ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 4, pp. 575–580. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © D.A. de Vekki, E.A. Kuchaev, M.V. Afonin, S.A. Simanova, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 4, pp. 594–599.

Catalytic Properties of Platinum(II) Immobilized on Polymethylene Sulfide in the Hydrosilylation Reaction

D. A. de Vekki, E. A. Kuchaev, M. V. Afonin, and S. A. Simanova

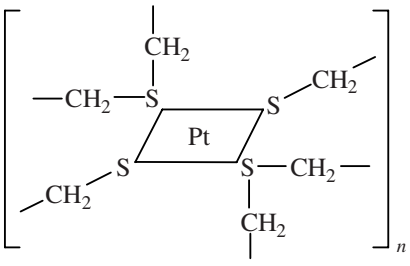
St. Petersburg State Institute of Technology,
Moskovskii pr. 26, St. Petersburg, 190031 Russia

Abstract—Hydrosilylation of 1,1,3,3-tetramethyl-1,3-divinyldisiloxane with 1,1,3,3-tetramethyldisiloxane in the presence of platinum(II) immobilized on polymethylene sulfide is studied.

DOI: 10.1134/S1070363208040105

Catalytic properties of complexes with sulfur-containing ligands, that is organic sulfides and sulfoxides, still attract much interest. Among these compounds, effective homogenous [1–9] and heterogenous [10] hydrosilylation catalysts have been found. Sulfur in such catalysts acts as the coordinating atom of a neutral ligand. At the same time, the catalytic activity of coordination compounds simultaneously containing a sulfide and an alkanethiolate (RS^- type anion) ligands have never been studied.

In this connection we have studied hydrosilylation in the presence of platinum(II) immobilized on polymethylene sulfide (complex **A**). The choice of polymethylene sulfide was motivated by the uniform distribution of its sulfur atoms over the sorbent matrix (sulfur content ~69 wt %), which endows it with properties of a macroligand and, in addition, prevents dissolution of the immobilized catalyst in the reaction mixture.



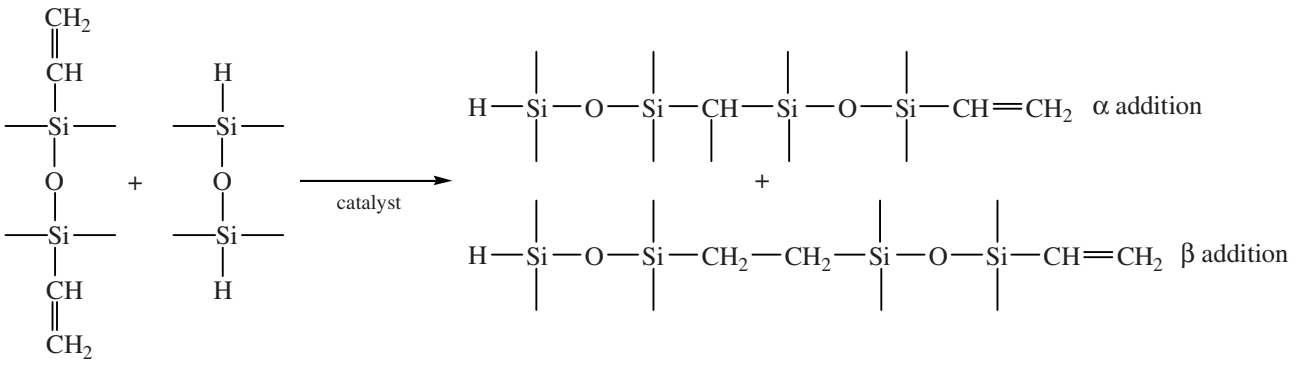
A

The catalytic activity was explored in one of thoroughly studied reactions: hydrosilylation of 1,1,3,3-tetramethyl-1,3-divinyldisiloxane [$(VinMe_2Si)_2O$] with 1,1,3,3-tetramethyldisiloxane [$(HMe_2Si)_2O$] [6, 9, 11].

