ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 8, pp. 1613–1620. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © I.V. Mel'nik, N.V. Stolyarchuk, L.I. Kozhara, V.P. Goncharik, Yu.L. Zub, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 8, pp. 1384–1391.

FROM MATERIALS OF ALL-RUSSIAN CONFERENCE "CHEMISTRY OF SURFACE AND NANOTECHNOLOGY"

Synthesis of Bridged Polysilsesquioxane Xerogels with Thiourea Groups

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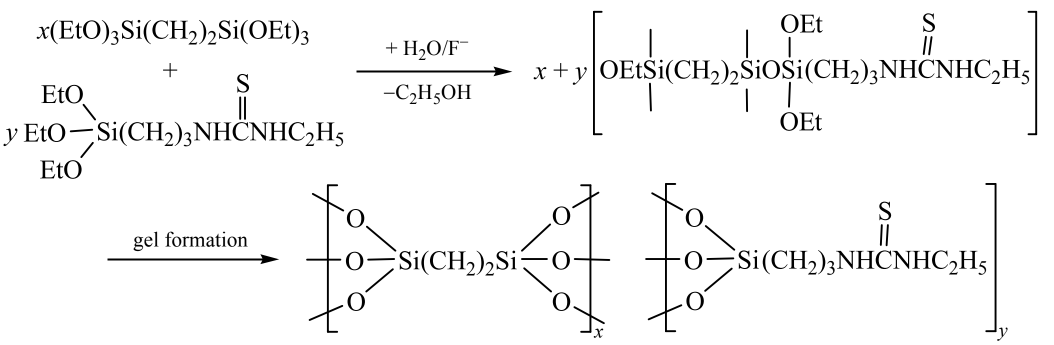
Received January 14, 2013

Abstract—Two xerogels with the ligand groups concentration 1.0 and 1.8 mmol g^{-1} were prepared by sol-gel method from 1,2-bis(triethoxysilyl)ethane and trifunctional silane with thiourea groups [$\equiv Si(CH_3)_2NHC(S)\cdot NHC_2H_5$]. It is shown that the increase in relative amount of structuring agent does not cause the increase in the specific surface value and the other parameters of porous structure. It arises from the significant increase in gel formation time in this system. It is found that synthesized xerogels can adsorb Hg^{2+} ions from the acidified water solutions. In this case in the surface layer formation of complexes of mercury(II) of different composition and with coordination sphere of different nature is possible due to thione-thiol tautomerism characteristic of thiourea group.

DOI: 10.1134/S1070363213080240

Hybride organo-inorganic materials in the course of last several years attract growing interest due to their unique properties [1–3]. Among these materials special place is occupied by bridged polysilsequioxane xerogels which are prepared by hydrolytic polycondensation of molecular building blocks. Such molecular blocks contain organic bridge of certain nature which is bound with two (or more) trialkoxysilyl groups by covalent Si–C bond. Using such organosilicon compounds as precursors permits the preparation of three-dimensional network materials where the organic bridge remains in the composition of xerogel scaffold. Physicochemical and adsorption properties of such polysilsesquioxane xerogels originate from the nature of the bridge as well as the conditions of performing the reaction of hydrolytic polycondensation and the conditions of final formation of structure (washing, drying, etc.) [2, 4].

Bridged polysilsesquioxane xerogels exhibit as a rule non-specific adsorption properties. At the same time the sol-gel method which is used for their synthesis permits using multicomponent (with respect to alkoxysilanes) systems and to prepare xerogels with complex-forming functional groups in one stage. In another words, sol-gel method permits preparation of targeted nature of organic groups on the surface as well as inside the matrix, and to construct xerogels with the necessary porous structure and necessary specific sorption properties [5]. Hence, the development of methods of synthesis of adsorbents using bis-silanes as the structuring agents and establishing the main factors influencing the process of structure formation with the purpose of obtaining sorbtion-active materials with the given parameters of porous structure and chemical nature of surface is urgent. Therefore in this work we aimed to develop procedures for preparing bridged polysilsesquioxane xerogels containing thiourea complex-forming group of the composition $\equiv Si(CH_3)_2NHC(S)NHC_2H_5$ [6, 7] and to establish the factors affecting the structure-adsorption characteristics of such materials and their sorption properties with respect to heavy metal ions by an example of mercury(II) ions.



