Mesoporous silica containing $\equiv$Si(CH$_2$)$_3$NHC(S)NHC$_2$H$_5$ functional groups in the surface layer

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ABSTRACT

One-step synthesis technique of mesoporous SBA-15 type silica with thiourea $\equiv$Si(CH$_2$)$_3$NHC(S)NHC$_2$H$_5$ groups in the surface layer was developed. According to elemental analysis, the content of surface groups is 1.25 mmol/g, which is consistent with TGA data. FT-IR spectra of the obtained sample contain characteristic absorption bands of thiourea groups (—NH—C(S)—NH—), as well as polysiloxane network ($\equiv$Si—O—Si$\equiv$). The synthesized sample was studied by XRD, TEM, SEM, and adsorption method. It was demonstrated that the sample features porous microspheres $\sim$0.5 µm with well-ordered internal spatial structure of the hexagonal lattice type due to the usage of template P123 during synthesis. According to XRD and TEM, the diameter of pores is 4.2–5 nm and the wall thickness between them is 2.6 nm. These data are consistent with the structural-adsorption characteristics calculated from nitrogen adsorption–desorption isotherms: $S_{sp.}$ = 510 m^2/g, V_s = 0.47 cm^3/g, and d = 4.3 nm. Equilibrium is established within 60 min during sorption of silver(I) and mercury(II) ions from acidified aqueous solutions for this sample, and with the complexes are formed 1.1/1 for Ag$^+$ and 0.8/1 for Hg^{2+} at metal/ligand ratio.

1. Introduction

The appearance of publications [1–3] in the early 1990s started a new approach to obtaining porous inorganic materials. It is based on coprecipitation of soluble forms of silicates with surfactants. In the original solution, surfactant formed micelles of different shapes (depending on the synthesis conditions) and acted as formative agent (template). That is, the formation of silica layer occurred due to the polycondensation of precursors on the surfaces of the already formed micelles. Calcination of the obtained sediments (mesophases) led to the template removal and the formation of porous regularly-structured materials, in which the pore shape and size was conditioned by the geometry of micelles [2]. Variation of template nature and synthesis conditions allowed to obtain mesoporous silica with different types of ordered channels (pores), for example, MCM-41, MCM-48, etc. [4].

Later, Mann with his co-workers [5] proposed to use tetraethoxysilane with trifunctional silanes (RO)$_3$SiR′, where R′ is an organic radical connected to silicon atom with hydrolytically stable bond $\equiv$Si—C$\equiv$, as precursors during template synthesis. Clearly, the different complexing groups can also be used as R′. However, in this case, the template should be removed by extraction with nonaqueous solvents (e.g., boiling in acidified ethanol) to preserve the organic functional layer on the pore surface. The materials obtained as above-described have a wider perspective of practical application.

However, using long-chained ammonium salts as templates produces materials with low mechanical strength because of the relatively thin pore walls [6]. In 1998 [7], it was proposed to use triblock copolymers as templates (such as Pluronic 123) to obtain mesoporous silica. Hydrolytic polycondensation of tetraethoxysilane in acidic medium in the presence of template, followed by its removal, makes it possible to obtain highly organized phases with hexagonal structure, named SBA-15, which are analogous to MCM-41 materials [2], but have several advantages. The most important of them is high mechanical stability, due to relatively thick walls (3.1–6.4 nm) between mesopores. In addition, these materials were characterized by well-developed porous structure (S_{sp} = 400–1040 m^2/g) [7,8].

