=== **ARTICLES** ===

Application of Silica Chemically Modified by Sulfur-Containing Groups to the Separation and Determination of Platinum and Rhenium in Catalysts Based on Aluminum Oxide

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Abstract—Adsorbents based on silica chemically modified by sulfur-containing groups (dithiocarbamate, thiodiazolethiol, mercaptophenyl, and aminobenzothiazole) quantitatively extract (recovery ≥99%) platinum(IV) from solutions ranging from 4 M HCl to pH 6. Under the conditions of the adsorption separation of platinum(IV), rhenium(VII) is not extracted and remains in the solution. The subsequent quantitative (98−99%) adsorption of rhenium(VII) is achieved in the presence of a 1000-fold excess of tin(II) chloride. Adsorption on the surface of adsorbents leads to the formation of platinum(II) complexes with sulfur-containing groups, luminescent at 77 K on irradiation with UV light. The luminescence spectra of surface platinum(II) complexes are located in the region of 550−700 nm. In the adsorption of rhenium(III) in the presence of tin(II) chloride, intensely colored brown complexes of rhenium formed on the surface of adsorbents. Electron paramagnetic resonance showed that, in the surface complexes, rhenium is in the oxidation state 2+. Silicas chemically modified by sulfur-containing groups were used in the development of procedures for the sequential isolation and determination of platinum and rhenium in solutions after the decomposition of aluminum−platinum−rhenium catalysts.

Aluminum−platinum−rhenium catalysts are used in petrochemical industry to produce high-quality gasolines. Depending on the type of feed for reforming, catalysts with different concentrations of platinum and rhenium on aluminum oxide are used [1]. The composition of the catalysts affects their catalytic activity, which necessitates the control of the concentration of platinum and rhenium in them. To determine platinum and rhenium in aluminum oxide-based catalysts, inductively coupled plasma atomic emission spectrometry [2−4], atomic absorption spectrometry [4], X-ray fluorescence analysis [5], neutron activation analysis [6], and coulometry [7] are used.

The photometric and luminescence methods for determining elements are characterized by the simplicity of operations and high sensitivity and selectivity; they do not require complex or expensive equipment. For the photometric determination of platinum and rhenium, a wide range of organic and inorganic reagents was proposed [8].
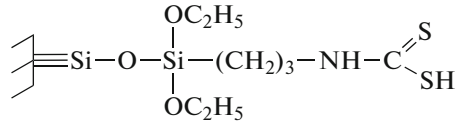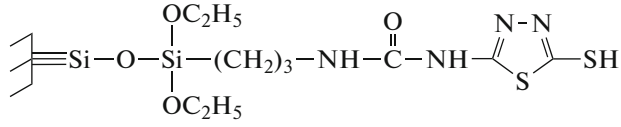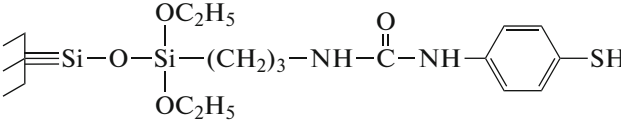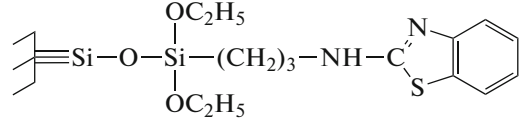
To increase the sensitivity and selectivity of photometric and luminescence determination of elements,

their preliminary separation and preconcentration are used [9]. Among the broad range of adsorbents, silica with chemically grafted sulfur-containing groups, characterized by mechanical strength of particles, relatively high chemical stability, and lack of intrinsic color or luminescence, are the most promising for the preconcentration and determination of platinum and rhenium; they enable the determination of elements directly in the adsorbent phase using luminescence and photometric methods of analysis.

Procedures for the sequential isolation and adsorption−luminescence determination of platinum and adsorption−photometric determination of rhenium in an aluminum−platinum−rhenium catalyst, using silica chemically modified by *N*-allyl-*N*'-propylthiourea, were developed [10].

The goal of this work was to develop procedures for the sequential adsorption separation of platinum(IV) and rhenium(VII) from solutions obtained after the decomposition of aluminum−platinum−rhenium catalysts, using silica chemically modified by sulfur-containing functional groups, and the adsorption−

Table 1. Functional groups, their surface concentration, and the designation of adsorbents