Chemisorption of platimum on polymethylene sulfide was carried out by a standard procedure [12], starting from K_2PtCl_6 or K_2PtCl_4. In both cases, immobilization is accompanied by cleavage of all Pt–Cl bonds (the difference IR spectrum contains no Pt–Cl stretching vibration bands and the XPS spectrum contains no Cl2$p_{3/2}$ signals) and formation of new Pt–S bonds. The XPS spectrum shows new Pt4$f_{7/2}$ (E_b 73.4 eV), thiolate S2$p_{3/2}$ [E_b(S2$p_{3/2}$) 162.8 eV], coordinated sulfide S2$p_{3/2}$ [E_b(S2$p_{3/2}$) 165.1 eV], and C [E_b(C1s) 287.2 eV] signals in a 13.5 : 3.4 : 1.5 : 9.6 ratio (at %). Uncoordinated S2$p_{3/2}$ [E_b(S2$p_{3/2}$) 164.0 eV] and polymethylene sulfide C [E_b(C1s) 285.9 eV] signals are also observed. The XPS data well agree with the electron binding energies of Pt^{2+} (4$f_{1/2}$) and ionic and coordinated sulfur (2$p_{3/2}$), reported in [13, 14]. The IR spectrum of the resulting compound contains strong bands at 705, 735, 745, 1013, 1178, and 1367 cm^{-1} characteristic of uncoordinated sulfur atoms and polymethylene sulfide CH_2 group. Taken together, the above evidence suggests that it is compound **A** that is formed by chemisorption of potassium platinates.

Hydrosilylation of $(VinMe_2Si)_2O$ with a triple molar excess of $(HMe_2Si)_2O$ in the presence of complex **A**, as well as other platinum catalysts [6, 11], initially provides α- and β-adducts of $(HMe_2Si)_2O$ at one of the vinyl groups of $(VinMe_2Si)_2O$, the β-adduct (CH_2, δ 0.41 ppm) prevailing.

According to GLC data, the monoadducts undergo fast transformation to α,α-, α,β-, and β,β-adducts, the



latter prevailing. In their turn, these compounds enter further hydrosilylation. Therewith, gradual increase of the viscosity of the reaction mix-ture and of the molecular weight of carbosiloxanes obtained takes place. For example, after 5 h reaction at 50°C the molecular weight of the products reaches 850–900. Such a fast growth of the silicon chain is characteristic of hydrosilylation of siloxanes [10, 11].

The operating temperature range of Pt(II) chemisorbed on polymethylene sulfide in siloxanes under investigation is more than 50°C (Fig. 1) and depends both on the amount of platinum on the immobilizate (mol g^{-1} sorbent) and on the amount of platinum per mole of the reaction mixture (Fig. 2). As the temperature is reduced (45°C), an induction period appears (Fig. 1, curve *4*), probably due to slow formation of a true catalyst of the process.

Varying the concentration of platinum on the sorbent and the amount of platinum per mole of the reaction mixture showed that, in terms of minimization of the concentration of platinum on the sorbent, optimal is the *C* 5.95×10^{-5} mol l^{-1} reaction mixture value at C 8.5×10^{-5} mol g^{-1} polymethylene sulfide [Fig. 2, the reference time is the time of complete conversion of $(VinMe_2Si)_2O$]. Increase in the platimun concentration on the sorbent (above 8.5×10^{-5} mol g^{-1} polymethylene sulfide) does not significantly shortens the time of complete conversion of $(VinMe_2Si)_2O$, while decrease in the platinum concentration significantly decelerates hydrosilylation. For example, the conversion of $(VinMe_2Si)_2O$ after 4 h reaction at *C* 4.2×10^{-5} mol g^{-1} polymethylene sulfide is 37% against 100% after 2 h reaction at *C* 8.5×10^{-5} mol g^{-1} polymethylene sulfide.

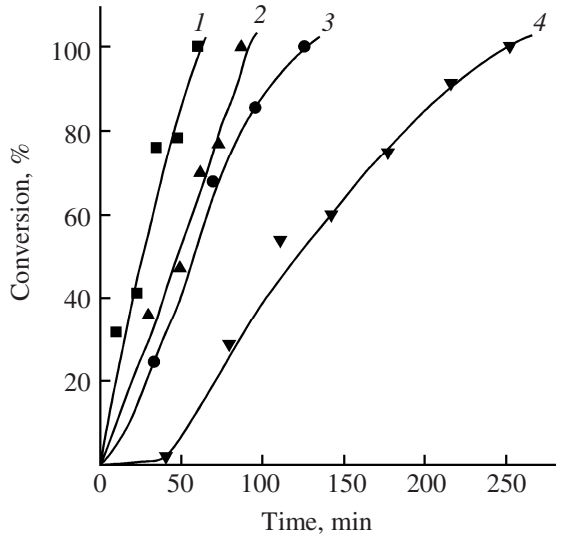


Fig. 1. Conversion of $(VinMe_2Si)_2O$ vs. time for the reaction with $(HMe_2SI)_2O$ [$(VinMe_2Si)_2O$: $(HMe_2Si)_2O$ molar ratio 1:3] in the presence of complex **A** (*C* 8.5×10^{-5} mol g^{-1} polymethylene sulfide, 5.9×10^{-5} mol l^{-1} reaction mixture) at (*1*) 60, (*2*) 55, (*3*) 50, and (*4*) 45°C.