It should be mentioned that two-component systems (according to alkoxysilanes) can also be used for one-stage synthesis of such materials as SBA-15, containing functional groups in the surface layer of pores [9]. This time, the obtained sorbents are characterized by highly-ordered porous structure and a relatively high content of functional groups. Moreover, these features are preserved with the increase in pore diameter up to 30 nm, which is very important from practical point of view. But only some sorption materials of SBA-15 type with complexing groups received by

one-stage synthesis have been described so far [10]. Primarily, this is due to the lack of an extensive range of commercially available trifunctional silanes $(RO)_3SiR'$, where R' stands for sulfur- or sulfur/nitrogen-containing complexing groups. However, materials with such functional groups can exhibit high selectivity in the extraction of ions of heavy and noble metals [11]. Previously, we developed one-step technique for the synthesis of mesoporous materials MCM-41 containing thiourea groups [12] and showed their ability to remove mercury(II) ions from aqueous solutions [13]. The aim of current work is to develop an one-step technique for the synthesis of SBA-15 type materials with $\equiv Si(CH_2)_3$-$NHC(S)NHC_2H_5$ complexing groups [14] and evaluate their sorption capacity.

2. Experimental

The following substances were used as precursors: tetraethoxysilane, $Si(OC_2H_5)_4$ (TEOS, 98%, Aldrich); 3-aminopropyltriethoxysilane, $(C_2H_5O)_3Si(CH_2)_3NH_2$ (APTES, 98%, Aldrich); ethylisocyanate, C_2H_5NCS (EtNCS, 97%, Fluka); poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$, P123, Aldrich); and absolutized ethanol. The following substances were used to study sorption: $Hg(NO_3)_2 \cdot H_2O$, $AgNO_3$, 25% NH_4OH water solution – analytical grade; NH_4Cl, $NaNO_3$, $NaCl$ – chemically pure (Macrochem, Ukraine); HNO_3, HCl, $MgSO_4 \cdot 7H_2O$, EDTA – fixanal concentrates (Reachem); and eriochrome black T – analytical grade (Reanal).

2.1. Synthesis of trifunctional silane $(C_2H_5O)_3Si(CH_2)_3NHC(S)NHC_2H_5$ (ETUS)

The synthesis was conducted in the flow of argon. The solution of 0.05 mol of C_2H_5NCS in 20 cm^3 of ethanol was added under vigorous stirring to 0.05 mol of APTES dissolved in 30 cm^3 of absolute ethanol in the Schlenk flask. Exothermic reaction was observed. The solution was boiled for 1 h and, after cooling to room temperature, the solvent was removed from it at low pressure. The emerging pale yellow oily substance, after treatment with vacuum, soon turned to solid white substance. The yield was 15.05 g. ETUS melting point is 80–82 °C. Elemental analysis data: anal. calc. for $C_{12}H_{28}N_2O_3SSi$, % (mass): C, 46.72; H, 9.15; N, 9.08; S, 10.39; found, % (mass): C, 44.96; H, 9.76; N, 9.32; S, 11.71. ^{1}H NMR (CDCl$_3$, δ/ppm): 0.66 (t, SiCH$_2$), 1.22 (s, CH$_3$CH$_2$O, CH$_3$CH$_2$), 1.73 (t, SiCH$_2$-CH$_2$), 3.44 (s, Si(CH$_2$)$_2$CH$_2$N, CH$_3$CH$_2$), 3.81 (qua, CH$_2$O), 5.82 (m, NHC$_2$H$_5$), 6.02 (m, (CH$_2$)$_3$NH). ^{13}C NMR (CDCl$_3$, δ/ppm): 7.40 (SiCH$_2$), 14.19 (CH$_3$CH$_2$N), 18.18 (CH$_3$CH$_2$O), 22.36 (SiCH$_2$CH$_2$), 39.20 (CH$_3$CH$_2$N), 46.15 ((CH$_2$)$_2$CH$_2$N), 58.43 (CH$_2$O), 181.27 (C=S). MS, m/z (%): 163(6), 263(50), 308(100), 337(25), 617(6).