Functional group (designation of adsorbent)	Structure of functional groups	Concentration of immobilized groups, mmol/g
Dithiocarbamate (DTCS)	$\equiv$Si$-$O$-$Si$-$(CH$_2$)$_3$$-NH-C\begin{smallmatrix} S \\ SH \end{smallmatrix}$ (OC$_2$H$_5$, OC$_2$H$_5$)	0.16
N-(1,3,4-thiodiazol-2-thiol)-*N*'-propylurea (TDTS)	$\equiv$Si$-$O$-$Si$-$(CH$_2$)$_3$$-NH-$C(=O)$-NH-$[N-N thiadiazole]$-$SH (OC$_2H_5$, OC$_2H_5$)	0.13
Mercaptophenylpropylurea (MPS)	$\equiv$Si$-$O$-$Si$-$(CH$_2$)$_3$$-NH-$C(=O)$-NH-$[phenyl]$-$SH (OC$_2H_5$, OC$_2H_5$)	0.10
Aminobenzothiazolepropyl (ABTS)	$\equiv$Si$-$O$-$Si$-$(CH$_2$)$_3$$-NH-$C[benzothiazole N,S] (OC$_2H_5$, OC$_2H_5$)	0.10

luminescence determination of platinum and adsorption−photometric determination of rhenium directly in the phase of adsorbents using one type of adsorbent.

EXPERIMENTAL

A stock solution of platinum(IV) (1 g/L) was prepared by dissolving an accurately weighed portion (0.1000 g) of PlAP-1 metal platinum powder (99.9%) in a mixture of HCl and HNO$_3$ (3 : 1) upon heating. After dissolving the metal, the solution was evaporated to wet salts, twice treated with conc. HCl under heating to remove nitrogen oxides, transferred to a 100-mL volumetric flask, and adjusted to the mark with 2 M HCl.

A stock solution of rhenium(VII) (10 g/L) was prepared by dissolving an NH$_4$ReO$_4$ preparation (cp grade) in 2 M HCl. Working solutions with lower rhenium concentrations were prepared by diluting the stock solution.

We also used tin(II) chloride (analytical grade), conc. HCl (high-purity grade), Michler's thioketone (technical grade), and hydrazine hydrochloride (analytical grade).

Silica gel 60 (Merck; particle size, 0.1–0.16 mm; specific surface area, 270 m^2/g; average pore size, ~12 nm) chemically modified by dithiocarbamate (DTC; adsorbent DTC–silica (DTCS)), thiodiazole-thiol (TDTS), mercaptophenyl (MPS), and amino-benzothiazole (ABTS) groups were used as adsorbents.

γ-Aminopropyltriethoxysilane, γ-(triethoxysilane)propyl isocyanate, 4-aminothiophenol, 2-aminothiophenol, and carbon disulfide (Aldrich) and 2-amino-1,3,4-thiadiazole-2-thiol (Fluka) were used in the synthesis of the adsorbents.

DTCS was synthesized by treating aminopropylsilica with carbon disulfide according to the procedure described in [11]; TDTS was prepared according to the procedure [12] by fixing a modifier, previously obtained in an organic solvent by the interaction of γ-(triethoxysilane)propyl isocyanate with 2-amino-1,3,4-thiadiazole-2-thiol, on the silica surface. MPS and ABTS were prepared in a manner similar to the preparation of TDTS, but 4-aminothiophenol and 2-aminothiophenol were used to react with γ-(triethoxysilane)propyl isocyanate, respectively. The characteristics of the adsorbents are presented in Table 1.

The adsorption of platinum(IV) and rhenium(VII) was studied at 25 and 95°C in the range of media of 6 M HCl–pH 6 in static mode in thermostated test tubes, mounted in cells of a WU-4 mechanical vibrator and connected with a UTU-2 thermostat by a rubber hose.

To study the adsorption of platinum(IV), the required amount of platinum(IV) was placed into the tube as a solution in 2 M HCl; conc. HCl or NaOH was added to create the necessary acidity, and the mixture was diluted with water to 10.0 mL. A 0.1-g portion

of adsorbent was added; the tube was capped, heated to 25 or 95°C, and stirred for 1–60 min. The adsorbent was separated from the solution by decantation, transferred to a steel cuvette, and cooled to 77 K; the luminescence intensity of the surface complexes of platinum(II) was measured using a unit assembled on the basis of a MDR-4 monochromator with a cell compartment, allowing measurements at 77 K. An SVD-120A mercury–quartz lamp with an UFS-2 light filter was used as an excitation source.

To study the adsorption of rhenium(VII), the required amount of rhenium was placed into the test tube as a solution in 2 M HCl; conc. HCl or NaOH was added to create the necessary acidity, a 0.2 M tin(II) chloride solution in an amount from 1.0 to 5.0 mL was introduced, and the mixture was diluted with water to 10.0 mL. A 0.1-g portion of adsorbent was added; the tube was capped, heated to 25 or 95°C, and stirred for 1–60 min.

The adsorbent was separated from the solution by decantation and transferred to a fluoroplastic cuvette; diffuse reflectance spectra (DRS) of surface rhenium complexes were recorded in the region 380–720 nm using a Pulsar spectrophotometer. The spectra are given in the coordinates of the Gurevich–Kubelka–Munk function of $F(R) = (1 - R)^2/2R$–wavelength (nm), where R is the diffuse reflectance coefficient.