Bridged polysilsesquioxane xerogels containing thiourea group were obtained by the reaction of hydrolytic polycondensation of 1,2-bis(triethoxysilyl)-ethane as structuring agent and trifunctional silane with thiourea group $(C_2H_5O)_3Si(CH_2)_3NHC(S)\cdot NHC_2H_5$-, as the functionizing agent (see the scheme below). Molar ratio of reacting alkoxysilanes was 2:1 and 4:1.

In Table 1 the results of elemental analysis of obtained samples are presented. As seen, for both samples a good agreement is observed between the content of functional groups calculated from the elemental analysis of sulfur and nitrogen. It shows that functional groups retain their composition. Overestimation of carbon content as compared to the calculated one from the ratio of reacting alkoxysilanes is most probably connected with the presence of residual ethoxysilyl groups.

In Fig. 1 the IR spectra of xerogels synthesized are presented. The absorption band of medium intensity at 1550–1560 cm^{-1} corresponding to ν_{as}(NCN) vibration of –NH–C(S)–NH– fragment shows the presence of thiourea group in the composition of both samples [8]. In the IR spectra of xerogels two sharp absorption bands at ~1270 cm^{-1} and ~1414 cm^{-1} are observed. They can be attributed to $\omega(CH_2)$ and $\delta(CH_2)$ of $\equiv Si–CH_2–CH_2–Si\equiv$ bridge. Yet the starting trifunctional silane also contains a group of absorption bands in the range 1300–1500 cm^{-1} (Fig. 1, spectrum *1*). Therefore the band at ~1414 cm^{-1} most probably refers to the deformation vibrations $\delta(SiCH_2)$ of $\equiv Si(CH_2)_3NHC(S)NHC_2H_5$ group [9]. A weak band $\delta(CH_2)$ of $\equiv Si–CH_2–CH_2–Si\equiv$ is masked by the absorption bands of ethyl and propyl substituents of the functional group. The presence of these groups causes the appearance of absorption bands also at 2890–2970 cm^{-1} in the IR spectra of both samples corresponding to the symmetric and asymmetric stretching vibrations of C–H bonds (Fig. 1). In the range of 1050–1200 cm^{-1} IR spectra of xerogels contain the most intense absorption band with the high-frequency shoulder. Apparently its appearance is connected with the formation of siloxane bonds [10]. The synthesized sorbents contain also water, therefore in the range above 3300 cm^{-1} a broad and intense absorption band is identified. It is probably a superposition of two absorption bands, ν(OH) of sorbed water and ν(NH) of thiourea fragment. Besides, $\delta(H_2O)$ absorption band characteristic of water is observed at 1630 cm^{-1}. The presence of an absorption band at ~3730 cm^{-1} undoubtedly shows the presence of silanol groups in the xerogels [11]. Hence, IR spectroscopy indicates the presence of thiourea groups, siloxane bonds, ethylene bridges, silanol groups, and water in the composition of xerogels obtained.

In Table 1 parameters of porous structure of synthesized samples calculated from the isotherms of low temperature nitrogen adsorption are presented (Fig. 2). As a rule, the xerogels obtained from 1,2-bis-

Table 1. Composition of xerogels synthesized and content of functional groups in them

Sample	Elemental analysis data, wt %				Concentration of functional groups		S_{sp}, $m^2\ g^{-1}$	V_s, $cm^3\ g^{-1}$	*d*, nm
	C	H	N	S	$c_{f.gr}$, mol g^{-1a}	$c_{f.gr.}$, mmol g^{-1b}			
A	20.1	4.9	5.2	5.9	1.8	1.8	108	0.09	3.6
B	26.0	4.8	3.0	3.2	1.0	1.1	75	0.07	4.6

[a] Calculated from the elemental analysis data on S. [b] Calculated from the elemental analysis data on N.