2.2. Synthesis of SBA-15 silica with thiourea groups (TEOS/ETUS molar ratio in the initial solution was 10/1)

Firstly, 6.7 cm^3 (0.03 mol) of TEOS was hydrolyzed in 18.8 cm^3 of 2M hydrochloric acid at 40 °C for 3 h. Separately, 3 g of P123 was dissolved in 70 cm^3 of 2M HCl under constant stirring for 1 h on water bath (40 °C). To the resulting solution, still under stirring, there were added 0.93 g (0.003 mol) of ETUS solution in 5 cm^3 of ethanol, 4 cm^3 of 2 M HCl, and, finally, a solution of previously hydrolyzed TEOS. In 10 min, the formation of white precipitate was observed. The formed heterogeneous system was stirred another 4 h at 40 °C. The obtained mesophase was subjected to hydrothermal treatment (HTT) in the mother solution at 80 °C for 24 h. Then, the precipitate was filtered and dried in air for 8 h (sample 1). The template was removed by boiling mesophase in ethanol acidified with hydrochloric acid (100 cm^3 of C_2H_5OH and

1 cm^3 of HCl (conc.) per 1 g of mesophase) for 3 h. The procedure was repeated thrice. The obtained white product was dried in vacuum at 20 °C for 1 h and at 80 °C for 5 h [15]. Product yield was 3.66 g (sample 1a).

2.3. Characterization

Elemental analysis of both synthesized materials and ETUS precursor was performed by the certified Analytical laboratory of Institute of Organic Chemistry of National Academy of Science of Ukraine.

FT-IR spectra of synthesized materials were recorded on a Thermo Nicolet Nexus Fourier-transform infrared spectrometer in the 400–4000 cm^{-1} range, working in "Nexus Smart Collector" mode with a resolution of 8 cm^{-1}. The samples were previously ground with solid KBr (Fluka, for IR spectroscopy). The sample/KBr mass ratio was 1/30. The spectra were analyzed using software "OM-NIC". The spectrum of TEOS was recorded in liquid form between KRS plates.

X-ray diffraction experiments were conducted on diffractometer DRON-4-07, using Cu Kα-radiation. Scanning was carried out within 0.4–10.0 $2\theta/°$.

Morphology of the obtained samples was studied by JEOL JSM-6060LA Analytical Scanning Electron Microscope (Jeol, Japan) using secondary electrons at accelerating voltage of 30 kV. The samples were fixed on the surface of objective table with previously deposited adhesion coating. To prevent the accumulation of the positive charges and to receive contrasting images, the surface of the samples was covered with thin continues layer of gold by cathodic sputtering in vacuum. Microphotographs of the sample were also recorded using Transmission Electron Microscope Tecnai G2 F20 S-TWIN (FEI) at accelerating voltage of 200 kV. A drop of the suspension of mesoporous silica ultrasonically dispersed in ethanol was deposited on a copper-grid-supported transparent carbon foil (20–30 nm thick) and examined in transmission regime.

Thermal stability of the synthesized samples was studied using derivatograph Paulik–Paulik–Erdey Q (Q-1500D) operating in the 20–1000 °C temperature range, with a heating rate of 10 °C min^{-1}.

Low-temperature (77 K) nitrogen adsorption and desorption isotherms were measured on ASAP-2405N (Micromeritics). The sample was preliminary degassed at 120 °C. Specific surface area was determined using BET equation [16], and pore size distributions was evaluated by BJH method [17] and DFT method modified by Gun'ko [18].
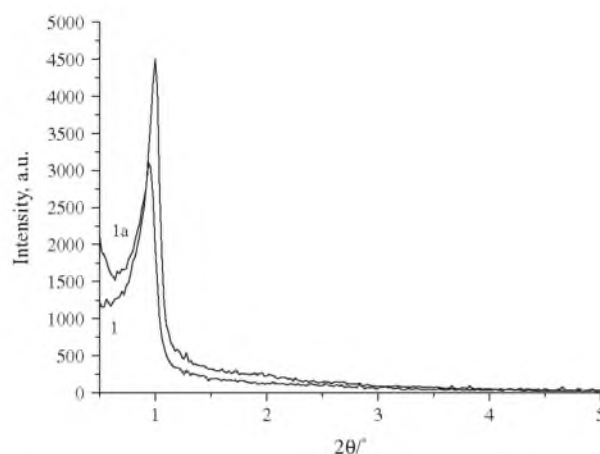