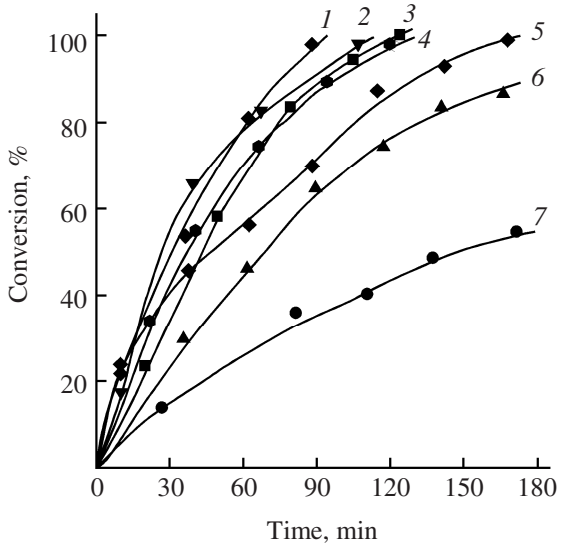


Fig. 2. Conversion of $(VinMe_2Si)_2O$ vs. time for the reaction with $(HMe_2Si)_2O$ [$(VinMe_2Si)_2O$: $(HMe_2Si)_2O$ molar ratio 1:3, 50°C] in the presence of complex **A** (C_{Pt} 8.5×10^{-5} mol g^{-1} polymethylene sulfide) at *C* 10^5 mol l^{-1} reaction mixture (*1*) 14.7, (*2*) 11.9, (*3*) 5.95, (*4*) 7.37, (*5*) 7.65, (*6*) 9.07, and (*7*) 3.4.

The activation energy and pre-exponential factor at C 5.9×10^{-5} mol l^{-1} reaction mixture were evaluated analytically from the Arrhenius equation as 82.2 ± 1.5 kJ mol^{-1} and ln k_0 25.6, respectively. These values are several times higher as compared to hydrosilylation of siloxanes in the presence of effective homogenous catalysts, such as dichlorobis(methyl *p*-tolyl sulfoxide) platinum(II) [E_A 18.3 ± 0.9 kJ mol^{-1} (ln k 4.99) at C 3.4×10^{-6} mol l^{-1} reaction mixture] and dichloro[η^4-1-methylcycloocta-1,5-diene]platinum(II) [E_A 33.6 ± 1.6 kJ mol^{-1} (ln k_0 10.72) at C 5.0×10^{-6} mol l^{-1} of reaction mixture] [6]. This result is evidently explained by different mechanisms of action of homogenous and immobilized platinum catalysts and by different rate-limiting stages of the process (the platinum center in homogenous catalysts is more accessible than in immobilized ones).

The selectivity of addition in the presence of Pt(II) chemisorbed on polymethylene sulfide proved to be slightly lower as compared to the methyl *p*-tolyl sulfoxide catalyst. The selectivities of β-addition at 50°C in the presence of compound **A** (C 8.5×10^{-5} and 17.0×10^{-5} mol g^{-1} polymethylene sulfide, respect-ively) are 87 and 80%, respectively, against 92% in the presence of the methyl *p*-tolyl sulfoxide complex [6]. At the same time, it is higher as compared to that observed with the methylcyclooctadiene complex (75%) [6]. Decrease in the reaction temperature increases the addition selectivity. For example, the selectivity at 45° C is 90%. Multiple use of catalyst **A** has almost no effect on the addition selectivity: The fraction of β-addition after four-run use of the catalyst at C 8.5×10^{-5} mol g^{-1} polymethylene sulfide is, according to ^{1}H NMR data, 86–87% at 50°C).

