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Bridged Polysilsesquioxane Xerogels Functionalizated by Amine- and Thiol- Groups: Synthesis, Structure, Adsorption Properties

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Abstract. Bridged polysilsesquioxane xerogels containing amine ($-NH_2$; $-NH(CH_2)_2NH_2$; $=NH$) and thiol ($-SH$) groups were synthesized by hydrolytic polycondensation of 1,2-bis(triethoxysilyl)ethane, 1,4-bis(triethoxysilyl)benzene and appropriate trifunctionalized silanes in the presence of a fluoride-ion catalyst in an ethanol solution. ^{29}Si CP/MAS NMR give indication of the molecular framework of these materials formed by structural T^1, T^2 and T^3 units. 3-aminopropyl or 3-mercaptopropyl groups accessible to proton or metal ions are fixed to the xerogel surface by the siloxane bonds. IR and ^{13}C CP/MAS NMR data clearly show that 3-aminopropyl groups form hydrogen bonds. The same data testify that all xerogels contain non-condensed silanol groups and some fraction of non-hydrolyzed ethoxygroups.

Functionalized polysilsesquioxane xerogels obtained by means of organic spacers have a porous structure (500–1000 m^2/g) and a high content of functional groups (1.0–2.7 mmol/g). AFM data indicate that xerogels are formed by aggregating primary particles—the size of such aggregates is in the range 30–65 nm. It was established that the main factors influencing the structure and adsorption properties considered hybrid materials are: the nature and geometrical size of the functional groups, spacer flexibility and, in some cases, the ratio of the reacting alkoxysilanes and the ageing time of the gel.

Keywords: sol-gel method, functionalized bridged, polysilsesquioxane xerogels, porosity, hybrid materials

1. Introduction

Modern sorption technologies use adsorbents with high advanced porous surfaces, high values of static sorption capacity, selective properties and stability in aggressive environments (Dabrowski, 2001). The techniques of synthesis of such adsorbents should be simple and easy for reproduction. Furthermore, the methods underlying the synthesis of such materials should give an opportunity for affecting physico-chemical and structure-adsorption characteristics of the final product. From this point of view the bridged polysilsesquioxane (BPS) xerogels are attractive compounds which can be obtained by the sol-gel method (Loy and Shea, 1995). The sol-gel method deals with one-stage process and the possibility of using “mild” conditions of synthesis (Brinker and Sherer, 1990).

BPS xerogels are a class of hybrid organic–inorganic materials, formed by molecular building blocks. Such building units include a bridge of organic origin which links two or more Si atoms by forming hydrolytically stable Si—C bonds. The simplest precursors of BPS xerogels can be presented as bis(trialkoxysilanes) structures $(RO)_3Si-R'-Si(OR)_3$, where R is the methyl or ethyl radical, and R' denotes the organic bridge (spacer). By means of the appropriate precursors in the reaction of hydrolytic polycondensation it is possible to design on a molecular level the considered materials keeping control over their characteristics (Shea et al., 2001; Cerveau et al., 2001). Bridges (R′) between alkoxysilyl groups can have a different nature, e.g. they can be representative of homologue series of saturated hydrocarbons (Oviatt et al., 1993) or aromatic hydrocarbons (Shea et al., 1992). In addition, apart from a different composition, they have a different length, form and, in consequence, rigidity. Hence, changing the nature and geometry of organic bridges it is possible to influence, both the chemical and physical properties, including structure–adsorption characteristics. For example, an increase of the length of a carbon backbone chain in homologue series alken–bridged polysilsesquioxane xerogels results in a reduction of the value of a specific surface area: from 729 m^2/g (for two methylene units in chain) to 94 m^2/g (for 10 units in chain) (Oviatt et al., 1993). Xerogels obtained in the acid medium are non porous if the number of carbon atoms in organic bridge is more than five. Xerogels synthesized in the alkaline medium with the same number of carbon atoms keep a high value of a specific surface area. Furthermore, at the same length of the organic bridge, formation of mesoporous materials is observed in the alkaline medium, while in the acid medium—formation of microporous ones. Thus, pH of the reactionary medium (the nature of the catalyst) essentially influences the textural characteristics of BPS xerogels, which is typical of the sol-gel method based on the hydrolytic polycondensation reaction. The influence of both factors mentioned above—as well as other factors—on textural characteristics of BPS xerogels has been described previously in the literature (Shea et al., 2001; Cerveau et al., 2001).

BPS xerogels are widely used in sorption technologies so there is a high demand for advanced synthesis methods, especially sol-gel methods. BPS xerogels functionalized by different functional groups during the reaction of hydrolytic polycondensation become specific materials for sorption technologies. Fuctionalized BPS xerogels keep the advantages proper to BPS xerogels (genetically connected with them). Obviously, the set of factors influencing the physico-chemical and structure-adsorption characteristics of the functionalized xerogels are different than in the case of BPS xerogels.

The main goal of this work is to use the sol-gel method for a synthesis of the BPS xerogels functionalized by amine- and thiol- organic groups, and to find the factors influencing the formation of the porous structure of such nitrogen- and sulfur-containing adsorbents.

2. Experimental Part

Initially the following compounds were used: 1,2-bis(triethoxysilyl)ethane, $[(C_2H_5O)_3Si]_2C_2H_4$ (BTESE, 96%, Aldrich); 1,4-bis(triethoxysilyl)benzene, $[(C_2H_5O)_3Si]_2C_6H_4$ (BTESB, obtained according to the method described in (Shea et al., 1992)); 3-aminopropyltriethoxysilane, $(C_2H_5O)_3Si(CH_2)_3NH_2$ (APTES, 98%, Aldrich); bis[3-(trimethoxysilyl)propyl]amine, $[(CH_3O)_3Si(CH_2)_3]_2$-NH (BTMPA, 95%, ABCR); *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH_2$ (TMPED, 97%, Aldrich); 3-mercaptopropyltrimethoxysilane, $(CH_3O)_3Si(CH_2)_2SH$ (MPTMS, 95%, Aldrich); NH_4F (98%, Aldrich). Ethanol was absolutizated before according to (Gordon et al., 1972).

Synthesis of xerogels with 3-aminopropyl functional group (structure-forming agent—BTESE; ratio BTESE/APTES = 4:1 and 2:1—samples **1** and **2** respectively). To the solution of 0.04 mol (or 0.025 mol in the case of sample **2**) BTESE in 15 cm^3 ethanol (or 7 cm^3 in the case of sample **2**) a solution of NH_4F was added (0.9×10^{-3} mol NH_4F in 0.135 mol water (or 0.63×10^{-3} mol in 0.094 mol)). After 5 min to this mixture 0.01 mol APTES in 15 cm^3 ethanol (or 0.0125 mol in 7 cm^3) was added. Stirring stopped after a minute. Transparent gel formed in a few minutes, opalescence was observed. After 30 days, the gel was pounded and dried in vacuum at 20/50/105 °C for 2 h at each temperature.

Synthesis of other amino-containing xerogels (structure-forming agent—BTESE; ratio BTESE/BTMPA and BTESE/TMPED = 4:1—samples **3** and **4** respectively). To the solution 0.04 mol BTESE in 15 cm^3 ethanol a solution of NH_4F (1×10^{-3} mol NH_4F in 0.15 mol water (or 0.9×10^{-3} mol in 0.135 mol water in case of a sample **4**)) was added. After 5 min to this mixture 0.01 mol BTMPA (or 0.01 mol TMPED) in 15 cm^3 ethanol was added. Stirring stopped after a minute. Transparent gel formed in a few minutes, opalescence was observed. After 30 days the gel was pounded and dried in vacuum similarly to the previous samples.

Synthesis of xerogels with 3-mercaptopropyl functional group (structure-forming agent—BTESE; ration BTESE/MPTMS = 4:1 and 2:1—samples **5** and **6** respectively). To the solution 0.04 mol (or 0.025 mol) BTESE in 15 cm^3 ethanol (or in 7 cm^3 in the case of a sample **6**) a solution of NH_4F (0.9×10^{-3} mol NH_4F in

0.135 mol water (or 0.63×10^{-3} mol in 0.094 mol)) was added. After 5 min to this mixture 0.01 mol MPTMS in 15 cm^3 ethanol (or 0.0125 mol in 7 cm^3) was added. Transparent gel formed in a few minutes, opalescence was observed. After 30 days the gel was pounded and dried in vacuum at 20/50/105 °C for 2 h at each temperature.

Synthesis of xerogels with 3-aminopropyl functional group (structure-forming agent—BTESB; ratio BTESB/APTES = 4:1 and 2:1—samples **7** and **8** respectively). The techniques of synthesis of these samples were similar to the techniques of synthesis of samples **1** and **2** respectively, with the exception of the ageing time of the gels, which amounted to 14 days.