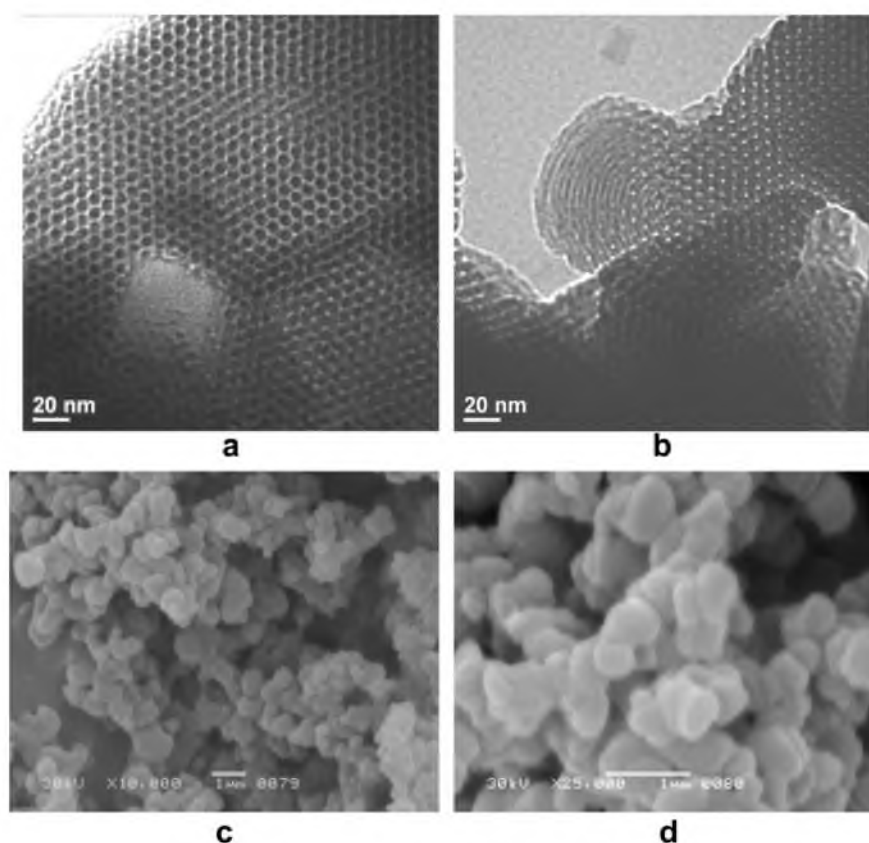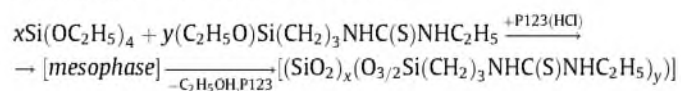**Fig. 1.** XRD of mesophase (1) and sample without template (1a).

Fig. 2. TEM (a and b) and SEM (c and d) microphotographs of mesoporous silica **1a**.

2.4. Sorption

Silver(I) and mercury(II) ions sorption from nitric acid solutions was conducted in static mode (the sorbent batch was 0.05 g, total solution volume ~20 cm³, pH value of the initial solution ~2.0, $t = 20$ °C). Ionic strength of the solution (0.1M) was created with 1M NaNO₃. Ag⁺ concentration in the initial solutions and in the filtrate was determined by atomic absorptive analyzer using 242.8 nm resonance signal on spectrophotometer C-115-M1 in depleted flame (acetylene/air mixture). The source of resonance radiation was spectral lamp LS-2. Mercury(II) content both in the initial solution and filtrate was determined by back compleximetric titration of the excessive EDTA with 0.05 M solution of MgSO₄ [19].