The amount of adsorbed platinum and rhenium was determined by the difference in their concentrations before and after adsorption. The concentration of platinum and rhenium in solutions before and after adsorption was determined by inductively coupled plasma atomic emission spectrometry (ISP AES) using an Optima 5300DV device (Perkin-Elmer, United States) with a Scott spray chamber made of Rayon plastic with a Game Tip Cross-Flow nebulizer. Operating parameters of the device are selected in accordance with the manufacturer's recommendations for these nebulizer and chamber. In determining the concentration of platinum and rhenium, the emission lines at 265.945 and 197.248 nm, respectively, having the highest intensity, were used.

In the determination of platinum as a mixed-ligand complex of platinum(II) with grafted sulfur-containing groups and Michler's thioketone, the necessary amount of platinum(IV) in the form of a solution in 2 M HCl was introduced into a thermostated test tube with a ground stopper, and 2 M HCl was added to 10.0 mL. A 0.1-g portion of ABTS was added; the tube was stopped, heated to 95°C, and stirred for 1–60 min. The solution was decanted; the adsorbent is washed with 10.0 mL of distilled water. Ten milliliters of a 1×10^{-5}–5×10^{-4} M Michler's thioketone solution in 50% ethanol was added to the adsorbent, and the mixture was stirred for 5 min and washed with 10.0 mL of 50% ethanol to remove the adsorbed Michler's thioketone. The adsorbent was taken out

and placed in a fluoroplastic cuvette; the diffuse reflectance coefficient was measured at 550 nm.

Electron paramagnetic resonance (EPR) spectra were recorded using an Elexsys E580 instrument (Bruker, Germany).

RESULTS AND DISCUSSION

We demonstrated earlier [13, 14] that platinum(IV) was quantitatively extracted (98–99%) from solutions with acidity in the range of 4 M HCl–pH 6 by DTCS at room temperature and by TDTS at 95°C. The time for reaching an adsorption equilibrium under these conditions was 20 min for DTCS and 40 min for TDTS.

The quantitative extraction of platinum(IV) by MPS and ABTS is also achieved in the acidity range of 4 M HCl–pH 6 at 95°C and the time for reaching adsorption equilibrium not exceeding 10 min.

In the process of adsorption, complex platinum compounds are formed on the surface of the adsorbent, which have intense orange-red luminescence at 77 K on irradiation with ultraviolet light. Similar luminescence is characteristic of complex compounds of platinum in the oxidation state 2+ [15], including its complexes with sulfur-containing ligands [16, 17]. It can be concluded that, upon interaction with sulfur-containing groups covalently attached to the surface of silica, platinum(IV) is reduced to platinum(II) to form luminescent complex compounds of platinum(II) on the surface of DTCS, TDTS, and MPS. The spectra of luminescence excitation and luminescence of the surface platinum(II) complexes are broad bands located in the regions 300–500 and 550–750 nm, respectively (Fig. 1). The maxima of the luminescence spectra of the surface platinum(II) complexes with sulfur-containing ligands are located at 600 nm for DTCS, at 620 nm for TDTS, and at 645 nm for MPS.

With increasing concentration of platinum on the surface of DTCS, TDTS, and MPS, luminescence intensity proportionately increased. This effect was used to develop procedures for the low-temperature adsorption–luminescence determination of platinum using DTCS, TDTS, and MPS adsorbents. The detection limits for platinum, calculated by the 3s test and the linearity ranges of calibration dependences are given in Table 2. The relative standard deviations are not higher than those indicated in Table 2 in determining the concentration of platinum in the adsorbent phase, which are ten or more times exceed the detection limits. The lower luminescence intensity of platinum(II) complexes on the surface of DTCS and MPS results in higher detection limits for platinum and a narrower range of its detectable concentrations. The adsorption preconcentration of platinum from 2 M HCl and its subsequent luminescence determination on the surface of TDSD and MPS does not interfered with 10^5-fold amounts of l(III), 10^4-fold amounts of

I_{lum}, rel. unit
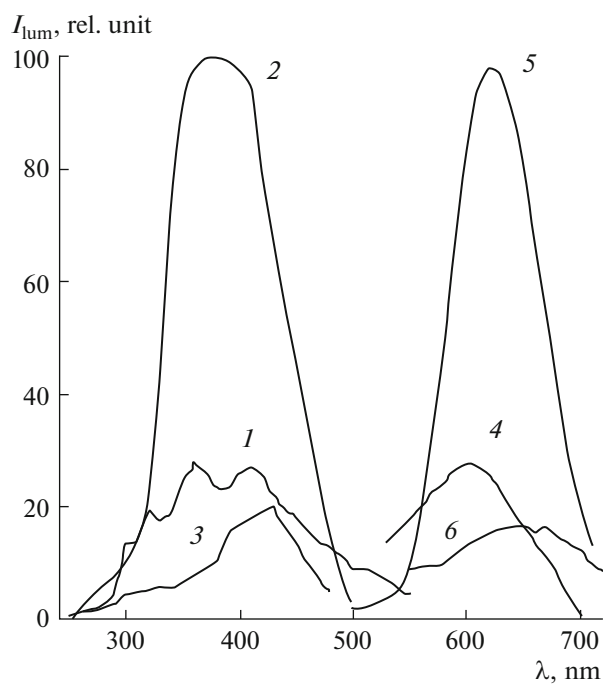
Fig. 1. Spectra of (*1–3*) luminescence excitation and (*4–6*) luminescence of platinum(II) complexes on the surface of (*1* and *4*) DTCS, (*2* and *5*) TDTS, and (*3* and *6*) MPS; c_{Pt} = 10 µg, adsorbent weight, 0.1 g.