Synthesis of xerogels with a secondary amino group (structure-forming agent—BTESB; ratio BTESB/BTMPA = 4:1—sample **9**). The technique of synthesis of this sample was similar to the techniques of synthesis of sample **3** with the exception of the ageing time of the gels, which amounted to 14 days.

Synthesis of xerogels with 3-mercaptopropyl functional group (structure-forming agent—BTESB; ration BTESB/MPTMS = 4:1 and 2:1—samples **10** and **11** respectively). The techniques of synthesis of these samples were similar to the techniques of synthesis samples **5** and **6** respectively with the exception of the ageing time of the gels, which amounted to 14 days.

Synthesis of sample **12** at a ratio BTESB/MPTMS = 2:1 carried out like the synthesis of sample **11**, but the ageing time of the gel was 30 days.

The contents of the amino groups in the obtained samples were determined by reverse acid–base titration (Zub et al., 2002). Concentration of the thiol groups was determined by a method of reverse complexometric titration of an excess of the standard solution of silver nitrate by unitiol in 0.1 M HNO_3 medium. As a metallochrome indicator di(*p*-sulfophenyl)thiocarbazone was used (Pilipenko et al., 1989).

Scanning electron micrographs (SEM) were recorded on the Tesla BS301 microscope (Czech Republic) upgraded with the digital imaging system "Satellite". In order to avoid the electrostatic effect the studied samples were coated with thin layer gold/palladium film on Polaron SC 7640 sputter coater (U.K.). TEM micrographs of the samples were carried out using the Tesla BS 540 (Czech Republic) apparatus. The investigated samples were prepared by the platinum-carbon replication method with evaporation of platinum and a low amount of carbon on the adsorbent surface then treated in hydrofluoric acid to dissolve the inorganic silica matrix. AFM images were received using MultiMode Scannig Probe Microscope "Nanoscope III" (Digital Instruments). The imaging technique was TappingMode. Characteristics of TappingMode Etched Silicon Probes were: spring constant (k) 20–100 N/m; resonant frequency 200–400 kHz; the nominal tip radius of curvature was 5–10 nm; the cantilever length was 125 μm; cantilever configuration was a single beam; reflective coating was uncoated (optional Al coating). The scan size was 500 or 1000 nm.

The DRIFT spectra were recorded on the Thermo Nicolet Nexus FT-IR at 4 cm^{-1} resolution using the Spectra Tech collector diffuse reflectance accessory at room temperature. The samples were mixed with KBr (1:30) and were used to fill the DRIFT sample cup before measurements. All the solid-state NMR measurements were completed on a Bruker Avance 300 MHz spectrometer. The settings for acquiring the ^{13}C CP/MAS NMR at 75.5 MHz were as follows: the relaxation delay was 3.0 s, contact time was 1.00 ms. The number of scans was 1024–2048 and the spin rate was 8800 Hz. The settings for ^{29}Si CP/MAS NMR at 59.7 MHz were as follows: the relaxation delay was 3.0 s and contact time 2.5 ms. The number of scans was 1024–4096 and the spin rate was 8800 Hz. TMS was used as the standard for the NMR experiments.

Nitrogen adsorption isotherms were measured at −196°C by using an ASAP–2405N adsorption analyzer (Micromeritics, Inc.) and used to evaluate the BET specific surface area (Brunauer et al., 1938). Prior to adsorption measurements each sample was degassed (at 150°C for samples containing amino groups and at 120°C for samples containing thiol groups). The BET surface area (S) was evaluated in the 0.05–0.35 range of relative pressures. The total pore volume (V) was calculated by converting the amount adsorbed at a relative pressure about 0.99 to the volume of liquid adsorbate. The average pore size was estimated using the BJH method, which is valid for cylindrical pores. Pore size distributions were estimated using the same approach (Barrett et al., 1951).

3. Results and Discussion

For obtaining BPS xerogels functionalized by amino— and thiol— groups the reaction of hydrolytic polycondensation of BTESE (or BTESB) and amino-containing alkoxysilan (or MPTMS) was used (see scheme below).

$$\begin{aligned}&(C_2H_5O)_3Si - R' - Si(OC_2H_5)\\&+ (RO)_3Si(CH_2)_3R'' \xrightarrow[-ROH]{+H_2O/F^-}\\&\longrightarrow [(O_{3/2}Si)_2R']_x(O_{3/2}Si(CH_2)_3R'')_y,\end{aligned}$$

where R = Me or Et; $R' = (CH_2)_2$ or C_6H_4, and $R'' = -NH_2$; $-NH(CH_2)_2NH_2$; 1/2 = NH; −SH.

The molar ratio of "bis(trialkoxysilane)/trifunctional silane" in reacting systems was 2:1 and 4:1. The choice of such a ratio was caused, first of all, by a desire to achieve the high maintenance of functional groups in the final xerogel. On the other hand, such a molar ratio allows the search for the optimal mode of synthesis of the xerogels. It means, for example, avoidance of momentary formation of gels at the mixing of the reactionary solutions that is often observed at the increase in the reacting system of the relative quantity of trifunctional silane. Because of the presence a basic amino ($-NH_2$; $-NH_2(CH_2)_2NH_2$; = NH) groups in samples **1**–**4**, **7**–**9** and an acidic thiol (−SH) groups in samples **5**, **6**, **10**–**12** it was impossible to use only acidic or basic catalyst in all samples. To keep similar conditions of synthesis at differ acid-base nature of the functional groups such a strong nucleophil as fluoride-ion (F/Si = 1–1.5/100 (mol)) was used as a catalyst (Cerveau et al., 2001). Previous investigations had also shown that when a solvent was missing from the systems like BTESE/APTES inhomogeneous gelation was observed. Therefore in future ethanol will be used in all cases while carrying out the reaction of hydrolytic polycondensation. The choice of such a non-aqueous solvent was made because of its low toxicity, good solvate ability regarding to the majority of alkoxysilanes, the ability of retarding a path of the hydrolysis reaction of ethoxysilanes. Moreover, it was determined (Shvaykovska et al., 2004) that a pre-hydrolysis of BTESE and BTESB is necessary—in this case a smooth transition was observed from sol to gel at the subsequent introduction of trifunctional silanes in the system. The above-mentioned transition, i.e. the gelling time amounted to 1–40 min. But even during the prior hydrolysis of bis(triethoxysilanes) the minimal ageing time was 14 days—in the case of BTESB as a structure-forming agent—and 30 days in the case of BTESE as a structure-forming agent. When the ageing time of gels decreased, the polycondensation process was observed as incomplete, what produced formation of low-polymeric products of a different structure, volatile in the vacuum (Shvaykovska et al., 2004). It must not be ruled out that the ageing time is determined by the quantity of water taken for hydrolysis—in the present conditions of synthesis it makes 1/2 of stoichiometric quantity (i.e. the quantity necessary for carrying out the hydrolysis of all the alkoxygroups). However, most likely, the essential influence on the ageing time of gels in such systems causes the presence of trifunctional silanes since at the gelation of a one-component system the ageing time of the gel for BTESB is only 48 days (Shea et al., 1992), and for BTESE–14 days (Oviatt et al., 1993). During the time in the obtained gels opalescence was observed; synergism practically was not observed. Drying in vacuum the milled glassy gels resulted in the required xerogels.

The synthesized xerogels are white (or yellow—in the case of samples **3** and **4**) powdery compounds, insoluble in water and non-swelling in nonaqueous solvents. SEM microphotographies of some xerogels are represented in Fig. 1. At small magnification it can be seen that they consist of irregularly-shaped particles of different sizes (Fig. 1, samples **4**, **6**, **7**, **12**). Most of these particles have a glassy fracture (see e.g. samples **2**, **6**, and **12** on Fig. 1). At a higher magnification (see for example Fig. 1, samples **11** and **12**) for all samples on a smooth surface, as a rule, granularity appears caused by compactly packed particles of the spherical form.

The content of functional groups in the synthesized xerogels was estimated in terms of the back titration and is presented in Table 1. For all samples this content is close to the estimated values based on the ratio of the reacting alkoxysilanes. Thus, the ratio of the Si-containing components given at the beginning of synthesis is practically the same as in the final xerogels. But in all cases, especially at the ratio 2:1 of the reacting alkoxysilanes, the content of the functional groups in the xerogels is several times greater than for samples obtained by the method of surface modification of silica by APTES or MPTMS (Lisichkin, 2003; Zaitsev, 1997; Vansant et al., 1995).