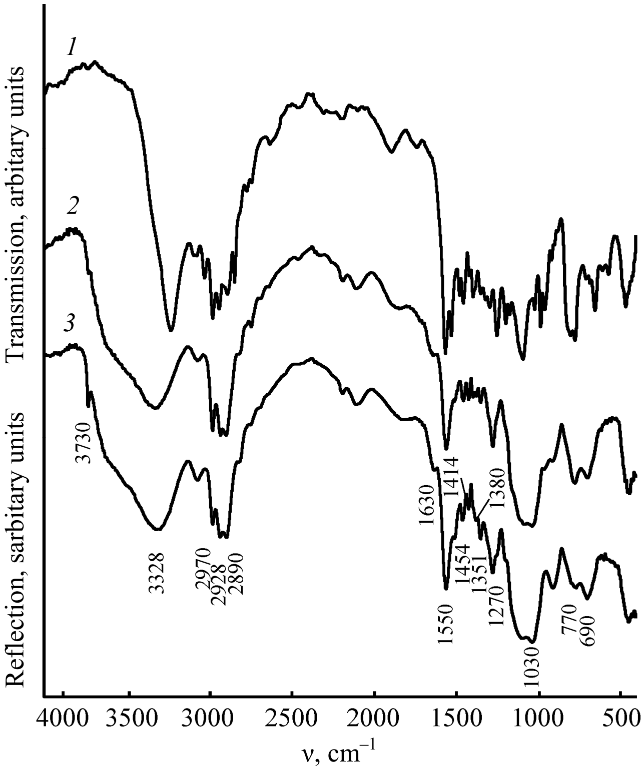


Fig. 1. IR spectra of (*1*) starting silane and synthesized samples (*2*) **A** and (*3*) **B**.

(triethoxysilyl)ethane are highly porous [12, 13]. The increase in content of structuring component usually leads to the increase in the specific surface of xerogel [12]. But for the samples synthesized this tendency is not preserved (see Table 1). Note that in the case of xerogel **A** gel is formed in the course of 10 min, while in the case of xerogel **B** only after 6 days. Therefore in the last case the formation of larger globules must be expected, which explains the difference in the parameters of porous structure of these xerogels.

Nevertheless, using of 1,2-bis(triethoxysilyl)ethane instead of tetraethoxysilane permits to obtain xerogels with more developed porous structure [14]. This effect is observed also in the case of thiourea group. Hence, xerogel obtained at the molar ratio of 1,2-bis(triethoxysilyl)ethane and trifunctional silane equal to 2:1 is not porous [15] unlike xerogel **A** (see Table 1). On the other hand, while using functional groups whose geometrical size is smaller as compared to $-(CH_2)_3NHC(S)HNC_2H_5$ (for example, 3-aminopropyl and 3-mercaptopropyl) bridged xerogels at the above-mentioned ratio of alkoxysilanes have the specific surface area to 600–900 m^2 g^{-1} [13]. Note also that xerogels synthesized are characterized by a low sorption volume of pores (see Table 1). According to microphotographs obtained by scanning electron microscopy (Fig. 3) the obtained xerogels consist of angular particles of irregular form and contain the admixture of low porous fraction.

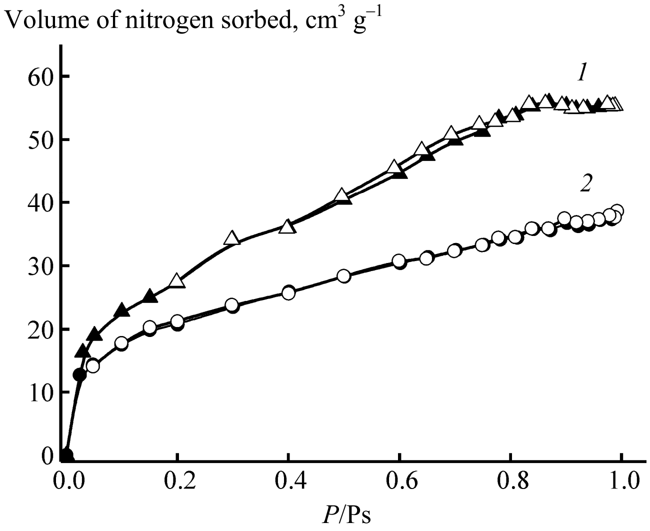


Fig. 2. Isotherms of low temperature adsorption-desorption of nitroges for the xerogels obtained: (*1*) **A** and (*2*) **B**.