Fe(III), Co(II), Ni(II), Zn(II), and Mn(II), and a salt background up to 150 g/L for NaCl.

Platinum(II) complexes formed on the surface of ABTS do not exhibit intense luminescence, and their weak yellow color is not suitable for the adsorption–photometric determination of platinum directly on the surface of the adsorbent. To determine platinum, the formation of mixed-ligand surface complexes of platinum(II), containing immobilized sulfur-containing ligands and Michler's thioketone in the inner coordination sphere, was used. This approach was previously used for the adsorption–photometric determination of palladium and gold [18].

When treating ABTS with adsorbed platinum with Michler's thioketone solutions, the adsorbent is colored red. Diffuse reflection spectra of the surface mixed-ligand complexes of platinum(II) is a broad band with maxima at 480 and 550 nm (Fig. 2). The shape of the spectrum does not depend on the concentration of platinum on the ABTS surface. The maximum intensity of the adsorbent color is achieved when it is treated with 5×10^{-5}–5×10^{-4} M Michler's thioketone solutions, and the color intensity increases with the platinum concentration on the surface, which is used in the development of the adsorption–photometric procedure for determining platinum.

The performance characteristics of the procedure for the adsorption–photometric determination of platinum are presented in Table 2. The adsorption preconcentration of platinum from 2 M HCl and its subsequent adsorption–photometric determination in the form of a mixed-ligand complex is not interfered by 10^5-fold excess of Al(III), 10^4-fold excess of Fe(III), Co(II), Ni(II), Zn(II), and Mn(II), and a salt background up to 150 g/L for NaCl. Gold(III) and palladium(II) interfere with the adsorption preconcentration and the adsorption–photometric determination of platinum in the form of a mixed-ligand complex; however, their absence in catalysts makes it possible to use this adsorbent to determine platinum using Michler's thioketone.

Rhenium(VII) as ReO_4^- is not extracted from 0.5–6 M HCl by of DTCS, TDTS, MPS, or ABTS at room and elevated (95°C) temperatures. In the complexation of rhenium(VII) with ligands of various types, tin(II) chloride is used as a labizing agent [19].

In the presence of a 1000-fold excess of tin(II) chloride, DTCS, TDTS, MPS, and ABTS quantitatively (the extraction ratio is ≥98%) recover rhenium(VII) from 0.5–6 M HCl solutions at room temperature with the time for reaching adsorption equilibrium of 5 (DTCS), 10 (TDTS), 30 (MPS), and 60 min (ABTS). At 95°C, the time for reaching adsorption

Table 2. Performance characteristics of the procedures for the adsorption–luminescence and adsorption–photometric determination of platinum (n = 5, P = 0.95)

Adsorbent	c_{HCl}, M	T, °C	Phase contact time, min	Detection limit*, µg/0.1 g	Analytical range*, µg/0.1 g	RSD, %	Reference
Adsorption–luminescence determination							
DTCS	0.5–2	20	20	0.3	1–30	5	[12]
TDTS	0.5–2	95	40	0.1	0.3–100	6	[13]
MPS	0.5–2	95	20	0.3	1–50	7	Present work
Adsorption–photometric determination as a mixed-ligand complex							
ABTS	0.5–2	95	20	0.1	0.5–25	7	Present work