All the synthesized xerogels were identified by IR spectroscopy. It should be noted that the IR spectra of samples which were synthesized using the same bis(triethoxysilane) are similar (see Fig. 2, samples **2**, **6** and **8**, **11**). A characteristic property of the IR spectra of all xerogels is the presence of the most intensive and widest absorption band in the region 1010–1075 cm^{-1} which, as a rule, has a high-frequency

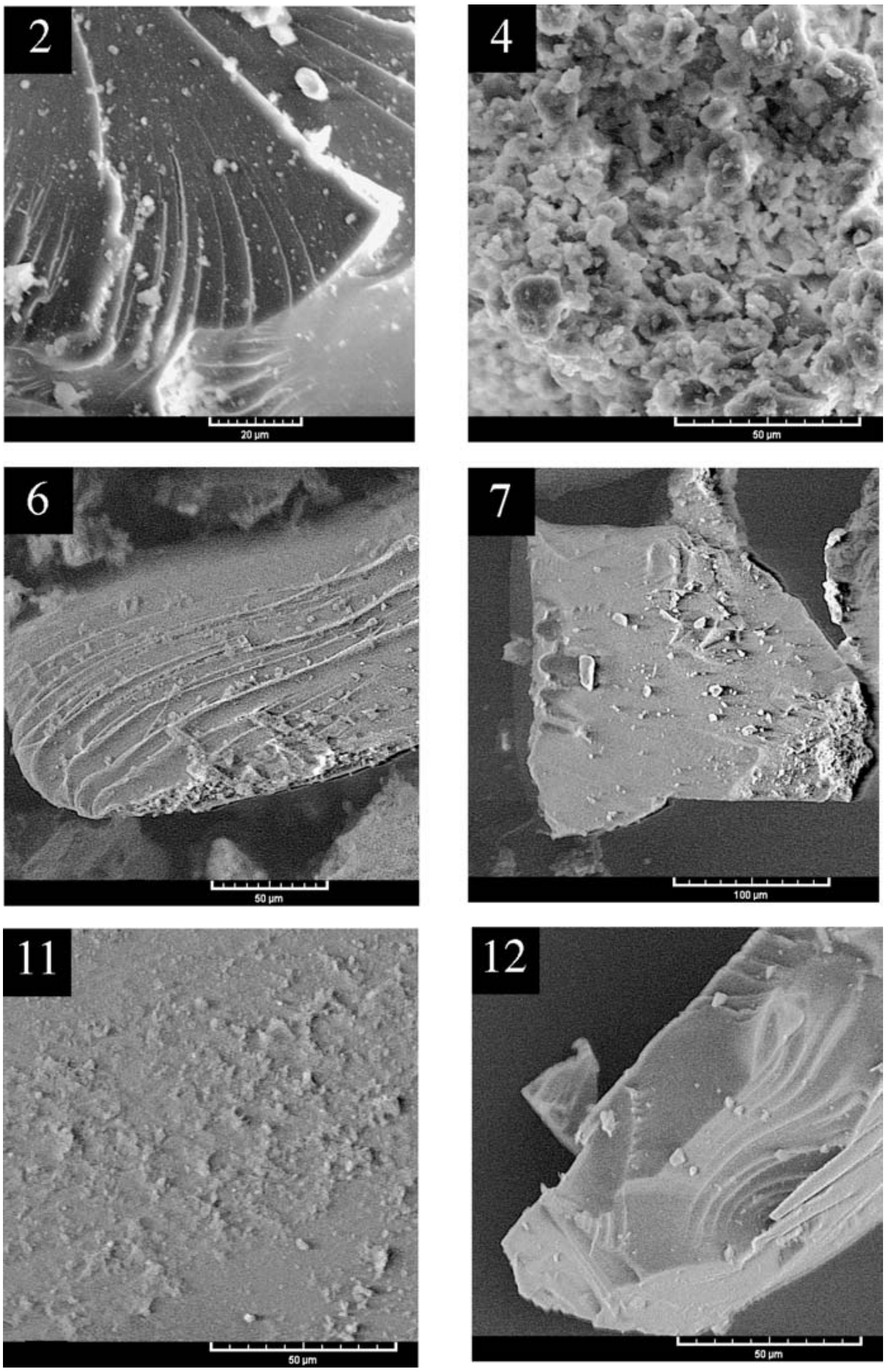


Figure 1. Scanning electron micrographs of xerogels obtained: **2** (2000×), **4** (1600×), **6** (1000×), **7** (680×), **11** (1600×), and **12** (1600×).

shoulder at 1100–1130 cm^{-1}. The occurrence of this absorption band in the IR spectra of functionalized polysiloxanes is connected with stretching the vibrations of the $\equiv$Si—O—Si$\equiv$ bonds of siloxane framework, which carry the carbofunctional group Si—C$_n$—R$''$ (Finn et al., 1975). In the spectra of xerogels obtained using BTESE, this band is in the region of 1014–1027 cm^{-1}. This fact testifies to considerable influence

Table 1. Some synthetic conditions and structure-adsorption characteristics of obtained xerogels

						Structure-adsorption characteristics		
Sample	Spacer (R')	Functional group (R'')	Initial ratio of alkoxysilanes	Ageing time (days)[a]	Content of functional groups (R''), (mmol/g)	S_{sp} (m^2/g)	V_s, cm^3/g	*d* (nm)
1	$-C_2H_4-$	$-(CH_2)_3NH_2$	4:1	30	1.4[b] (1.6)[c]	611	1.490	15.0
2	$-C_2H_4-$	$-(CH_2)_3NH_2$	2:1	30	2.5 (2.8)	638	0.946	7.8
3	$-C_2H_4-$	$=[(CH_2)_3]_2NH$	4:1	30	1.7 (1.6)	565	1.137	7.1
4	$-C_2H_4-$	$-(CH_2)_3NH(CH_2)_2NH_2$	4:1	30	1.3 (1.6)	516	1.015	6.0
5	$-C_2H_4-$	$-(CH_2)_3SH$	4:1	30	1.9 (1.6)	834	0.543	2.8
6	$-C_2H_4-$	$-(CH_2)_3SH$	2:1	30	2.5 (2.8)	630	0.418	3.0
7	$-C_6H_4-$	$-(CH_2)_3NH_2$	4:1	14	1.4 (1.2)	911	0.717	3.0
8	$-C_6H_4-$	$-(CH_2)_3NH_2$	2:1	14	2.6 (2.2)	926	0.823	3.2
9	$-C_6H_4-$	$=[(CH_2)_3]_2NH$	4:1	14	1.0 (1.1)	654	0.503	3.0
10	$-C_6H_4-$	$-(CH_2)_3SH$	4:1	14	1.0 (1.2)	968	0.601	3.6
11	$-C_6H_4-$	$-(CH_2)_3SH$	2:1	14	2.7 (2.2)	932	0.684	3.0
12	$-C_6H_4-$	$-(CH_2)_3SH$	2:1	30	2.1 (2.2)	698	0.424	2.8

[a] Influence of the ageing time on the structure of gels was discussed in the text.
[b] From the data of titration.
[c] Theoretical content of the functional groups.

of cyclic organosiloxane structures on the architecture of the material frame (Loy, Carpenter et al., 1999). In the IR spectra of xerogels obtained using BTESB, this band is in the region of higher frequencies (1041–1074 cm^{-1}). Furthermore, for these samples a specific spectral curve is observed, namely: with an additional maximum at 1153 cm^{-1}, which practically has identical intensity to the basic catalyst. This picture is characteristic also of the phenyl-containing xerogels obtained using tetraethoxysilane (TEOS) as a structure-forming agent (Finn et al., 1975).

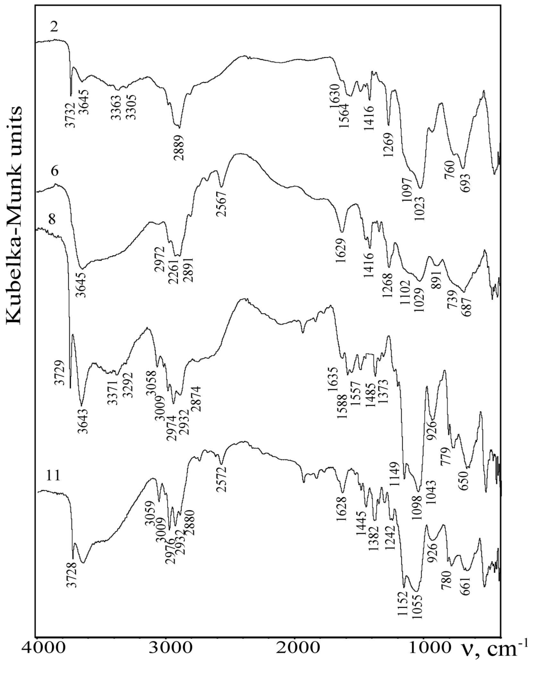


Figure 2. IR spectra of xerogels **2**, **6**, **8** and **11**.

