditions: 4 h, 60°C, 0.1 g of catalyst, and one-shot addition of 0.4 mL of H_2O_2.

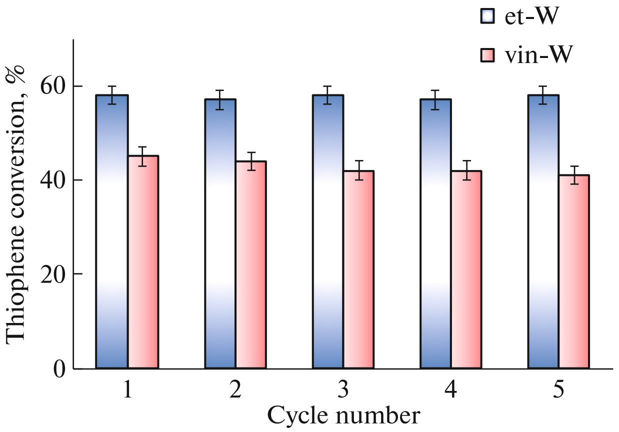


Fig. 6. Stability of the SILP catalysts in the oxidation of thiophene upon fractional addition of hydrogen peroxide (0.2 + 0.2 mL). Reaction conditions: 4 h, 60°C, and 0.1 g of catalyst.

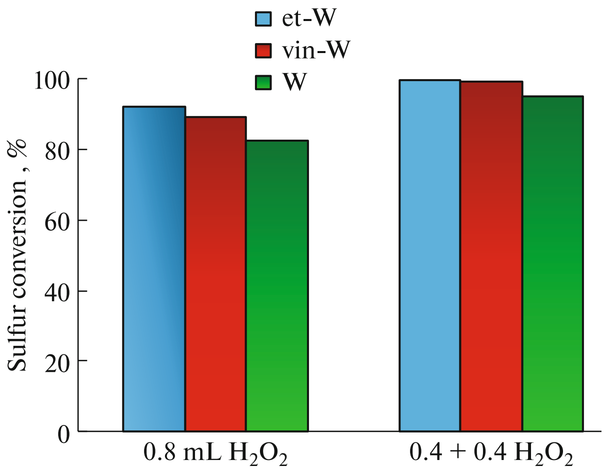


Fig. 7. Oxidative desulfurization of diesel fuel (1080 ppm sulfur) with different ways of hydrogen peroxide loading (0.4 + 0.4 and 0.8 mL). Reaction conditions: 60°C, and 0.04 g of catalyst.

CONCLUSIONS

A method is proposed for the synthesis of heterogeneous SILP catalysts based on ionic liquids protonated with phosphotungstic heteropolyacid, namely, ionic liquids 4-(3'-ethylimidazolium)-butanesulfonate and 4-(3'-vinylimidazolium)-butanesulfonate. It is found that the use of protonated ILs in the active phase of the catalyst increases the stability of PTA heteropolyanions on the surface of silica gel. The most active catalyst is et-W, which shows high stability in thiophene oxidation in five repeated reaction cycles. The fractional loading of the oxidant promotes an increase in the degree of conversion of thiophene and ODS of diesel fuel. Diesel fuel with a sulfur content of less than 10 ppm is obtained using SILP catalysts.

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