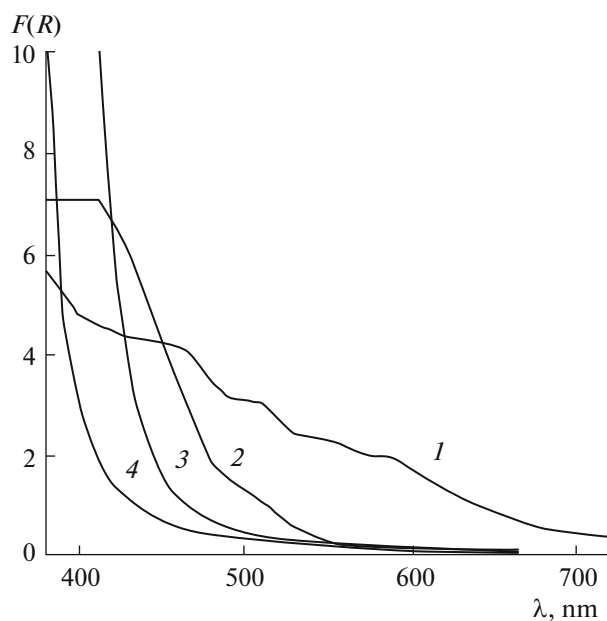* Ten milliliters of solution is used.
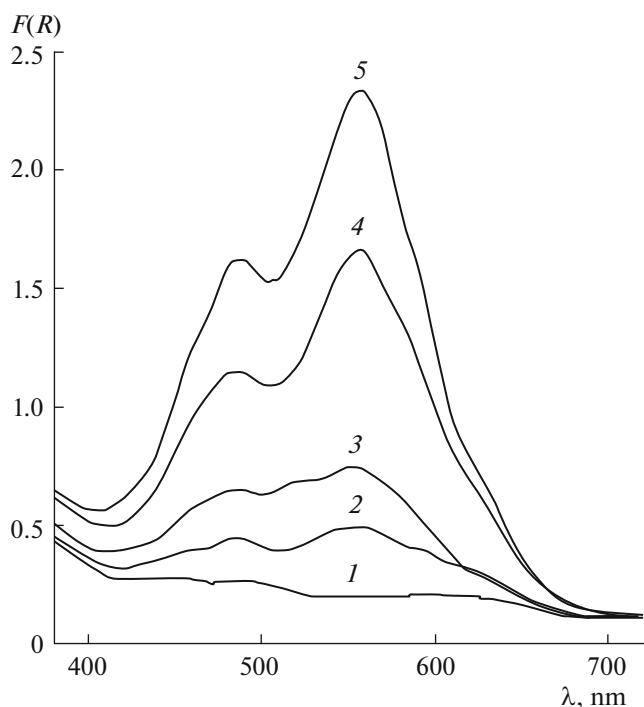
Fig. 2. Diffuse reflectance spectra of a mixed-ligand complex of platinum(II) with aminobenzothiazole groups and Michler's thioketone (Mtk) on the surface of ABTS; c_{Pt}, μg: (*1*) 0, (*2*) 1, (*3*) 2, (*4*) 5, (*5*) 10; $c_{Mtk} = 5 \times 10^{-5}$ M; adsorbent weight, 0.1 g.

Fig. 3. Diffuse reflectance spectra of rhenium(II) complexes on the surface of (*1*) DTCS, (*2*) TDTS, (*3*) MPS, and (*4*) ABTS; $c_{Re} = 10$ μg, adsorbent weight, 0.1 g.

equilibrium for adsorbents MPS and ABTS does not exceed 10 min.

The diffuse reflectance spectra of rhenium complexes on the surface of MPS and ABTS are descending curves located at the boundary of the ultraviolet and visible regions. In the diffuse reflectance spectra of rhenium complexes on the surface of TDTS, a maximum at 420 nm and a shoulder at 510 nm are observed, and on the DTCS surface, there are weakly expressed maxima at 460, 510, and 580 nm (Fig. 3). The maximum intensity of the color of the adsorbents is achieved by using a 1000-fold excess of tin(II) chloride (Fig. 4).

In the interaction of rhenium(VII) with a number of sulfur-containing ligands in the presence of tin(II) chloride, coordination compounds are formed, in which rhenium is in the oxidation state 4+ [19, 20]. To determine the oxidation state of rhenium in complexes on the surface of silica chemically modified by dithiocarbamate and thiodiazolethiol groups, EPR spectra were recorded. In the EPR spectra of rhenium complexes on the surface of DTCS and TDTS, a number of signals are observed (Fig. 5). The EPR spectra of the complex rhenium compounds formed on the surface of adsorbents have distinctive features, depending on the nature of the functional group of the adsorbents. The observed signals of rhenium complexes on the DTCS surface (Fig. 5, spectrum *1*) have a charac-

teristic multiplicity due to the hyperfine structure from the rhenium nuclei, which confirms the presence of paramagnetic complex forms in the low-spin state [20]. The complex nature of the multiplet signals in the EPR spectrum is due to the presence of various rhenium coordination states, which differ in the symmetry of the nearest environment (axial or orthorhombic) and the composition of the ligand environment. Complexes with a hyperfine structure are observed against a background of a broad band with an average g factor of 2.2, the presence of which is caused by the interaction between paramagnetic rhenium ions at a sufficiently high concentration on the surface of the adsorbent.