The presence of the $-CH_2-$ link in the ethylene spacer, and also in the propyl chain, which attaches thiol- and amino-groups to silicon surface atoms of the synthesized xerogels, is indicated by a group of absorption bands in the region 2875–2980 cm^{-1}. They are characterized by stretching vibrations of $\nu_{s,as}$(CH). The presence of $\equiv Si-CH_2-CH_2-Si\equiv$ bridge also is indicated by bands in the region ~1270 cm^{-1} and ~1416 cm^{-1}, which can be referred to $\omega(CH_2)$ and to $\delta(CH_2)$. In the IR spectra of samples **7**–**12** in the region 3000–3060 cm^{-1} the absorption bands of ν(CH) are presented, which testify to the presence of an aromatic fragment $\equiv Si-C_6H_4-Si\equiv$. It was verified by identification in the IR spectra of these samples and others of medium adsorption bands (e.g. at 779 cm^{-1}) which are proper to the derivative BTESB. It should be noted that in the interval ~2973–2977 cm^{-1} of the IR spectra of all xerogels a sharp absorption band is fixed, which exists in both initial bis(triethoxysilanes). Its intensity—in comparison with other absorption bands in this region—grows at the increase in a ratio of "bis(triethoxysilane)/trifunctional silane" in an initial solution. Undoubtedly, this band is linked up with the stretching vibrations of C—H bonds of the ethoxygroup. It is indirectly testified by the gradual decrease of its intensity at the increase in the ageing time of gels (Shvaykovska et al, 2004). Therefore, the presence of this band is evidence of the presence of the ethoxy-groups. At the same time, in the IR spectra of all samples at ~3730 cm^{-1} a sharp medium intensity absorption band is identified (Fig. 2) whose occurrence is caused by valence vibrations of ν(OH) silanol groups that were formed as a result of a hydrolysis of the ethoxysilyl groups. Below this band, up to 3100 cm^{-1}, in the IR spectra of all samples a wide absorption band with an intensive peak is fixed at ~3645, which is attributed to the valence vibrations of ν(OH) for the adsorbed water. Against a background of this band in the region of 3300–3370 cm^{-1} the occurrence of two low-intensity absorption bands typical for the valence vibrations of the $\nu_{s,as}$(NH) amino groups is observed. Besides, in the IR spectra of samples **1**, **2**, **4**, **7** and **8** in the region 1550–1590 cm^{-1} one or two low-intensity absorption bands are identified which can be related to $\delta(NH_2)$, as in the IR spectra of initial alkoxysilanes - BTESE, BTESB and APTES. In this area there are no absorption bands (low-intensity absorption bands at ~1630 cm^{-1} in the IR spectra of xerogels correspond to $\delta(H_2O)$). If we take into consideration the fact that in an IR spectrum of the initial APTES an absorption band which corresponds to $\delta(NH_2)$ is in a higher-frequency region (1602 cm^{-1}), it is possible to draw a conclusion about the participation of amino groups of xerogels in hydrogen bonding. Moreover, in some samples it is realized in two forms. A low-intensity absorption band at ~2570 cm^{-1} testifies to the existence of thiol groups in samples **5**, **6**, **10**–**12**, which refers to ν(SH). Thus the xerogels obtained contain adsorbed water, siloxane bonds, thiol and amine groups (the latter take part in the formation of hydrogen bonds) which were entered during a synthesis by corresponding trifunctional silane, residual silanol groups.

The above results are confirmed by solid-state NMR data. In Fig. 3 ^{13}C CP/MAS NMR spectra of xerogels **2** and **8** which contain 3-aminopropyl groups, and xerogels **6** and **11**, which contain 3-mercaptopropyl groups, are presented. Each of these spectra has one of the most intensive signals, which corresponds to the carbon atoms of the spacer. In the spectra of samples **2** and **6**, which contain the bridge of structure ≡Si—CH_2—CH_2—Si≡, this signal is at 5.1 and 4.8 ppm respectively, and in the spectra of samples **8** and **11**,

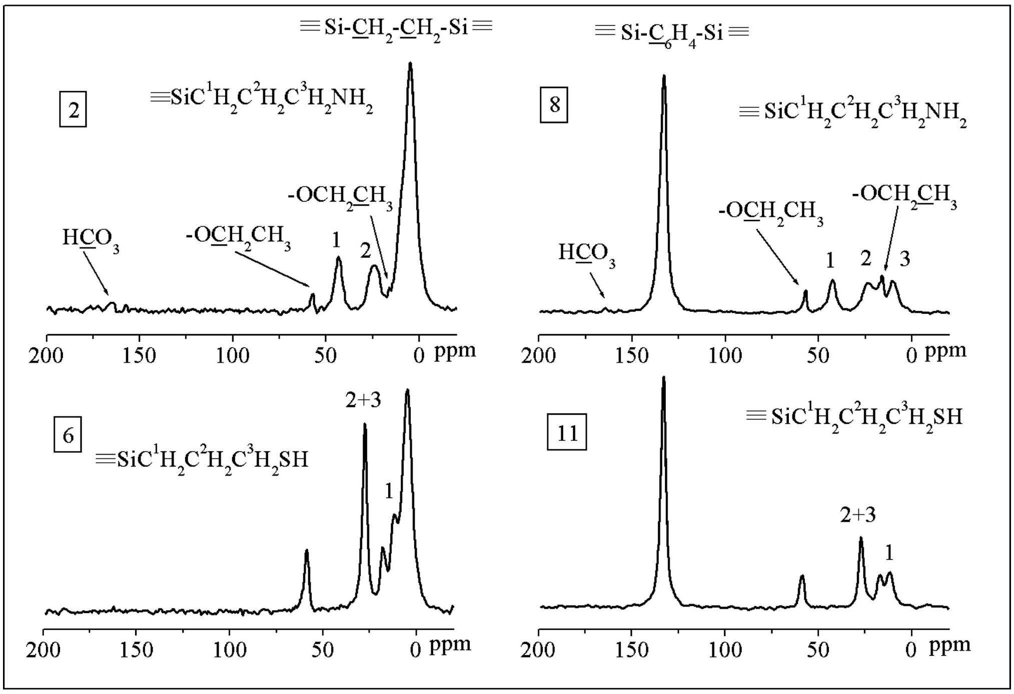


Figure 3. ^{13}C CP/MAS NMP spectra of xerogels **2**, **6**, **8**, and **11**.

which contain the bridge of structure ≡Si—C_6H_4—Si≡, it is at 133.2 ppm. It is necessary to note that all the spectra contain two low intensity signals at 16–18 and 57–59 ppm, which correspond to the carbon atoms of ethoxygroups. Since all the xerogels were dried in high vacuum, these signals betoken to the existence of non-hydrolized ethoxygroups. A similar situation is observed in the case of BPS xerogels (Shea et al., 1992; Oviatt et al., 1993).

It is known that the 3-aminopropyl group in the ^{13}C CP/MAS NMR spectra has three signals: at ∼10 (≡$SiCH_2$), ∼22–28 (CCH_2C) and ∼43 ppm (CH_2NH_2) (Maciel, 1998). However, in the spectra of sample **2** the first signal is not identified as it is masked by an intensive and wide signal of the carbon atom of the ethylene spacer (Fig. 3). In the spectrum of sample **8**, where the signal of atom *C* of the phenylene-spacer comprises in another region, this signal is observed at 10.7 ppm (Fig. 3). The signals of the *C* atom of other methylene groups are located at 23.8 (**2**); 23.9 (**8**) and 43.3 (**2**); 42.7 (**8**) ppm respectively. The region of the location of a signal draws attention to itself from the central carbon atom of the 3-aminopropyl chain (∼23 ppm) and its broadening. It can betoken to a participation of the amino group in the non-uniform hydrogen bond (Maciel, 1998). This conclusion agrees with the conclusion which was reached on the basis of data IR spectroscopy (see below). A low-intensity signal at ∼165 ppm in the ^{13}C CP/MAS NMR spectra of amino-containing xerogels (samples **2** and **8**) most probably belongs to the C atom of a hydrocarbonate anion, which in a trace quantity is formed at the contact of xerogels with air. In the presence of water steam CO_2 is chemisorbed on their surface with the formation of alkylammonium hydrocarbonate which easily decomposes while heating the samples above 100deg;C (Culler et al., 1983). A similar fact was published both after investigation of silica modified by APTES (Zaper et al., 1985), and amino-containing xerogels synthesized using TEOS as a structure-forming agent (Zub, et al., 2002).

A 3-mercaptopropyl group often has not three, but only two signals in ^{13}C CP/MAS NMR unlike 3-aminopropyl groups (Maciel, 1998). A similar situation is observed in the spectra of samples **6** and **11**—they contain signals at 11.8, 11.7 and 27.5, 27.1 ppm respectively, which corresponds to atoms of carbon of the methylene groups ≡$SiCH_2$ and CCH_2C + CH_2SH (Fig. 3). As a consequence, the second signal is more intensive in comparison with the first one.