As known, thiourea group forms stable complexes with the ions of noble and heavy metals [16, 17]. Therefore we studied the sorption properties of obtained xerogels with respect to Hg^{2+} samples. The dependence of degree of extraction of Hg(II) on the time of contact for sample **A** is presented in Fig. 4a. The kinetic curve for sample **B** has the same shape. The analysis of these data leads to a conclusion that for such samples the equilibrium is established in the course of 144 h (6 days). Therefore the isotherms of sorption of Hg^{2+} ions with these xerogels in the static regime (Fig. 4b) were obtained under the conditions presented below (pH ~ 2, $\tau = 144$ h, ion strength 0.1). During the experiment variation in pH of the equilibrium solutions in the course of sorption was observed.

As is seen from the Fig. 4b for the xerogels synthesized a quick rise of isotherms in the range of low Hg(II) concentrations with the simultaneous reaching the plateau takes place. For the xerogel **A** more smooth rise of the isotherm is characteristic. The saturation of sorption layer of this xerogel proceeds at higher equilibrium concentrations of Hg^{2+} which are almost by an order of magnitude larger than in the case of sample **B**. Note that sorption of mercury(II) ions with both samples is accompanied by elimination of

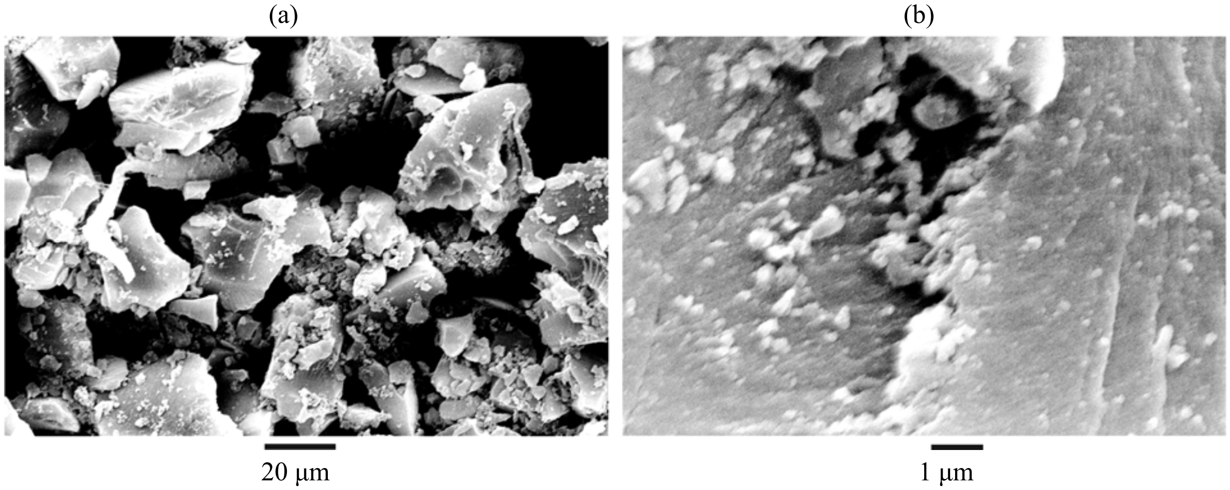


Fig. 3. Microphotographs of xerogels obtained by scanning electronic microscopy.