3. Results and discussion

Scheme of the synthesis of mesoporous sorbent with thiourea complexing groups is presented below.

$$x\mathrm{Si(OC_2H_5)_4} + y\mathrm{(C_2H_5O)Si(CH_2)_3NHC(S)NHC_2H_5} \xrightarrow{+P123(HCl)}$$
$$\rightarrow [mesophase] \xrightarrow[-C_2H_5OH,P123]{} [(\mathrm{SiO_2})_x(\mathrm{O_{3/2}Si(CH_2)_3NHC(S)NHC_2H_5})_y)]$$

It should be noted that there are two features of the developed technique of synthesis. Firstly, we used successive introduction of ETUS solution and the solution containing oligomeric TEOS hydrolysis products to the strongly acidic solution with P123 micelles. It was assumed that in this case, a significant part of complexing groups would be located on the inner, not the outer side of the silica framework enveloping these micelles. Secondly, HTT of mesophase was conducted, because the lack of such treatment leads to the formation of a spatially disordered structure.
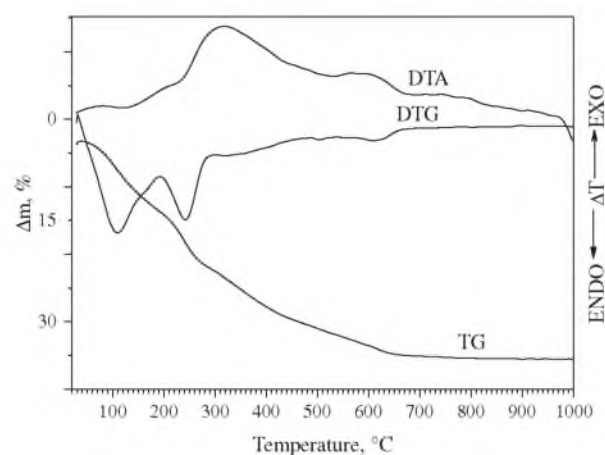

Fig. 3. Thermoanalytical curves for sample **1a**.