The analysis of the ^{29}Si CP/MAS NMR spectra of synthesized xerogels (some of them are displayed in Fig. 4) leads to the conclusion regarding the stability of

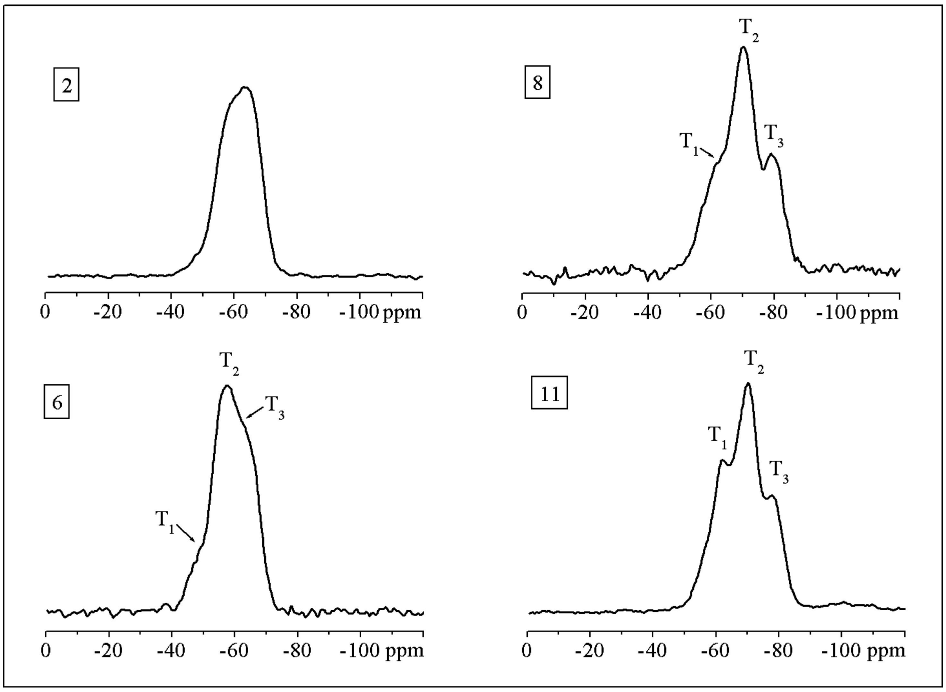


Figure 4. ^{29}Si CP/MAS NMP spectra of xerogels **2**, **6**, **8**, and **11**.

the ≡Si—C bond in alkoxysilanes during the reaction of hydrolytic polycondensation. The absence of any signals in the region of (−90)–(−110) ppm underlies such a statement. Secondly the presence of the group of intensive resonance signals in the range of (−48)–(−66) ppm in the case of samples **1**, **2** and **6** and in the region of (−60)–(−80) ppm in the case of samples **7**, **8** and **11** indicates the existence of structure units of a T^n type ($n = 1$, $-Si(OR)_2(OSi)$; $n = 2$, $-Si(OR)(OSi)_2$; and $n = 3$, $-Si(OSi)_3$, R = Et, Me or H) and the absence of completely non-hydrolyzed structure units of T^0 composition. It is well-defined in the case of three last samples with the bridge of $\equiv Si-C_6H_4-Si\equiv$ type. Thus the ^{29}Si CP/MAS NMR spectrum of sample **11** (Fig. 4) contains three well separated resonance signals at −61.7, −69.9 and −77.7 ppm, that are correspondent to the T^1, T^2 and T^3 structure units, respectively (Shea et al., 1992). The same signals are observed in the case of sample **8** (Fig. 4)—respectively at −62.0, −70.3 and −78.9 ppm. It should be noted that their position is close enough to the position of corresponding signals in the ^{29}Si CP/MAS NMR spectrum of xerogel synthesized in an alkaline medium using BTESB (Shea et al., 1992). But in the case of samples **1**, **2** and **6**, which contain a spacer of structure $\equiv Si-C_2H_4-Si\equiv$, these resonance signals begin to merge. This effect was observed also by (Oviatt et al., 1993) for ethylene-bridged xerogels. However, if in a ^{29}Si CP/MAS NMR spectrum of the last sample (Fig. 4) they can be identified (respectively at −49.5, −57.2 i −65.5 ppm, which practically coincides with the position of the same signals in a spectrum of xerogel synthesized in an alkaline medium using only BTESE (Oviatt et al., 1993)), then in the case of samples **1** and **2** (see Fig. 4, sample 2) one wide and dissymmetric resonance signal is observed. Obviously, it contains two signals of close intensity which overlap in the interval (−55)–(−65) ppm. Moreover, a low-intensity shoulder of one more signal is identified at –48 ppm. Thus, and in the case of xerogels with a bridge like $\equiv Si-C_2H_4-Si\equiv$ (samples **1**, **2** and **6**) their structure is a combination of the same units—T^1, T^2 and T^3. It should be noted that in the case of xerogels with an ethylene spacer signals from these structure units as products of BTESE hydrolysis and polycondensation (Oviatt et al., 1993) are situated in practically the same ranges as those from analogous structure units that are formed in the case of trifunctional silanes (e.g. APTES or MPTMS) hydrolysis and polycondensation (Maciel, 1998; Zub, et al., 2002). But in the case of xerogels with a phenylene spacer a range of signals T^n, which are the products of BTESB hydrolysis and polycondensation is situated in stronger fields (Shea et al., 1992). Therefore, ^{29}Si CP/MAS NMR spectra of type **8** and **11** samples presented two groups of T^n signals that will overlap to a certain extent. However, it was not observed in practice because of too broad signals and a low content of trifunctional silanes in the initial reaction solution (in comparison with bis(trietoxysilanes)). Only a structured shape of the resonance signal for T^1 structure unit for samples **8** and **11** was fixed (Fig. 4).

Considering that the analyzed ^{29}Si solid-state NMR spectra are cross-polarized, a calculation of xerogel polycondensation rate on the basis of peak areas from different structure units using the obtained spectra will be incorrect. However, it is claimed (Cerveau et al., 2001) that single-pulse NMR experiments do not show significant differences in relative intensities of silicon atom signals in comparison with the CP/MAS spectra of xerogels obtained using precursors containing different organic groups. Therefore after a deconvolution of the ^{29}Si CP/MAS NMR spectrum a contribution of each T^n structure unit may be estimated in the first approximation (±5%) and an extent of xerogel polycondensation may be estimated on that basis. Taking that into consideration it can be said that structure units of T^2 type are dominant in the framework of functionalized BPS xerogels containing phenylene spacers (44% for sample **8** and 41% for sample **11**), but structure units of T^1 and T^2 type are also present to a considerable degree (respectively 32% (34%) and 24% (21%) for sample **8** (**11**)). In this case a ratio of T^n structure units in all three xerogels is close enough. At the same time the framework of xerogels with ethylene spacers contains a significantly lower amount of T^1 type structure units (10% for sample **2** and 4% for sample **6**) and contributions of T^2 and T^3 structure units are dominant (respectively 33 and 57% for sample **2** and 65 and 29% for sample **6**). Therefore the extent of polycondensation in the case of xerogels with an ethylene spacer is higher than that of xerogels with phenylene bridges—independently of the nature of the functional group. It may be supposed that it is determined by a more flexible ethylene spacer in comparison with the phenylene spacer. Moreover, analyzing ^{29}Si CP/MAS NMR spectra of samples **2** and **6** (Fig. 4), it may be confirmed that in the case of a sample with an aminogroup (**2**) a ratio of T^n structure units has a slightly different character than that for a sample with a thiol group (**6**)—obviously in the first case a contribution of T^3 type structure units is larger. Therefore from our viewpoint the nature of the reaction medium that is created by functional groups—3-aminopropyl in the case of sample **2** and 3-mercaptopropyl in the case of sample **6**—has a certain effect. An analogous situation—a larger rate of polycondensation for xerogels obtained using a basic catalyst—was observed both for BPS xerogels synthesized using an ethylene-bridged monomer (Oviatt et al., 1993) and for xerogels obtained using tetraalkoxysilanes (Brinker et al., 1990).