To gain insight into the mechanism of the catalytic action of the immobilized platinum, we have studied the reaction of complex **A** with hydro- and vinyloxysilanes by spectral methods and then carried out comparative hydroxylation of the reaction products.

Heating of complex **A** with excess $(HMe_2Si)_2O$ or $(Vin_2Me_2Si)_2O$ produces changes in its XPS and IR spectra. The $(HME_2Si)_2O$ solution becomes yellowish green, while the color of the $(VinMe_2Si)_2O$ solution does not change. Coloration of siloxane solutions is usually connected with formation of a platinum-silicon hydride complex [15, 16].

The XPS spectrum of the solid product obtained by treatment of complex **A** with tetramethyldisiloxane for 1.5 h at 70°C and then thoroughly washed with CH_2Cl_2 contains Si2$p_{3/2}$ [E_b(Si2$p_{3/2}$) 102.7 eV], C [E_b(C1s) 285.0 eV], and O1s [E_b(O1s) 532.7 eV] signals of the Me_2SiO siloxane fragment; the relative fractions of the thiolate S [E_b(S2$p_{3/2}$) 162.8 eV] and Pt(II) (4$f_{7/2}$) decreases, and the Pt : coordinated S : thiolate S : Si ratio (at %) is 3.9 : 3.3 : 0.7 : 2.2, respectively. The IR spectrum acquires two bands of the siloxane methyl group at 805 and 1261 cm^{-1} and a band of the SiH group at 2300– 2400 cm^{-1}, and the band at 1626 cm^{-1} gets stronger. Upon longer heating with tetramethyldisiloxane (5 h at 80°C in a sealed ampule), black mottlings appear in the solid product, and its IR spectrum no longer shows SiH bands, the bands at 805 cm^{-1} and 1260 cm^{-1} get stronger, and a new band at 1078 cm^{-1} appears [probably, ν_{as}(Si–O–Si)]. At the same time, boiling of the starting polymethylene sulfide in $(HMe_2Si)_2O$ for 10 h does not cause changes in the IR spectrum of polymethylene sulfide and in the ^{1}H NMR spectrum of $(HMe_2Si)_2O$. Hence, the observed changes in the IR spectrum and decrease, by XPS data, in the amount of Pt(II)(4$f_{7/2}$) and S(2$p_{3/2}$) after treatment of complex **A** with tetramethyldisiloxane are caused by "washing-out" of platinum from polymethylene sulfide to the solution.

After analogous treatment of complex **A** with tetramethyldivinyldisiloxane, the XPS spectrum of the solid product acquires signals of Si [E_b(Si 2$p_{3/2}$) 102.4 eV], C [E_b(C1s) 285.0 eV], and O [E_b(O1s) 532,7 eV] from the siloxane Me_2SiO fragment, the signal of the thiolate S(2$p_{3/2}$) disappears, and the relative amount of Pt(II)(4$f_{7/2}$) decreases. The Pt : coordinated sulfur : Si ratio (at %) is 3.5 : 1.7 : 2.7, respectively. The IR spectrum acquires a strong band at 1373 cm^{-1} and bands of siloxane methyl groups at 799, 875, and 1255 cm^{-1}, and the bands at 1013 and 2880 cm^{-1} disappear. Boiling of the starting polymethylene sulfide in $(VinMe_2Si)_2O$ for 10 h causes no changes in the IR spectrum of polymethylene sulfide and in the ^{1}H NMR spectrum of $(VinMe_2Si)_2O$. Hence, the decrease in the Pt(II)(4$f_{7/2}$) content in polymethylene sulfide in this case, like with $(HMe_2Si)_2O$, is caused by washing out of the catalyst. The absence of the thiolate S signal in the XPS spectrum and the simultaneous preservation of the binding energy of Pt(II)(4$f_{7/2}$) electrons (73.3 eV) suggests cleavage of the Pt–S bond, which is not accompanied by a change in the oxidation state of the adsorbed platinum {for low-valent platinum complexes like the Karsted catalyst [Pt(0) vinylsiloxane complex], the Pt(4$f_{7/2}$) binding energy does not exceed 72.5 eV [14–17]}. It can be suggested that,

instead of Pt–S, a Pt–C or Pt–O bond is formed, because the formation of a Pt–Si bond should shift the Pt($4f_{7/2}$) binding energy to higher values [16, 17].