Template removal from mesophase (**1**) by boiling in acidified ethanol causes the appearance in the small 2θ angles region of diffractogram of the final product (**1a**) of more intense and narrower reflex ($d_{100} = 8.8$ nm) compared to the diffractogram of mesophase ($d_{100} = 9.4$ nm, see in Fig. 1). So, this procedure leads to the further spatial arrangement of the sample structure. X-ray diffraction analysis data were used to calculate the interplanar spacing d_{100}. This value and the sorption pore volume (see below) were used to calculate the size (diameter) of mesopores, which amounted to $d_{mesopores} = 7.6$ nm. The distance between the centers of pores $a_0 = 10.2$ nm, and the wall thickness between pores $h_w = 2.6$ nm. d_{100} and a_0 values for the synthesized sample (**1a**) are consistent
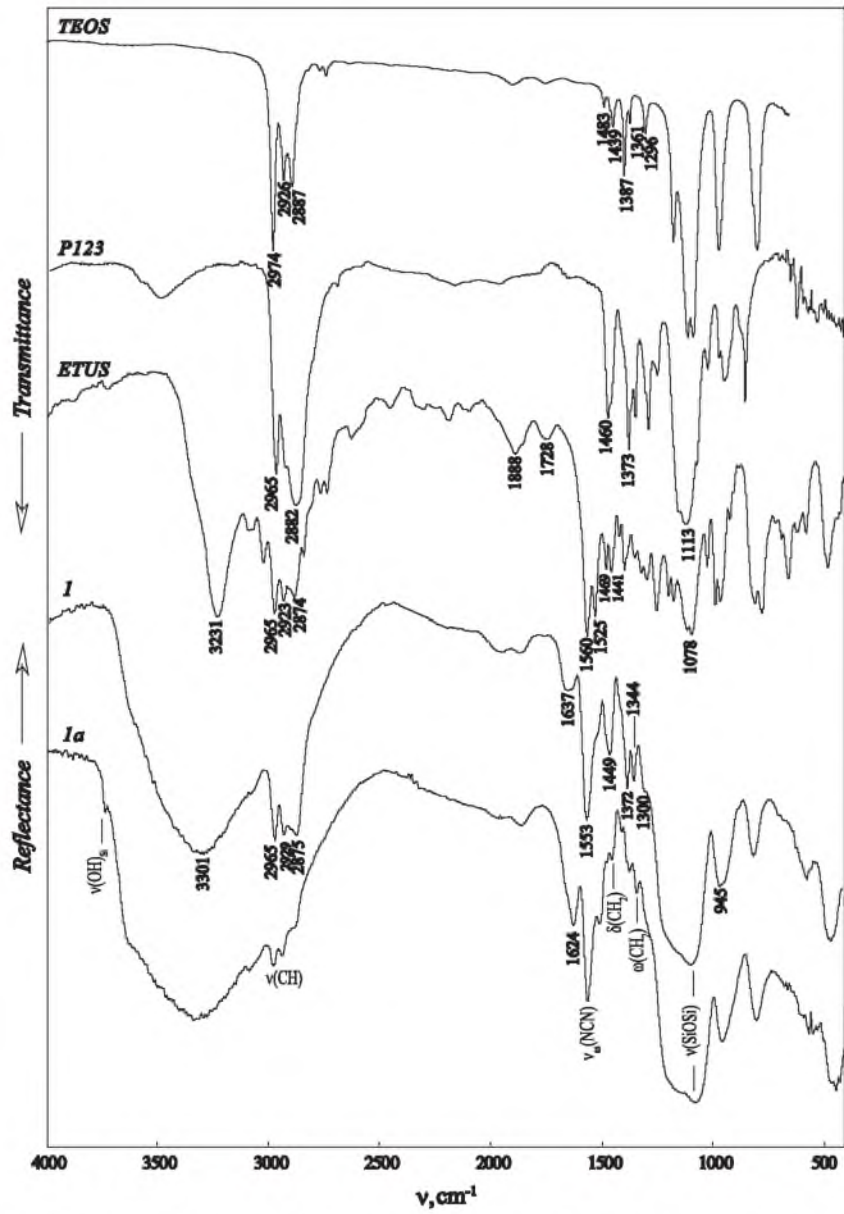
Fig. 4. FT-IR spectra of initial substances and synthesized samples: **1** – before template removal, **1a** – after template removal.
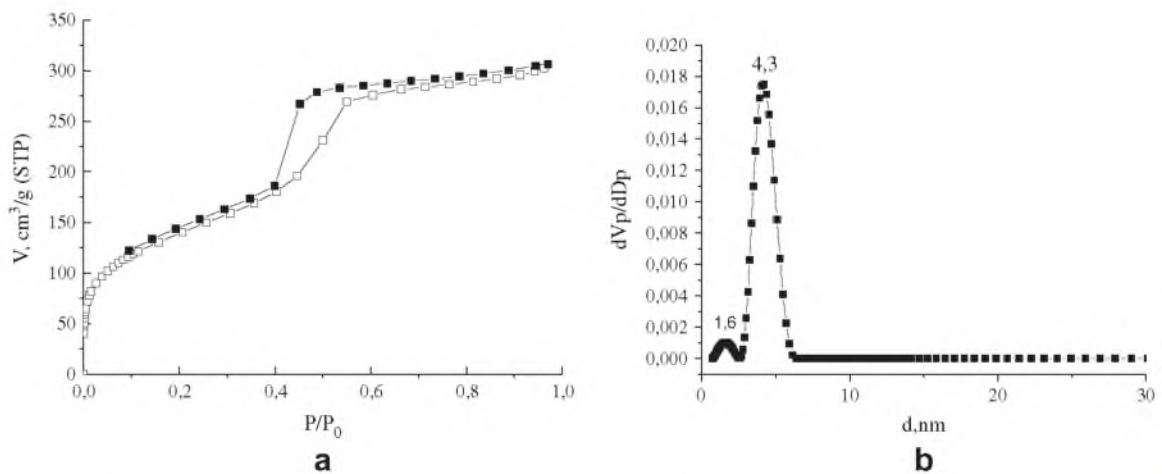