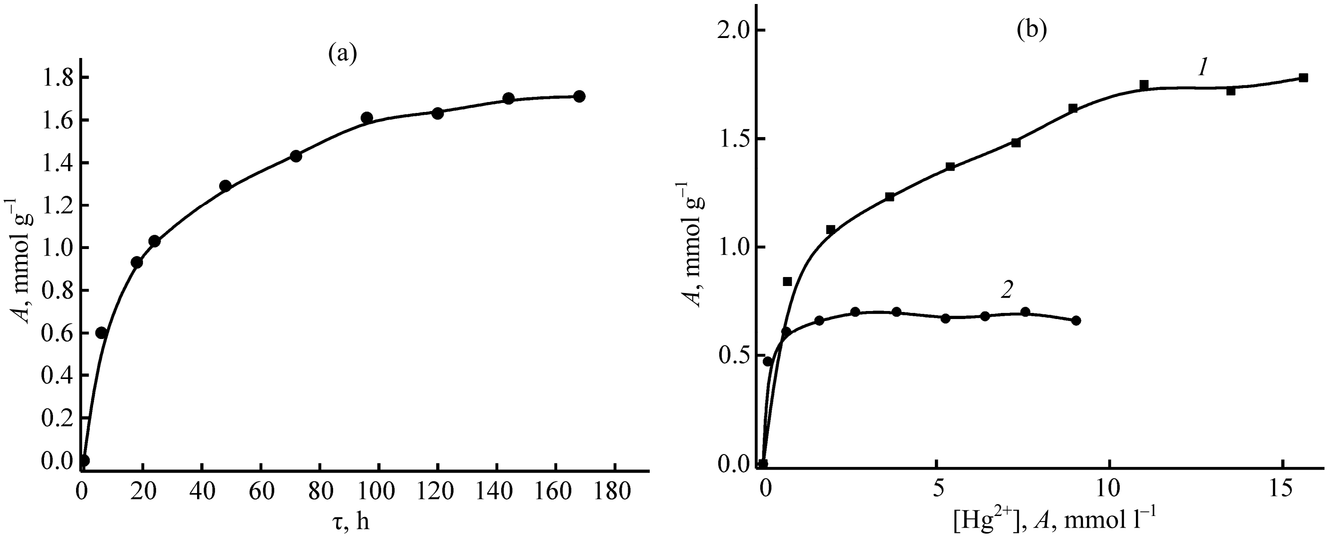
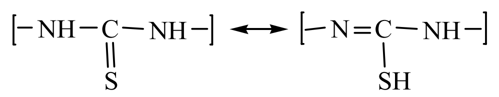


Fig. 4. (a) Effect of time of contact of the sample **A** with the solution on the amount of extracted mercury(II) and (b) isotherms of sorption of Hg^{2+} ions with xerogels (*1*) **A** and (*2*) **B**.

protons (Table 2). As is known, thiourea undergoes a thione-thiol tautomerism [18].



$$[-NH-\underset{\underset{S}{\|}}{C}-NH-] \longleftrightarrow [-N=\underset{\underset{SH}{|}}{C}-NH-]$$

Proceeding from this fact it is possible to assume that liberation of protons in the course of sorption of mercury with xerogels functionalized with thiourea groups is caused by substitution of proton in the thiol form of thiourea ligand with Hg^{2+} with the formation of strong coordination bond. This assumption agrees also with the results of investigation by the IR spectroscopy of samples corresponding to the points 1, 3, and 8 of the sorption series of xerogel **B** (Table 2) after absorption of mercury(II) ions. The analysis of the obtained spectra (Fig. 5) permits the detection in them of a new absorption band at ~1620 cm^{-1} which can be attributed to the vibrations of the double bond ν(C=N). Note that in these spectra the absorption band ν_{as}(NCN) at ~1560 cm^{-1} characteristic of the IR spectra of starting xerogels (Fig. 1) is also present. Besides, in the same spectra (Fig. 5) one more absorption band belonging to vibrations of nitrate ion [23] is identified at ~1380 cm^{-1}.