In the electronic absorption spectrum of the yellowish green $(HMe_2Si)_2O$ solution obtained after treatment of complex **A** with tetramethyldisiloxane, two small shoulders at λ 355 and 400 nm appear and in the electronic absorption spectrum of the $(VinMe_2Si)_2O$ solution, a shoulder at 241 nm and an absorption band at λ_{max} 267 nm. The presence of a plasmon band at λ 267 nm is characteristic of solutions containing platinum nanoparticles [16]. The ^{1}H NMR spectra of both siloxane solutions do not change, except that signals of 1,1,3,3,5,5-hexamethyltrisiloxane formed by disproportionation of $(HMe_2Si)_2O$ appear in the spectrum of the $(HMe_2Si)_2O$ solution (for more details on disproportionation, see [11]). We failed to isolate complexes formed in the siloxane solutions. Attempts to precipitate them or remove siloxanes in a high vacuum at low temperatures led to decomposition of the complexes (a black platinum precipitate and a white precipitate with a hydrogen sulfide odor are formed). Probably, platinum(0) nanoparticles stabilized either by the thiolate anion, like those obtained in [18], or by siloxanes are formed. In any case, the reaction of siloxanes with polymethylene sulfide-immobilized platinum leads to its partial extraction to the solution.

The catalytic activity of the solid product formed after treatment of complex **A** with tetramethyldisiloxane occurred to be significantly lower (50°C, conversion after 17 h reaction 95%) compared to the starting compound **A**. The selectivity of β-addition alters in parallel: It is as low as 78% at 100% conversion of $(VinMe_2Si)_2O$. The catalytic activity of the product formed by treatment of complex **A** with $(VinMe_2Si)_2O$ is even lower: The conversion after 17 h reaction at 50°C is as low as 26%, and 95% conversion is achieved only after 31 h.

At the same time, the colored $(HMe_2Si)_2O$ solution formed after treatment of complex **A** with tetramethyldisiloxane reacts with $(VinMe_2Si)_2O$ without a catalyst and at the same rate as in the presence of complex **A** (C 8.5×10^{-5} mol g^{-1} polymethylene sulfide; 14.7×10^{-5} mol l^{-1} reaction mixture). The reaction of the colorless $(VinMe_2Si)_2O$ solution with $(HMe_2Si)_2O$ without a catalyst proceeds extremely slowly even at 80°C (after 24 h the ^{1}H NMR spectrum shows only traces of β-adducts). The coincidence of kinetic curves for hydrosilylation with an $(HMe_2Si)_2O$ solution formed by boiling with complex **A** and for hydrosilylation in the presence of the starting complex **A** suggests that the true hydrosilylation catalyst is formed in the reaction mixture under the action of $(HMe_2Si)_2O$ and is a yellowish green platinum–silicon hydride complex.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker WM-400 spectrometer (400.13 MHz) in $CDCl_3$. All results are presented in ppm relative of TMS. The measurements were carried out without using additional reference substances against the signal of the deuterated solvent.

The IR spectra were registered on Shimadzu FTIR-8400S (4000–400 cm^{-1}) and Hitachi FIS-3 (400–100 cm^{-1}) spectrometers in KBr pellets.

The electronic absorption spectra were obtained on a Specord M-40 double-beam scanning spectrophotometer (200–800 nm) for solutions in $(HMe_2Si)_2O$ or $(VinMe_2Si)_2O$. The XPS spectra were measured on a Kratos Axis Ultra instrument with a monochromatic X-ray source ($Al_{K\alpha}$ wavelength, power 180 W). The surface charge was compensated for by slow electron bombardment. The vacuum of 3×10^{-7} Pa was maintained during mesurements. The spectra were processed using standard programs. The spectra were normalized by the C(1s) energy taken equal to 285 eV. The binding energies were determined with an accuracy of 0.2 eV.

Elemental analysis was carried out on a Leco CHN-932 analyzer.

Chromatographic analysis of hydrosilylation products was carried out on a Tsvet 104 chromatograph equipped with a thermal conductivity detector; column (3000 × 4 mm) packed with 10% SE-30 on Chromaton N-AW-DMCS; carrier gas helium (4 l min^{-1}); bridge current 100 mA; injector temperature 350°C. The oven temperature was programmed from 140 to 230°C at a rate of 10 deg min^{-1}.

