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New adsorbents based on bridged polysilsesquioxanes containing 3-mercaptopropyl functional groups

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Xerogels containing thiol groups (1.0–2.7 mmol g^{-1}) and having high specific surface areas of 630–970 m^2 g^{-1} were obtained by the sol–gel method using a structure-forming agent [1,2-bis(triethoxysilyl)ethane or 1,4-bis(triethoxysilyl)benzene] and a functionalising agent (3-mercaptopropyltrimethoxysilane).

Hybrid inorganic-organic materials are of interest because they combine the advantages of inorganic and organic components. Bridged polysilsesquioxanes (BPS), which are usually synthesised using a sol–gel technique, belong to this class of materials. The characteristic feature of BPS is the presence of an organic bridge (spacer) in their structure. This spacer binds two (or more) silicon atoms taking part in the formation of siloxane bonds. Arylene, alkylene, alkenylene, alkynylene and other groups are frequently used as such bridges (R′) in ≡Si–R′–Si≡ fragments of the BPS structure. Varying the spacer,

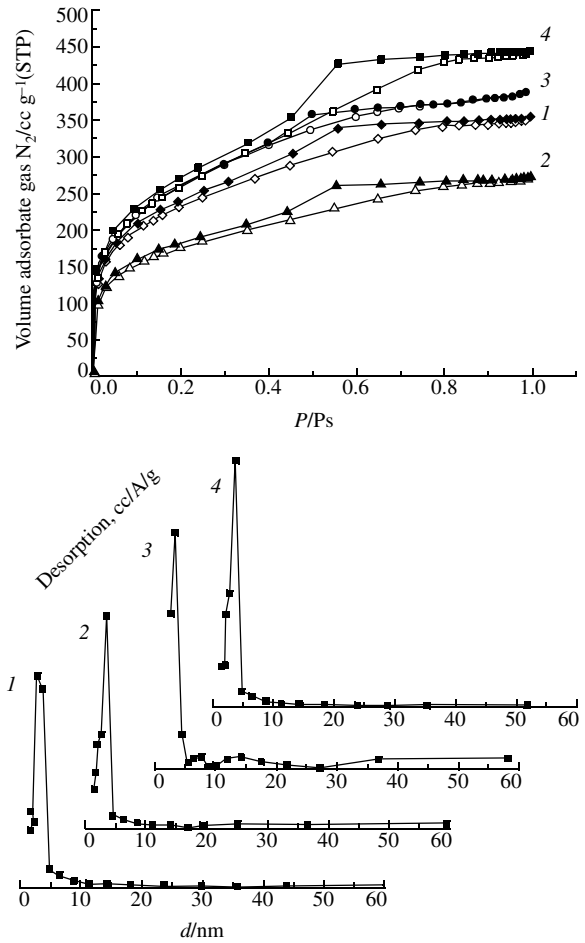

Figure 1 Nitrogen adsorption-desorption isotherms at –196 °C and PSDs for some xerogels.

one can influence the main chemical and physical properties of a final hybrid product, including structure-adsorptive characteristics.[1] From this point of view, it was of interest to examine BPS adsorbents functionalised with various ligands. 1,2-Bis(triethoxysilyl)ethane (BTESE) with a flexible ethylene spacer [R′ = –$(CH_2)_2$–] and 1,4-bis(triethoxysilyl)benzene (BTESB) with a rigid phenylene spacer (R′ = –C_6H_4–) were used as structure-forming agents.

Xerogels with thiol functional groups were synthesised by hydrolytic polycondensation of bis(triethoxysilanes) and 3-mercaptopropyltrimethoxysilane† (Table 1, samples **1** and **2** in case of BTESE and samples **3**–**5** in case of BTESB). The use of a non-aqueous solvent (ethanol) and the preliminary hydrolysis of bis(triethoxysilanes) in the presence of the fluoride ion as a catalyst are necessary to obtain homogeneous gels. Moreover, a minimal gel aging time required for complete structure-forming process in such systems is 30 days for samples **1** and **2** and 14 days for samples **3** and **4**. Xerogels were white powders insoluble in water and non-swelling in usual non-aqueous solvents. The content of thiol groups within surface layer calculated by back complexometric titration[2] is 1.0–2.7 mmol g^{-1} depending on the ratio of reacting alkoxysilanes (Table 1).