Note that the amount of protons liberated per one mercury atom in the course of sorption is always more than one (Table 2). Considering this fact and also the presence in the IR spectra after sorption of the absorption bands belonging to the nitrate ion, thione, and thiol forms of thiourea group (Fig. 5) it is possible

Table 2. Results of investigation of sorption of mercury(II) with bridge xerogels containing thiourea groups

Exp. no.	Taken Hg^{2+}, mmol	pH before sorption	pH after sorption	Found Hg^{2+} after sorption, mmol	Sorbed Hg^{2+}		Isolated H^+	
					mmol g^{-1}	Hg^{2+}/f.gr.	mmol g^{-1}	H^+/Hg^{2+}
Xerogel **A**								
1	0.098	2.34	2.08	0.014	0.84	0.47	0.967	1.15
2	0.147	2.33	2.01	0.039	1.08	0.60	1.310	1.21
3	0.196	2.32	1.96	0.073	1.23	0.68	1.590	1.29
4	0.245	2.31	1.91	0.108	1.37	0.76	1.908	1.39
5	0.294	2.31	1.89	0.146	1.48	0.82	2.055	1.39
6	0.343	2.34	1.88	0.179	1.64	0.91	2.219	1.35
7	0.392	2.33	1.91	0.217	1.75	0.97	1.965	1.12
8	0.441	2.28	1.88	0.269	1.72	0.95	2.042	1.18
9	0.49	2.22	1.85	0.312	1.78	0.99	2.085	1.17
Xerogel **B**								
1	0.049	2.34	2.19	0.0025	0.47	0.47	0.48	1.03
2	0.075	2.37	2.15	0.0133	0.61	0.61	0.72	1.18
3	0.098	2.34	2.11	0.0324	0.66	0.66	0.82	1.24
4	0.124	2.36	2.10	0.0531	0.7	0.7	0.92	1.31
5	0.147	2.36	2.09	0.077	0.7	0.7	0.96	1.38
6	0.173	2.36	2.09	0.1055	0.67	0.67	0.97	1.44
7	0.196	2.35	2.09	0.1281	0.68	0.68	0.94	1.38
8	0.221	2.35	2.08	0.1515	0.7	0.7	0.99	1.41
9	0.247	2.37	2.11	0.1807	0.66	0.66	0.90	1.36

to assume the formation of mercury complexes of the composition 1:1 as well as 1:2 in the surface layer of xerogels. Complexes of the composition 1:1 may be of two types, namely, with the thione and the thiol forms of thiourea ligand. Evidently it is impossible to establish the ratio of both forms of mercury complexes.

Analyzing the shape of isotherms (Fig. 4b) it can be suggested that in the surface layer of the sample **A** at low equilibrium concentrations of mercury complexes with two ligand groups are formed. At the increase in concentration of mercury(II) in solution its further sorption proceeds evidently due to the transformation of the biligand complex into the complex of 1:1 composition which corresponds to the smooth transition of the isotherm to the saturation.

The isotherm for sample **B** is characterized by a sharp occurrence of the saturation. The maximum sorption of mercury(II) corresponds to the metal : functional group ratio 0.7:1. It may be assumed that in this case a significant amount of mercury complexes with two surface ligands is formed. Large amount of evolving protons it indirectly indicates (see Table 2).

Note also that the distance between two silicon atoms of Si–O–Si fragment is equal to 3.2 Å or smaller if Si-O-Si angle is less than 180°. The calculations show that at the uniform distribution of functional groups on the surface of xerogel **A** the distance between the neighboring groups is 3.1 Å, and for xerogel **B** this distance should be 3.5 Å. In the simplest case the surface of this xerogels must be considered as flat polysiloxane net where each silicon atom is bound with functional group. Certainly, another location of functional groups is also possible, for example, in a form of oligomeric iselets, which from our point of view agrees better with the experiment. For example, from the data of Table 2 for xerogel **A** under the conditions of saturation a conclusion was made above on the formation of complex of the 1:1 composition because the amount of sorbed mercury (mmol g^{-1}) practically coincides with the content of functional groups (mmol g^{-1}). But the content of liberating protons (mmol g^{-1}) is considerably larger than the