Fig. 5. Nitrogen adsorption (□)-desorption (■) isotherm for sample **1a** (a) and pore size distribution curve (b), built according to [18].

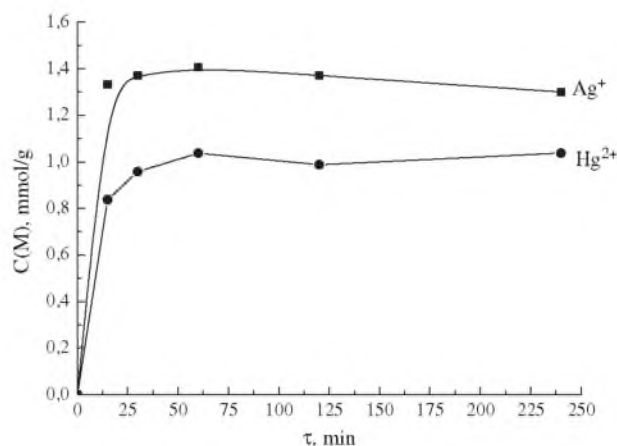**Fig. 6.** Kinetic curves of Ag$^+$ and Hg^{2+} ions sorption for sample **1a**.

with the results of other works on the synthesis of functionalized materials of SBA-15 type [20,21]. And the presence of one clear reflex in the region of small 2θ angles usually shows the formation of structure with hexagonal type lattice [22].

This conclusion is consistent with TEM data. The microphotographs in Fig. 2a and b clearly demonstrate the implementation of 2D structure in the synthesized sample, the elements of which are subjected to hexagonal symmetry. Fig. 2c and d presents SEM microphotographs of the same sample. According to them, it consists of small aggregates of almost spherical particles. The size of spherical particles is ~0.5 μm.

Thermogravimetry data analysis (Fig. 3) shows that in the range 100–130 °C with a maximum at ~110 °C, endothermic effect is observed. Obviously, its appearance is due to the removal of residual adsorbed water and ethanol. Moreover, the DTA curve registered no endothermic effect in this area. It is likely that this is due to the compensation processes of residual silanol groups condensation. The DTG registered clearly expressed exothermic effect in the range 200–300 °C with maximum at ~260 °C and recorded a significant weight loss. Rather, it is due to the oxidation and removal of sulfur-containing fragments. Finally, weight loss above 520 °C is associated with complete burnout of the organic residues, which is related to the appearance of exothermic effect in DTA curves. Thus, weight loss in the first region is 5%, in the second – 11%, and in the third – 16%, totaling to – 32% (Fig. 3). Note that surface layer of xerogels with similar groups burns out in the same temperatures ranges [23].

According to sulfur element analysis data (4.0% (mass)), the content of functional groups in the sample is 1.25 mmol/g. This value is close to group content calculated from the molar ratio of reacting alkoxysilanes (1.55 mmol/g) or from TGA data (1.45 mmol/g).