The hydrosilylation of siloxanes was carried out in a Pyrex temperature-controlled reactor. The catalyst was placed in the reactor, and a preliminarily prepared mixture of octamethylcyclotetrasiloxane and hydro- and vinylsiloxane in a 2:3:1 ratio was added. The reactor was evacuated, and the mixture was thermo-

stated with stirring. The platinum concentration was $(3–15) \times 10^{-5}$ mol l^{-1} reaction mixture at $C(4.2–17.0) \times 10^{-5}$ mol g^{-1} polymethylene sulfide. The conversion was evaluated by GLC (kinetically) against the internal standard (octamethyltetracyclosiloxane), and the selectivity was measured by GLC and NMR. In the last case, the selectivity was evaluated from the integral intensities of CH_3–C and CH_2–CH_2 signals of the α- and β-adducts at δ 1.02 (d, *J* 7.5 Hz) and 0.41 ppm.

1,1,3,3-Tetramethyldisiloxane and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane from Aldrich and octamethylcyclotetrasiloxane from Dow Corning were used.

Polymethylene sulfide was purchased from Pallada NPF OOO (Ufa, Russia). IR spectrum, ν, cm^{-1}: 2963, 2911, 2887 w, 1642, 1524, 1441, 1401, 1368 s, 1261 s, 1178 s, 1083 s, 1014 s, 930, 878, 803 s, 745 s, 734 s, 707 s.

Platinum(II) chemisorbed on polymethylene sulfide (complex A). A batch of K_2PtCl_4 or K_3PtCl_6 [$C(4.2–17.0) \times 10^{-6}$ M] was dissolved in 20 ml of 0.5 M HCl, and 0.1 g of polymethylene sulfide was added. The reaction mixture was heated at 90°C for 3 h. The precipitate that formed was filtered off and dried at 20°C. The yield was quantitative. IR spectrum, ν, cm^{-1}: 2957, 2910, 2868 w, 1630, 1442, 1367 s, 1304 w, 1228 w, 1178 s, 1013 s, 930, 878, 745 s, 735 s, 705 s, 674 w. XPS spectrum, E_b, eV: Pt($4f_{7/2}$) 73.4; S($2p_{3/2}$) 162.8, 164.0, 165.1; C (1*s*) 285.9, 287.2. Found, %: C 28.50; H 4.83, S 66.67. CH_2S. Calculated, %: C 26.06; H 4.37; S 69.57.

Solid product obtained by the reaction of complex A with $(HMe_2SI)_2O$ (after keeping in a vacuum). IR spectrum after heating for 1.5 h at 70°C, ν, cm^{-1}: 2959, 2911, 2880 w, 2342, 1626, 1367 s, 1304 w, 1256, 1178 s, 1013 s, 930, 878, 805, 745 s, 735 s, 707 s, 677. XPS spectrum, E_b, eV: Pt($4f_{7/2}$) 73.4; S($2p_{3/2}$) 162.8, 164.0, 165.1; C(1*s*) 285.0, 286.2, 287.4; Si($2p_{3/2}$) 102.7; O(1*s*) 532.7. IR spectrum after heating for 5 h at 80°C, ν, cm^{-1}: 3740, 2958, 2909, 2830 w, 1630, 1367 s, 1305 w, 1260, 1177 s, 1078 m, 1015 s, 930, 882, 803, 745 s, 735 s, 708 s, 676. Found, %: C 26.27; H 4.65; S 63.83. CH_2S. Calculated, %: C 26.06; H 4.37; S 69.57.

Solid product obtained by the reaction of complex A with $(VinMe_2Si)_2O$. IR spectrum after keeping in a vacuum, ν, cm^{-1}: 2958, 2907, 1640, 1373 s, 1367 s, 1304 w, 1256, 1175 s, 1035, 882, 799, 741 s, 733 s, 709 s, 669. XPS spectrum, E_b, eV: Pt($4f_{7/2}$) 73.3; S($2p_{3/2}$) 164.0, 165.1; C(1*s*) 285.0, 286.2, 287.5; Si ($2p_{3/2}$) 102.4; O(1*s*) 532.7. Found, %: C 30.38; H 4.80; S 64.82. CH_2S. Calculated, %: C 26.06; H 4.37; S 69.57.

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 06-03-32137-a), Administration of St. Petersburg (project no. PD06-1.3-62), and Development of the Scientific Potential of Higher School Departmental Target Program (project no. RNP.2.1.1.1277).

The authors express their gratitude to A.V. Shchukarev for measuring the XPS spectra.

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