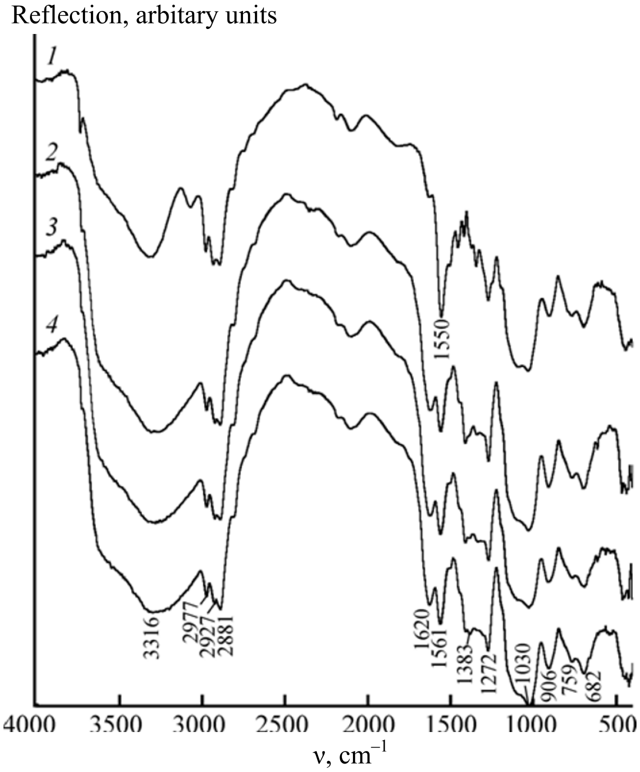


Fig. 5. IR spectra of the sample **B** (*1*) before sorption and after sorption in the points of isotherm (*2*) 1, (*3*) 3, and (*4*) 8 (see Table 2).

content of thiourea groups even at the assumption that all of them exist in the thiol form. Moreover, such assumption disagrees with the IR spectroscopy data which show the presence in the samples after sorption of metal of the thiol as well as of the thione forms of the ligand. Hence, in the surface layer of this xerogel may exist two complexes of mercury differing in the nature of coordination sphere. In the case of sample **B** even under the conditions of saturation the metal to functional group ratio is close to 0.7 (Table 2). But it does not mean that 0.3 mmol g^{-1} of thiourea ligands (from 1.0 mmol g^{-1}) does not take part in the complex formation. From our point of view, at the consideration of number of protons liberated per one mercury atom, in this case the formation of several complexes differing in the forms of ligands taking part in binding with metal also takes place.

Hence, the principle possibility of using sol–gel method for the synthesis of bridged polysilsesquioxane xerogels functionalized with thiourea groups of the composition $\equiv Si(CH_2)_3NHC(S)NHC_2H_5$ is shown. The obtained xerogels are characterized by relatively moderate parameters of porous structure (S_{sp} from 75 to 108 m^2 g^{-1}). Unlike the trend in the other xerogels the increase in the specific surface at the increase in the ratio of structuring agent in the reaction solution was not observed. The presence in the surface layer of xerogels of thiourea functional groups ($C_{C=S}$ ~1.0 and ~1.8 mmol g^{-1}) permits to use them for the extraction of heavy metal ions from water solutions as was shown by an example of a very toxic ion Hg^{2+}.

EXPERIMENTAL

For the preparation of functionalized xerogels the following substances were used (all reagents are from “Aldrich” if not specially indicated): 1,2-bis(triethoxysilyl)ethane $(C_2H_5O)_3Si(CH_2)_2Si(OC_2H_5)_3$ (ABCR, 97%), NH_4F (Fluka, 98%), anhydrous ethanol. Trifunctional silane with thiourea group $(C_2H_5O)_3Si\cdot(CH_2)_3NHC(S)NHC_2H_5$ was prepared according to the procedure [15].

While studying sorption properties of xerogels the following reagents were used: $Hg(NO_3)_2$ (pure for analysis grade, “Macrokhim), HNO_3 (chemically pure grade, “Reactiv”), Eriochrom black T (pure for analysis grade, “Reakhim”), $MgSO_4\cdot 7H_2O$ fixanal (Cherkasy State Plant of Chemical Reagents), NH_4Cl (chemically pure grade, “Macrokhim”), 25% NH_4OH (pure for analysis grade, “Macrokhim), trilon B fixanal (“Reakhim”), $NaNO_3$ (chemically pure grade, “Macrokhim”).