The presence of sulfur-containing groups $\equiv$Si(CH$_2$)$_3$NHC(S)NHC$_2$H$_5$ in the synthesized sample is confirmed by IR spectroscopy data. Thus, in the IR spectrum of the sample, washed from template (Fig. 4, spectrum **1a**), there is a narrow absorption band of medium intensity at 1556 cm^{-1}, which refers to ν_{as}(NCN) stretches of thiourea fragment —NH—C(S)—NH— [24]. In the spectrum of initial ETUS, it is located at 1560 cm^{-1}. The presence of ligand groups is proved by ν(NH) intense absorption band near 3300 cm^{-1} in the IR spectrum of the obtained sample, which is also typical for the original ETUS (Fig. 4). Presumably, it overlaps with ν(OH) absorption band of adsorbed water. Apart from this band, there are two absorption bands in the region 2875–3000 cm^{-1}, which can be attributed to the valence vibration of C—H bonds.

This indicates the presence of propyl and ethyl chains in the synthesized sample. The position and configuration of these bands differs significantly from those both in the IR spectra of mesophase (Fig. 4, spectrum **1**) and template (spectrum P123), which indicates the removal of template from mesophase. This conclusion is confirmed by a significant decrease in the intensity of three absorption bands in the 1340–1450 cm^{-1} region of IR spectrum of washed sample compared with the spectra of mesophase and P123.

Finally, it should be mentioned that the IR spectrum of synthesized sample has the most intense absorption band in the range 1077–1200 cm^{-1} with a high-frequency shoulder. Its presence is associated with the formation of three-dimensional polysiloxane framework [25]. This framework is connected not only to carbofunctional, but also to silanol groups; the existence of the latter is indicated by the presence of low-intensity absorption band at 3737 cm^{-1} in the IR spectrum of the washed sample (Fig. 4).

Nitrogen adsorption–desorption isotherm for synthesized sample presented in Fig. 5a has hysteresis loop of capillary condensation, which indicates the presence of mesopores. This is type IV isotherm according to the IUPAC classification [26] and is characteristic of SBA-15 type materials [27]. The following parameters of porous structure were calculated from the isotherm: $S_{sp.}$ = 510 m^2/g, V_s = 0.47 cm^3/g and d = 4.0 nm (calculated according to [17]) and 4.3 nm (according to [18]) (Fig. 5b). It should be noted that the calculated pore size is close to that assessed from TEM microphotographs (4.2–5 nm, Fig. 2b). The initial region of nitrogen adsorption isotherm (Fig. 5a) shows the presence of micropores in the sample, with average diameter of 1.6 nm according to the curve of pore size distribution (Fig. 5). These micropores can be formed in the walls of such type of samples [27].

We analyzed the sorption properties of the synthesized mesoporous sample with thiourea complexing groups on the example of silver(I) and mercury(II) ions. It was experimentally determined (see Fig. 6) that complete saturation of sample **1a** with silver(I) and mercury(II) ions was reached within 60 min. We can see that during 60 min sorb 1.4 mmol/g of silver(I) and 1.0 mmol/g of mercury(II) ions. In addition, it was easily calculated that the metal/ligand ratio was 1.1/1 for silver(I) and 0.8/1 for mercury(II), which is consistent with observations of other authors [28]. This ratio is related to the composition of the metal complexes. Finally, it should be noted that mesoporous samples containing thiourea groups are promising not only as sorbents. They may find application in catalysis [29] and other areas.

4. Conclusions

Thus, using surfactant P123 as template, it is possible to synthesize in strongly acidic environment mesoporous SBA-15 type silica with thiourea complexing group in the surface layer (at TEOS/ETUS ratio 10/1, group content reaches 1.25 mmol/g). According to TEM and XRD analysis, the obtained sample is characterized by highly-ordered spatial structure of the hexagonal lattice type. IR spectroscopy data confirm the presence of thiourea functional groups and three-dimensional framework of siloxane bonds ($\equiv$Si—O—Si$\equiv$) in the sample. Microspheres (about 0.5 μm in diameter) of the obtained functionalized silica adsorb 1.4 mmol/g of Ag(I) and 1.0 mmol/g of Hg(II) ions from acidified aqueous solutions for 60 min.

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