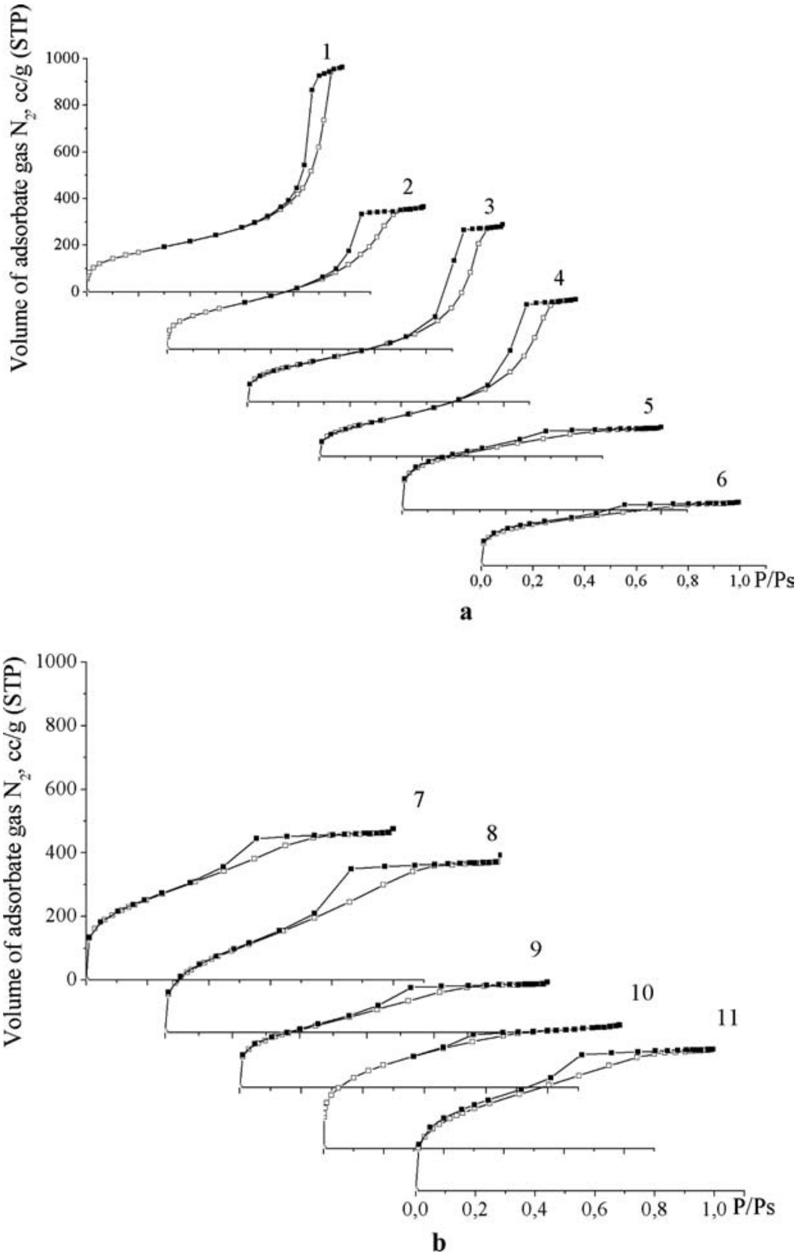
The following question arises here: could the obtained functionalized BPS xerogels save the general features of porous structures similar to BPS xerogels genetically connected with them, or would an addition of trifunctional silanes of APTES or MPTES type during synthesis cardinally change them? To answer this question we have examined isotherms of nitrogen adsorption-desorption of the synthesized samples. Figure 5(a), (b) shows isotherms for the xerogels examined. Obviously they are divided into two groups: the first group includes isotherms of xerogels containing amine functional groups and the second one includes isotherms of xerogels containing thiol groups. Isotherms of xerogels **1–4** (Fig. 5(a)) with an ethylene bridge stand out among the isotherms of the first group samples: they have an S-like character and belong to type IV according to IUPAC classification (Rouquerol et al., 1999). The presence of a well-defined hysteresis loop indicates the presence of mesopores in the structure of these xerogels. It should be mentioned that isotherms of samples **3** and **4** look like isotherms of the xerogel obtained in an alkaline medium using only BTESE (Oviatt et al., 1993). Isotherms of samples **7–9** containing aminogroups and a phenylene bridge have less defined hysteresis loops and their attribution to this group is conditional to a certain extent. Isotherms of samples from another group (xerogels **5**, **6**, **10–12**) look like Langmuir isotherms and they can be attributed to type *I* isotherms, which have small hysteresis loops (Fig. 5(a), (b)). This is in accord with the value of an average diameter of their pores, calculated using the isotherms mentioned. Obviously in the case of the second group samples the size of their pores is close to the border of meso-microporosity (2.0 nm). As the conditions of the synthesis of every xerogel were rather similar it may be supposed that the difference in the types of xerogels is determined first of all by the acid-base nature of the functional groups (more exactly by the nature of the medium created by these groups). It should be noted that the same situation applied to the xerogels obtained using an ethylene-containing monomer: type IV isotherm was fixed for the sample synthesized using a basic catalyst and type I—in the case of the sample obtained using an acid catalyst (Oviatt et al., 1993).

Attention is attracted by data shown in Table 1: a relatively high specific surface area of the adsorbents obtained—from 510 to 840 m^2/g in the case of xerogels with an ethylene bridge and from 650 to 970 m^2/g in case of xerogels with a phenylene bridge. The similar S_{sp} values were obtained by (Oviatt et al., 1993) and (Shea et al., 1992) for xerogels containing spacers of organic origin. These data were compared with those obtained for xerogels containing the same functional groups but during that synthesis TEOS was used as a structure-forming agent. It was found that for sample **2** the specific surface area is 4.5 times higher and for sample **8**–6 times than for an amino-containing xerogel synthesized using system TEOS/APTES (2:1; content of aminogroups is 3.6 mmol/g) (Zub, et al., 2002). Moreover, a sample with S_{sp} equal just 4 m^2/g was obtained using TMPED instead of APTES (Zub, et al., 2002). At the same time sample **4** (Table 1) with the same functional group (ethylenediamine) has S_{sp}, that is twice order as high as that mentioned above. An analogous situation is observed in the case of the 3-mercaptopropyl group: S_{sp} of sample **6** is nearly 3 times higher and for sample **11** it is more than 4.3 times higher than the specific surface area of the xerogel synthesized using the TEOS/MPTMS system (2:1; content of thiol groups is 4.5 mmlol/g) (Melnyk et al., 2002).

Sample **1**, which has a primary aminogroup on the surface, has the highest S_{sp} among the xerogels with aminogroups, the framework of those is formed by $\equiv Si-C_2H_4-Si\equiv$ bridges and the ratio of initial components was 4:1 (Table 1). As samples **1**, **3** and **4** were obtained in the same conditions and their functional groups have a similar chemical character it is clear that one of the main factors determining structure-adsorptive characteristics of these xerogels is the geometric sizes of the functional group and probably its nearest hydrophobic environment. The ratio of the reacting alkoxysilanes in the case of the 3-aminopropyl group (see, for example, samples **1** and **2** in Table 1) barely influences the value of the specific surface area and in contrast to systems in which TEOS was used as a structure-forming agent (Zub et al., 2002). However, it affects distinctly the volume and size of the pores. Thus both the pore volume and its average diameter increase with the increasing BTESE/APTES ratio. It may be supposed that in the case of xerogels **1** and **2** with similar sizes of globules (values of $S_{\text{пит}}$ is nearly the same) an increase of the relative content of APTES in the case of sample **2** leads to the partial filling in adsorbed area of 3-aminopropyl groups.

In contrast to these dependences an opposite situation is observed in the case of xerogels with a 3-mercaptopropyl group and $\equiv$Si—C_2H_4—Si$\equiv$ bridges. Thus an influence of the ratio of the reacting alkoxysilanes is clearly noticeable: a significant increase of S. (samples **5** and **6** in Table 1) is observed at an increasing relative amount of bis(trialkoxysilane) in the system. However, the pore volume and sizes do not change.

Comparing the porosity of samples **2** and **6** (Table 1), which have the same ethylene spacer, and the data of



a

b

Figure 5. Nitrogen adsorption-desorption isotherms for xerogels with the ethylene (a) or phenylene bridge (b) and PSD curves for xerogels 1–11(c).

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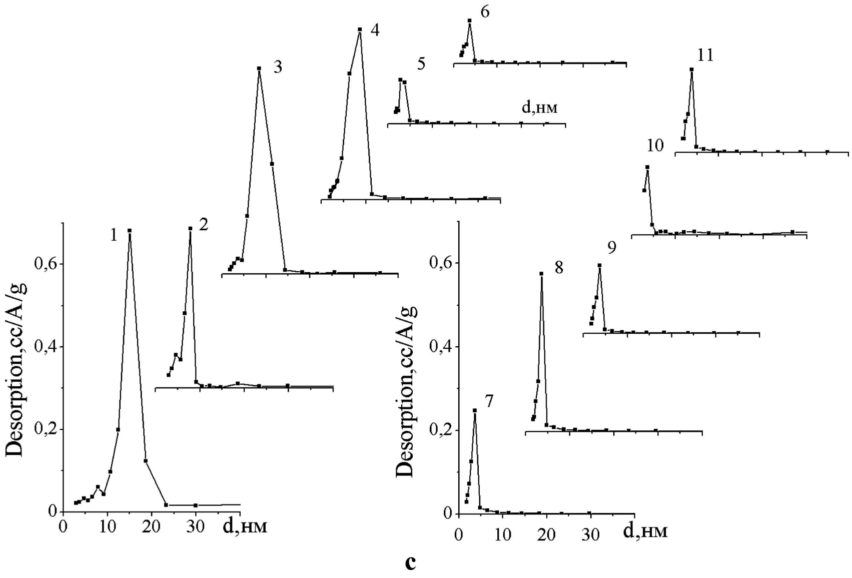

Figure 5. (*Continued.*)

^{29}Si CP/MAS NMR spectroscopy, it may be noted that in the case of a practically microporous sample **6** the dominating signal is a resonance signal from structure unit T^2, in the case of a mesoporous sample **2**—the signal is that from structure unit T^3. In other words, the greater extent of polycondensation in these xerogels is associated with mesoporous structures. A similar situation was observed earlier in the case of xerogels synthesized using only BTESE (Oviatt et al., 1993). However, it should be kept in mind that there is not a direct connection between the extent of polycondensation and texture characteristics of xerogels (Cerveau et al., 2001).