Synthesis of xerogel A (molar ratio of 1,2-bis-(triethoxysilyl)ethane and trifunctional silane 2:1). To a solution of 0.02 mol of 1,2-bis(triethoxysilyl)-ethane in 10 ml of ethanol a solution of 0.0148 g of NH_4F in 1.08 ml of water was added with stirring. Simultaneously a solution of trifunctional silane was prepared. To a solution of 3.0851 g of silane in 10 ml of ethanol a solution of 0.0037 g of NH_4F in 0.27 ml of water was added with stirring. After that the stirring of each solution was continued for extra 5 min. Then the solutions prepared were mixed and stirred for 5 min, and then the stirring was stopped. After 10 min the gel with slight opalescence was formed. This opalescence increased in time. After aging of gel for 30 days it was ground and dried in a vacuum at 20, 50, and 100°C for 2 h at each temperature. Yield of light yellow powder-like product was 4.7 g.

Synthesis of xerogel B (4:1). Synthesis was carried out analogously to preparing xerogel **A** with the following alterations. 1,2-Bis(triethoxysilyl)ethane was dissolved in 15 ml of ethanol, 1.5425 g of silane were dissolved in 5 ml of ethanol, and the amount of introduced catalyst (NH_4F) was 0.00185 g dissolved in 0.13 ml of water. Under these conditions the formation of gel (with slight opalescence) was observed after 6 days. Yield of the product 4.1 g.

Elemental analysis was carried out in the analytical laboratory of Parma University (Italy).

IR reflection spectra in the range 4000–400 cm^{-1} were obtained on a Nicolet NEXUS FTIR spectrometer using SMART Collector adapter of diffuse reflection. For recording of spectra the samples were ground with KBr ("Fluka", spectranal) in 1:20 ratio. In all cases 50 scans with the resolution 8 cm^{-1} were used. For the treating of spectra program of OMNIS supplier firm was used.

Nitrogen adsorption isotherms for all samples were measured by Kelvin-1042 sorbtometer. Before obtaining isotherms samples were degassed in the helium flow for 1 h at 110°C. Specific surface was calculated according to BET [19] in the range of relative pressures 0.05–0.35. Sorption volume of pores (V_s) was evaluated by the amount of adsorbate absorbed at relative pressure 0.99. Size of pores (d) and their size distribution was measured by BJH method [20].

Scanning electron microscopy microphotographs were obtained on a JEOL JSN-6060LA Analytical Scanning Electron Microscope (Jeol. Tokyo, Japan) under the secondary electron regime at the acceleration voltage 30 kV. The samples were assembled on a stand surface covered preliminary with adhesive. For preventing the accumulation of surface charge and obtaining of contrast image the surface of samples was covered in a vacuum with thin layer of gold by the cathode spraying.

Investigation of sorption of mercury(II) ions from nitric acid solutions was carried out in static regime (sorbent sample 0.1 g, total amount of solution 20 ml, pH of starting solution ~2.0, t 20°C). Fractions of xerogels with the particle size <0.063 mm were used. Considering that the surface of samples is hydrophobic, they were preliminary wetted with 0.1 ml of ethanol. Ionic strength of solution (0.1 M) was created by the addition of 1 M $NaNO_3$ solution. The distribution of metal ions was controlled by water phase. Sorbent was removed by filtration through the Schott glass filter. The equilibrium concentration of mercury ions in solution was evaluated by the reversed complexonometric titration with $MgSO_4 \cdot 7H_2O$. Content of metal ions in the phase of sorbent was evaluated as a difference between the starting concentration of ions in water phase and their concentration in filtrate. pH measurements were carried out on a U-500 ionometric converter.

ACKNOWLEDGMENTS

Authors express their gratitude to GTsNTP "Nanotekhnologii i nanomaterialy" (Nanotechnologies and Nanomaterials) for the financial support (project no 6.22.5.42).

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