In the EPR spectra of rhenium complexes on the surface of TDTS (Fig. 5, spectrum *2*), additional intense signals appear without a multiplet structure, which is due to the presence of exchange interactions between the rhenium complexes on the adsorbent surface (cluster formations). The features of the EPR spectra at high rhenium concentrations indicate the presence of additional different forms of rhenium (in the low-spin and high-spin states) also due to mutual association processes. The states of Re^{6+}, Re^{4+}, and Re^{2+} correspond to the configurations of d^1, d^3, and d^5, respectively; in addition, it is known that the existence of low-spin states is characteristic of $5d$ shells [20]. Therefore, Re^{3+} and Re^{5+} are usually in a diamagnetic state and do not appear in the EPR spectra. The d^1 electronic configuration is characterized by the presence of three values of the g factor of <2.00; for the low-spin state of the d^3 configuration, there are at least
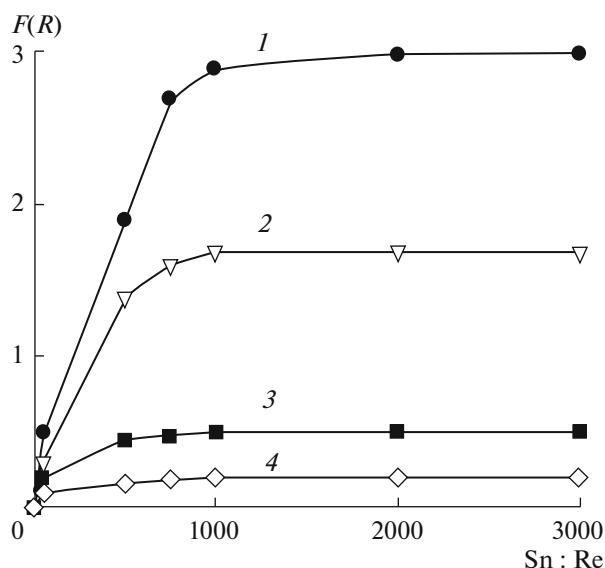
Fig. 4. Dependence of $F(R)$ of rhenium(II) complexes on the surface of (*1*) DTCS, (*2*) TDTS, (*3*) MPS, and (*4*) ABTS on the tin(II) chloride concentration; $c_{Pt} = 5$ μg, adsorbent weight, 0.1 g; λ, nm: (*1* and *4*) 460 and (*2* and *3*) 420.

Fig. 5. EPR spectra of rhenium complexes on the surface of (*1*) DTCS and (*2*) TDTS; c_{Re}, μg: (*1*) 250 and (*2*) 1000; adsorbent weight, 0.1 g; 77 K.
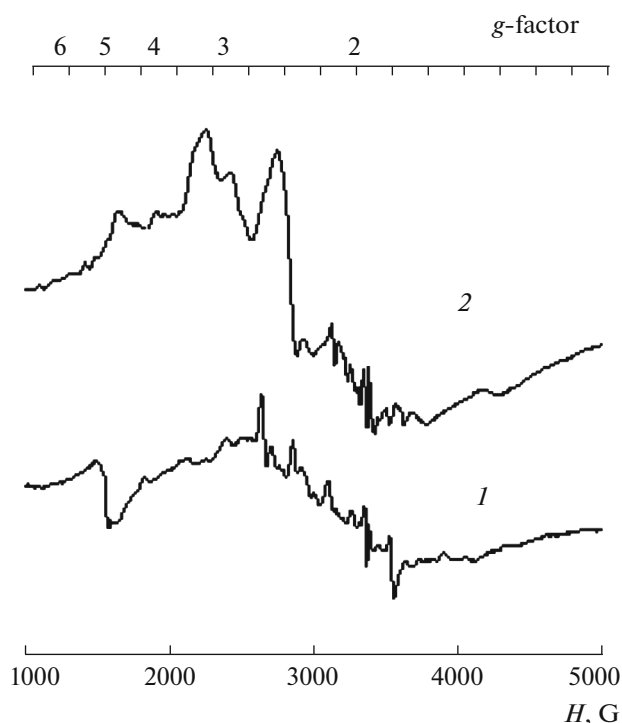
two values of the g factor of three that are <2.00; and for the low-spin state of the d^5 configuration, usually two values of the g factor are >2.00. In the EPR spectra (Fig. 5), two values of the g factor of the observed signals from rhenium complexes exceed 2.00.

The obtained EPR parameters (the values of the g factors and the hyperfine structure constants with allowance for quadrupole contributions) indicate the preferential formation of low-spin complex forms corresponding to the electronic configuration of rhenium of d^5 and the presence of rhenium in the composition of surface complexes in the oxidation state 2+.

To determine the role of tin(II) chloride in the interaction of rhenium(VII) with sulfur-containing groups immobilized on the surface of silica (for example, DTCS and TDTS), hydrazine, which reduces

Table 3. Extraction rate (%) of rhenium(VII) by DTCS and TDTS, using hydrazine and tin(II) chloride as reducing agents

Adsorption conditions	DTCS		TDTS	
	25°C	95°C	25°C	95°C
In the presence of 1 M hydrazine	0	60	0	0
After reduction of rhenium(VII) with 1 M hydrazine	0	60	0	0
After reduction of rhenium(VII) with 1 M hydrazine with addition of tin(II) chloride	60	60	25	25

rhenium(VII) to rhenium(IV), was used as a reducing agent [19]. Adsorption of rhenium(VII) by DTCS and TDTS was carried out in three ways:

—directly in the presence of a 1 M hydrazine solution;

—after preliminary reduction of rhenium(VII) to rhenium(IV) with a 1 M hydrazine solution, where the spectrophotometric method and comparison with the published data were used to control the process [19];

—by adding a 1000-fold excess of tin(II) chloride to the solution after reduction of rhenium(VII) to rhenium(IV) with a 1 M hydrazine solution.