All these dependences for aminocontaining xerogels stay unchanged to a certain extent in the case of aminocontaining samples whose framework is formed by $\equiv$Si—C_6H_4—Si$\equiv$ bridges (Table 1, samples **7**–**9**). However, in this case the influence of the functional group size becomes more explicit (samples **7** and **9**) and the change of the ratio of reacting alkoxysilanes fails to affect not only the specific surface area but also the sorption volume and the size of pores (samples **7** and **8**). Furthermore, an absence of the influence of the ratio of reacting alkoxysilanes on texture characteristics is observed in the case of samples with a 3-mercaptopropyl group (samples **10** and **11** in Table 1), and at the same time a contrary situation is observed for xerogels with a $\equiv$Si-C_2H_4-Si$\equiv$ bridge (see above). However, an increase of the ageing time—from 14 days (sample **11**, Table 1) to 30 days (sample **12**)—leads to a considerable worsening of the texture characteristics of the latter xerogel. With its parameters it is in fact an analogue to sample **6** (Table 1). Therefore as regards xerogels with a phenylene spacer and NH_2 and SH groups neither the ratio of reacting alkoxysilanes nor the nature of functional groups affects significantly their structure-adsorptive characteristics—xerogels with a high ($>900\,m^2/g$) and close enough specific surface area are formed in all cases. Moreover, the sizes of their pores are on the border of meso-microporosity regardless of the functional group nature (Table 1, samples **7**–**11**). This fact is also characteristic of xerogels synthesized using only BTESB (Shea et al., 1992). It may be claimed that the rigidity of the geometry of the phenylene spacer plays a certain role in this case. The supposition agrees with the conclusion on the basis of the data of ^{29}Si CP/MAS NMR spectroscopy of samples of this group (see above). The factors that influence structure-adsorptive characteristics in this case are the size of the functional group and gel ageing time (samples **7**, **9** and **11**, **12** respectively, Table 1). They have considerable influence on the specific surface area of samples and to a lesser extent on their pore size. It is believed that in this case (at long gel ageing time) the changes in the system are caused by the complicated colloid-chemical processes concerned with the change (an increase) of globule size. The influence of ageing time on the texture of thiolcontaining xerogels with a phenylene spacer described above is contrary to that observed for xerogels synthesized using only one monomer—BTESB, for example (Cerveau et al., 2001a, 2001b). This it indicates that an appearance of trifunctional silane (MPTMS) in the system affects substantially the passing of colloid-chemical processes mentioned above.

Finally, it should be noted that pore size distribution curves have a narrow character for all the synthesized xerogels (Fig. 5(c)). However, pore size distribution curves have a greater dispersion for aminocontaining xerogels synthesized using BTESE as a structure-forming agent (samples **1–4**, Fig. 5(c)).

The AFM microscopy was also used to characterize the morphology of the obtained xerogels. The functionalized BPS xerogels considered above are compositions of aggregated particles that look like olipsoides (Fig. 6). Their sizes are between 30 and 65 nm. It is interesting that in the case of aminocontaining xerogels with a phenylene spacer the sizes of these aggregated particles are slightly smaller (∼35–50 nm, Fig. 6, samples **7** and **8**) than in the case of aminocontaining xerogels with an ethylene bridge (∼50–65 nm, Fig. 6, samples **1** and **2**). It should be mentioned that the size of particles in xerogels with an ethylene spacer decreases almost doubly at the replacement of the amine

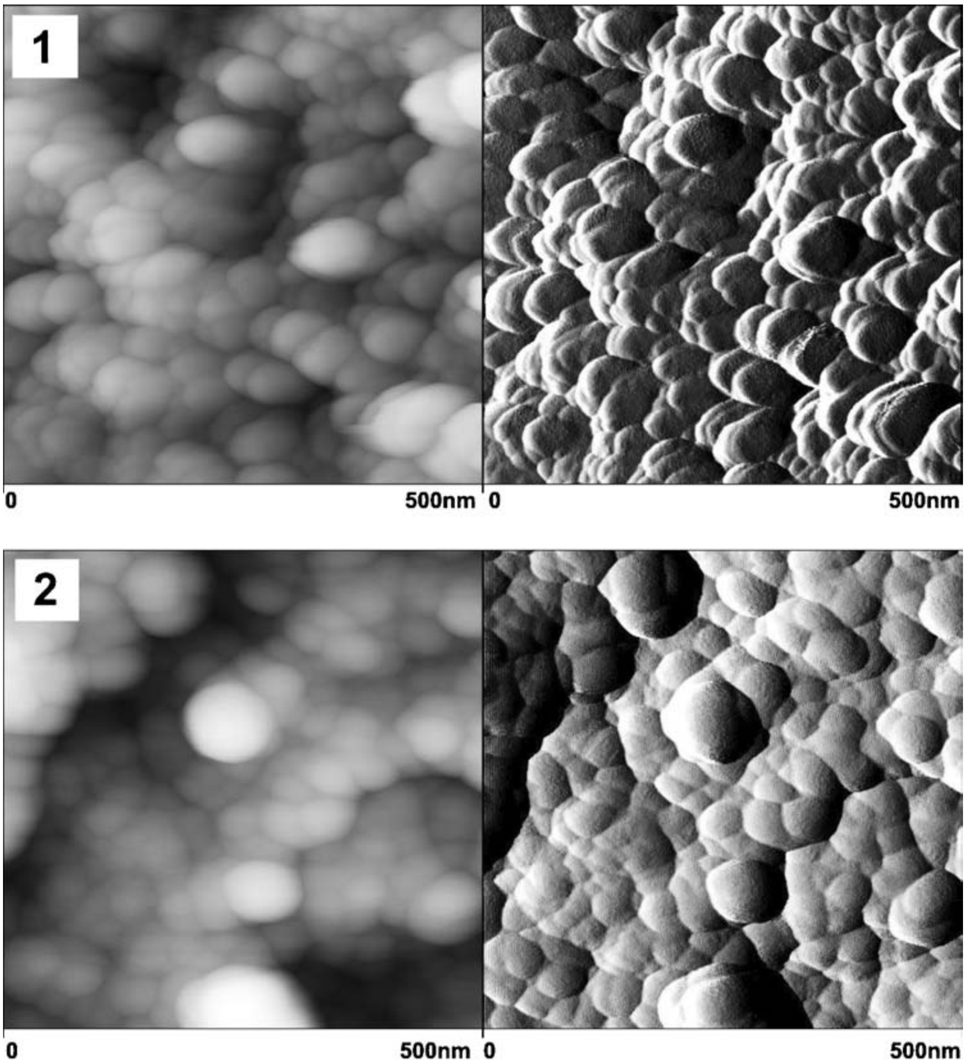

Figure 6. AFM images of some obtained xerogels.