The use of hydrazine as a reducing agent does not lead to a significant extraction of rhenium(VII) by DTCS or TDTS at room temperature (Table 3). At 95°C and the phase contact time of 60 min, the recovery of rhenium(VII) by DTCS is 60%, but the adsorbent remains colorless, and its diffuse reflectance spectra is identical to that of the initial adsorbent (Fig. 6).

The addition of a 1000-fold excess of tin(II) chloride to the solution containing rhenium(IV) after the reduction of rhenium(VII) with hydrazine leads to an increase in the recovery of rhenium at room temperature and the phase contact time of 60 min with DTCS up to 60%, and for TDTS, up to 25% (Table 3). Increasing the temperature to 95°C does not lead to an increase in the recovery of rhenium. Rhenium(IV)
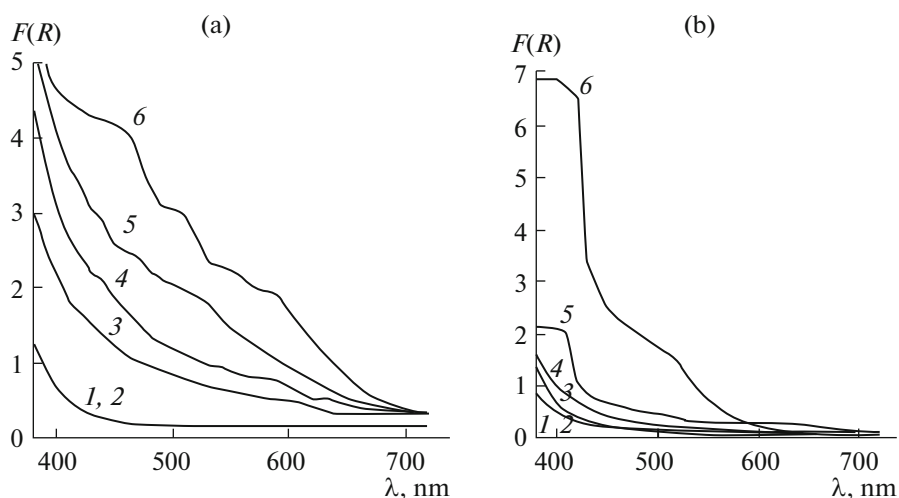
Fig. 6. Diffuse reflectance spectra of (a) DTCS and (b) TDTS (*1*) after adsorption of rhenium(VII) in the presence of hydrazine, (*2* and *3*) after reduction of rhenium(VII) with hydrazine, (*4* and *5*), after reduction of rhenium(VII) with hydrazine with addition of tin(II) chloride, and (*6*) in the presence of tin(II) chloride (6); $c_{Re} = 1$ μg/mL; $V = 10$ mL; adsorbent weight, 0.1 g; phase contact time, 60 min; T,°C: (*2, 4, 6*) 25 and (*1, 3, 5*) 95; 1 M hydrazine; 0.04 M SnCl$_2$.

complexes formed on the surface of DTCS and TDTS are colored brown. In this case, the color of the adsorbents and their diffuse reflectance spectra are similar to those obtained after the adsorption of rhenium(VII) in the presence of tin(II) chloride (Figs. 6a and 6b). The lower color intensity of DTCS and TDTC in this case is associated with a low recovery of rhenium(VII).

The formation of intensely colored surface complexes of rhenium was used to develop a procedure for its adsorption–photometric determination directly in the adsorbent phase using diffuse reflectance spectroscopy. The performance characteristics of the developed procedures are presented in Table 4.

The possibility of successive adsorption isolation of platinum(IV) and rhenium(VII) and the subsequent determination of platinum and rhenium directly in the phase of the adsorbent was used in their determination in samples of aluminum–platinum–rhenium catalysts.

Procedure for determining platinum and rhenium in catalyst. Weighed portions (0.5000 g) of catalyst samples were dissolved in 6 M HCl in a quartz autoclave in the presence of manganese dioxide according to the procedure described in [10]. The autoclave content was transferred to a 100-mL volumetric flask and diluted up to the mark with distilled water.

For the adsorption isolation of platinum(IV), 2.0-mL portions of the resulting solution are placed in four test tubes with ground stoppers and adjusted to a volume of 10.0 mL with 2 M HCl; 0.1-g weighed portions of DTCS, TDTS, MPS, and ABTS are added to the solutions one to each test tube, and the test tubes are tightly closed with stoppers. The contents of the tubes are stirred for 20 min at room temperature when DTCS is used, and in the case of TDTS, MPS, and ABTS, adsorption is carried out at 95°C for 40 min (TDTS) or 20 min (MPS and ABTS). Adsorbents DTCS, TDTS, and MPS are separated from the solutions by decantation, washed with 10.0 mL of 2 M

Table 4. Performance characteristics of the procedures for the adsorption–photometric determination of rhenium ($n = 5$, $P = 0.95$)

Adsorbent	c_{HCl}, M	Phase contact time, min		Detection limit*, μg/0.1 g	Analytical range*, μg/0.1 g	RSD**, %
		25°C	95°C			
DTCS	0.5–2	5	5	0.1	0.4–30	5
TDTS	0.5–2	10	10	0.1	0.4–100	6
MPS	0.5–2	30	10	0.3	1–50	7
ABTS	0.5–2	50	10	0.3	1–100	8

 * Ten milliliters of solution is used.

** The relative standard deviations in the determination of the concentration of rhenium in the adsorbent phase, which are ten or more times exceed the detection limit.

Table 5. Determination of the concentration (wt %) of platinum and rhenium in RB-33U, RB-44U, and KR-110 catalysts based on aluminum oxide ($n = 5$, $P = 0.95$)

Adsorbent	RB-33U		RP-44U		KR-110	
	Pt	Re	Pt	Re	Pt	Re
Adsorption−photometric method						
DTCS	0.29 ± 0.01	0.29 ± 0.01	0.25 ± 0.01	0.38 ± 0.01	0.35 ± 0.01	0.17 ± 0.01
TDTS	0.30 ± 0.01	0.30 ± 0.01	0.25 ± 0.01	0.39 ± 0.01	0.33 ± 0.01	0.18 ± 0.01
MPS	0.29 ± 0.01	0.30 ± 0.01	0.24 ± 0.01	0.38 ± 0.01	0.34 ± 0.01	0.18 ± 0.01
ABTS	0.30 ± 0.01	0.31 ± 0.01	0.24 ± 0.01	0.39 ± 0.01	0.35 ± 0.01	0.18 ± 0.01
ICP AES						
	0.30 ± 0.01	0.30 ± 0.01	0.25 ± 0.01	0.39 ± 0.01	0.34 ± 0.01	0.18 ± 0.01

HCl, placed in steel cuvettes, and cooled to 77 K; their luminescence intensity is measured at 600 nm (DTCS), 620 nm (TDTS), and 645 nm (MPS). The concentration of platinum is determined by the calibration curve obtained under similar conditions.

After adsorption of platinum(IV), ABTS is separated from the solution by decantation and washed with 10.0 mL of distilled water. Ten milliliters of a 5×10^{-5} M Michler's thioketone solution in 50% ethanol is added to the adsorbent, and the mixture is stirred for 5 min. The solution is then decanted; the adsorbent is washed with 10.0 mL of 50% ethanol to remove the adsorbed Michler's thioketone; the adsorbent is placed in a fluoroplastic cuvette, and its diffuse reflection coefficient is measured at 550 nm. The concentration of platinum is determined by the calibration curve obtained under similar conditions.

For the adsorption separation of rhenium(VII), aliquot portions (8.0 mL) of solutions after the adsorption separation of platinum(IV) are transferred to four test tubes with ground stoppers; 2.0 mL of a 0.2 M tin(II) chloride solution in 2 M HCl are added; and 0.1-g weighed portions of DTCS, TDTS, MPS, and ABTS are placed one to each test tube. The tubes are tightly closed with stoppers, heated to 95°C, and shaken for 10 min. The adsorbents are separated from solution by decantation and transferred to a fluoroplastic cuvettes; excess water is removed with filter paper. The diffuse reflectance of wet adsorbents is measured at 420 nm (TDTS and MPS) and 460 nm (DTCS and ABTS). The concentration of rhenium is determined by the calibration curves obtained under similar conditions.

The results of the determination of platinum and rhenium in the catalysts are presented in Table 5. The precision of the results is confirmed by ICP AES.

The developed procedures enable the sequential isolation of platinum(IV) and rhenium(VII) from one sample of a solution, using one type of adsorbent, and the determination of them directly on the adsorbent surface with good precision and reproducibility. The use of TDTS decreases more than twofold the detec-

tion limit of platinum and expanded twice the analytical range compared to the silica-based adsorbent chemically modified by *N*-allyl-*N*'-propylthiourea (ATMS) [10]. The use of DTCS and TDCS adsorbents makes it possible to lower fourfold the detection limits of rhenium in comparison with ATMS at a comparable analytical range. The achievable detection limits of platinum and rhenium are comparable to the detection limits obtained by flame ionization atomic absorption spectrometry and ICP AES.

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