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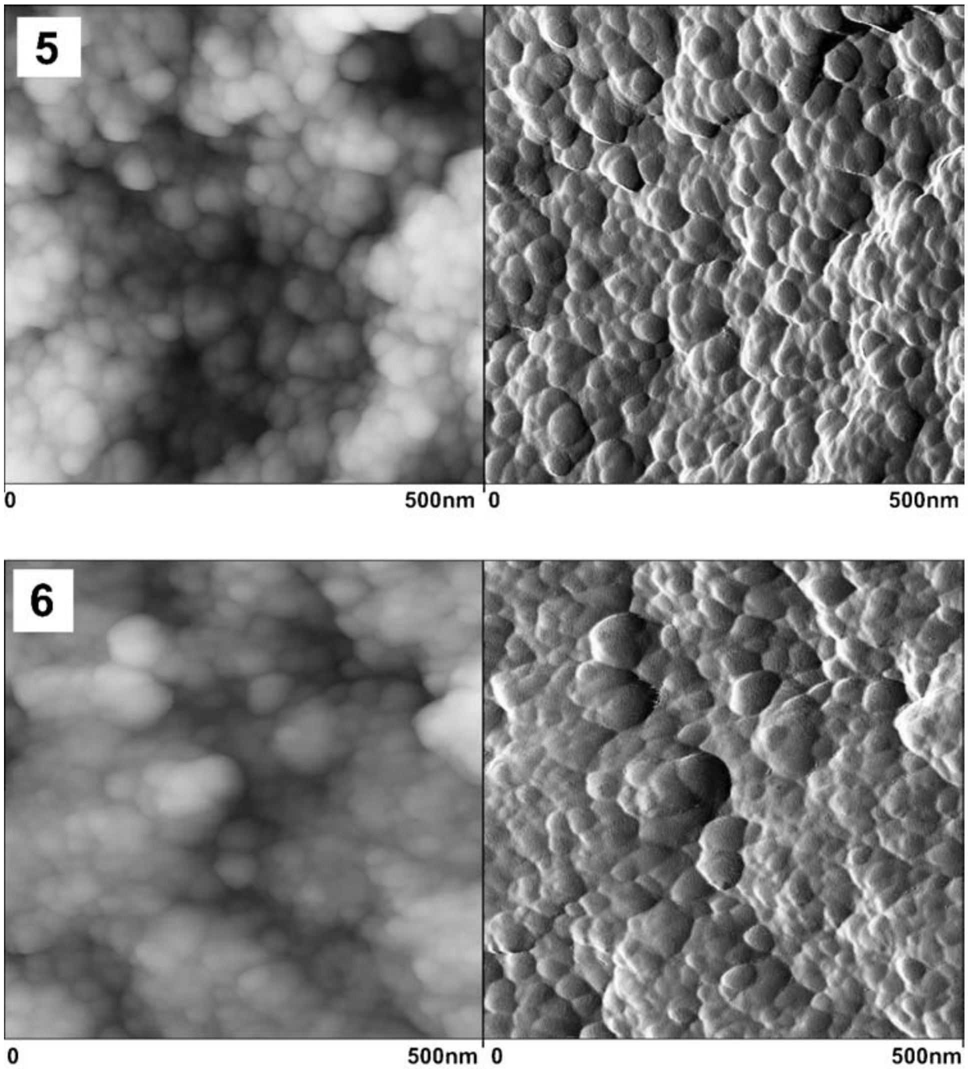
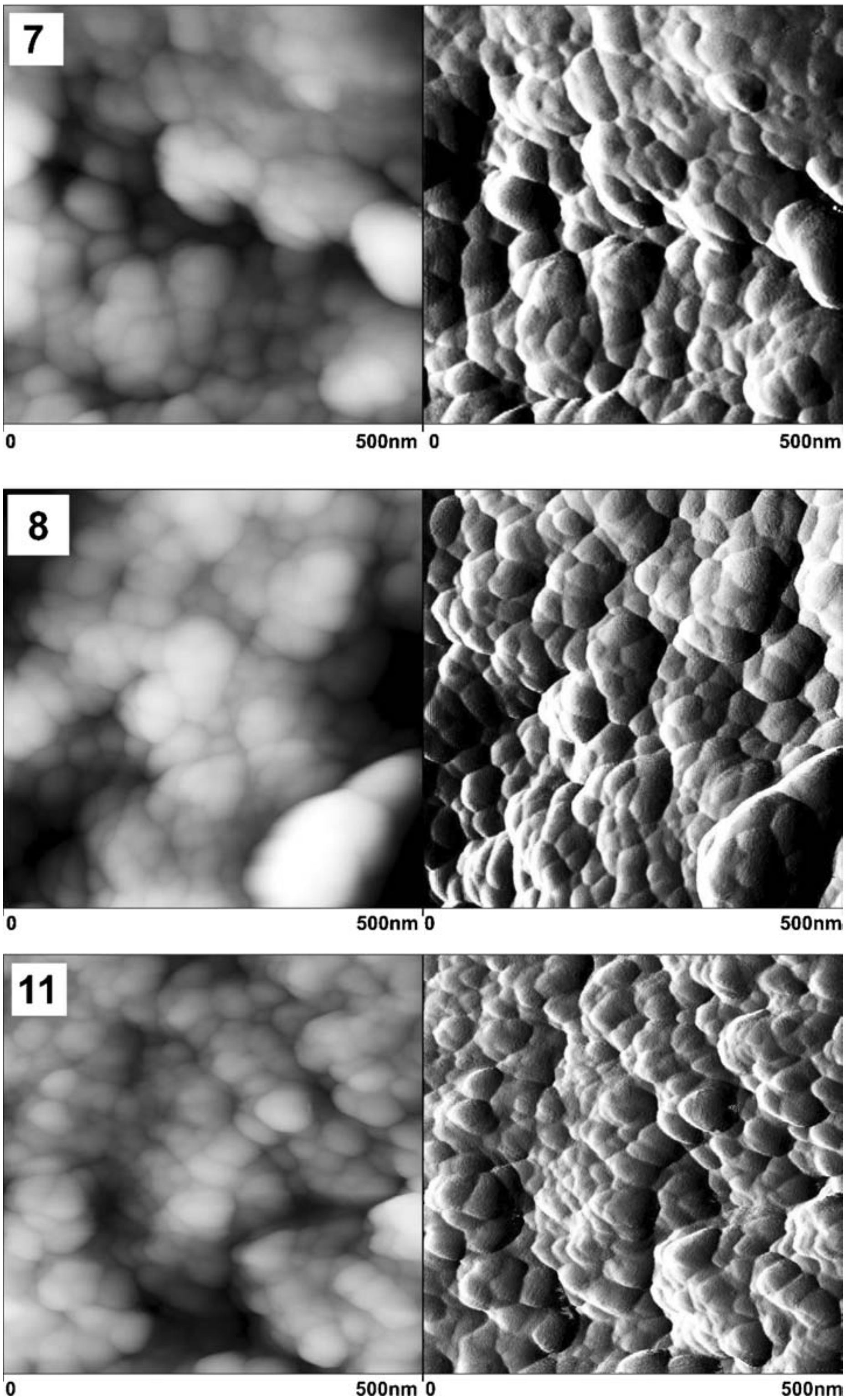


Figure 6. (*Continued.*)

functional group with a thiol one (Fig. 6, samples **1**, **2** and **5**, **6**). However, this is not observed in the case of xerogels with a phenylene bridge. In conclusion, it should be said that the change of the ratio of reacting alkoxysilanes practically does not affect the sizes of such aggregated particles. These particles (by TEM data that are not given here) consist of smaller particles (globules). An analogous situation was observed earlier for BPS xerogels that contain phenylene spacers (Shea et al., 1992).

Therefore the sol-gel method is aimed at the synthesis of not only porous inorganic oxides (Brinker and Scherer, 1990), functionalized polysiloxane xerogels (Slinyakova and Denisova, 1988; Zub and Parish, 1996; Voronkov et al., 2000; Zub, 2002), bridged hybrid inorganic-organic materials (Shea et al., 2004) etc. but also functionalized polysilsesquioxane xerogels with the spacers of various nature as it was shown in the present work. The possibility of using organic bridges of different nature and geometry and functional groups of various nature, various conditions of hydrolytic polycondensation reaction in a wide range (the ratio of reacting alkoxysilanes, the nature of a solvent, an acidity of a medium, etc.) and the regime of gel treatment gives a significant prospect in the molecular design of new porous materials with predetermined



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characteristics. This conclusion is confirmed by the results that were recently published (Aliev et al., 2000; Jurado-Gonzalez et al., 2001).

4. Conclusions

The principal features have been shown of amino- and thiol-containing polysilsesquioxane xerogels obtained in the reaction of hydrolytic polycondensation of BTESE (or BTESB) with trifunctional silanes APTES, BTMPA, TMPED or MPTMS as carriers of functional groups (solvent– ethanol, catalyst– fluoride-ion, ratio bis(triethoxysilane)/trifunctional silane = 2:1 and 4:1). The molecular frame of these materials (^{29}Si CP/MAS NMR spectroscopy data) is formed by structural T^1, T^2 and T^3 units. Functional groups accessible (to proton or metal ions)—3-aminopropil or 3-mercaptopropil type—are fixed on its surface by siloxane bonds. The first of these (IR and ^{29}Si CP/MAS NMR spectroscopy data) takes part in the making of a heterogeneous hydrogen bond. The data of IR, ^{13}C and ^{29}Si CP/MAS NMR spectroscopy testify to the presence in the xerogel structure of silanol and ethoxy groups.

Using BTESE and BTESB as structure-forming agents allows us to obtain functionalized polysilsesquioxane xerogels with a developed porous structure (500–1000 m^2/g) and with high contents of accessible functional groups (1.0–2.7 mmol/g). Taking into account the structure–adsorption characteristics the xerogels with an ethylene spacer seems the best for their use as specific adsorbents. They have relatively high specific surface area but the widest range of average pore size diameter, what make them very attractive potential adsorbents.

AFM data confirm that xerogels are formed by particle aggregates; the size of aggregates equals 30–65 nm. The principal agents which influence structure–adsorption properties of such hybrid materials are the nature and the geometrical sizes of the functional group, the extent of spacer flexibility, and in some cases—the ratio of reacting alkoxysilans and the ageing time of gel. Then, by fixing the aforementioned factors it is possible to control the texture of bridged polysilsesquioxane adsorption materials with nitrogen– and sulfur–containing functional groups.

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