The IR spectra‡ of all xerogels (Table 1) exhibit the most intense absorption band at 1030–1072 cm^{-1} having a shoulder at 1153–1150 cm^{-1}. This band is attributed to siloxane bond stretchings.[3] The presence of –CH_2– groups in the ethylene spacer and the propyl chain (attaching the thiol group to the surface) is reflected in the IR spectra as a group of absorption bands in the region 2884–2935 cm^{-1} related to $\nu_{s,as}$(CH) stretchings. Two sharp absorption bands at ~1270 and ~1416 cm^{-1} can be attributed to $\omega(CH_2)$ and $\delta(CH_2)$, respectively, and they indicate the presence of ≡Si–CH_2–CH_2–Si≡ bridges. In the IR spectra of samples **3**–**5**, ν(CH) absorption bands are present in the region 3006–3064 cm^{-1}, which indicate the presence of an aromatic fragment. Note that a sharp absorption band at ~2974–2978 cm^{-1} appeared in the IR spectra of all of the xerogels. It is attributed to the C–H bond stretchings of ethoxy groups. The IR spectra of all samples contain an absorption band at ~3730 cm^{-1} related to ν(OH) stretchings of silanol groups. In a lower-frequency region, a broad intense absorption band at ~3645 cm^{-1} is detected, which is typical of ν(OH) of adsorbed water. A low-intensity ν(SH) absorption band at ~2570 cm^{-1} indicates the presence of thiol groups. Therefore, the xerogels contained organic spacers, thiol groups, and also a part of non-condensed silanol groups, non-hydrolysed ethoxysilyl groups and adsorbed water.

These conclusions are confirmed by solid-state NMR spectroscopy.‡ In the ^{13}C CP/MAS NMR spectrum of sample **2** (not given here), the most intense signal at 4.8 ppm corresponds to carbon atoms of the ethylene spacer. 3-Mercaptopropyl group gives two signals[4] at 11.7 (≡Si*C*H_2) and 27.1 ppm (*C*CH_2C + + *C*H_2SH). As a consequence, the latter signal is more intense than the former. Moreover, the spectrum contains two low-intensity signals at 16.8 and 58.5 ppm attributed to carbon atoms of ethoxy groups. The ^{13}C CP/MAS NMR spectrum of sample **4** is identical to that of sample **2** except for the signal of the –C_6H_4– spacer at 133.2 ppm. An analysis of the ^{29}Si CP/MAS NMR spectrum of sample **4** indicates the stability of the ≡Si–C bond during the sol–gel synthesis (as there are no signals from –90 to –110 ppm). The presence of three well-separated signals at –67.7, –69.9 and –77.7 ppm in the spectrum indicates the existence of the following structure units[4] in the xerogel: T^1 [–Si$(OR)_2$(OSi)], T^2 [–Si(OR)$(OSi)_2$] and T^3 [–Si$(OSi)_3$], (R = Et, Me or H). In the spectrum of sample **2**, corresponding unresolved signals appear at –49.5, –57.2 and –65.5 ppm. Nevertheless, the structure of this xerogel is apparently composed of the same structure units.

Shapes of nitrogen adsorption–desorption isotherms‡ of the xerogels (Figure 1) are between I and IV types[5] according to the IUPAC classification. Pore-size distribution curves have a narrow maximum. Structure-adsorptive characteristics of all

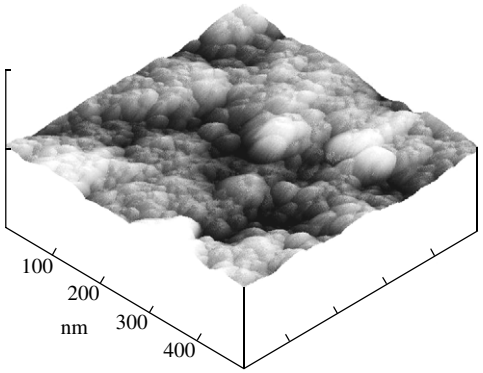

Figure 2 AFM image of sample **2**.

† BTESE, $(EtO)_3Si(CH_2)_2Si(OEt)_3$ (ABCR, 97%), BTESB, $(EtO)_3SiC_6H_4$-$Si(OEt)_3$ (synthesised by known technique[7]), MPTMS $(MeO)_3Si(CH_2)_2SH$ (Aldrich, 95%), absolute ethanol, NH_4F (Aldrich) were used to synthesise xerogels. An example of the synthesis (ratio BTESE/MPTMS = = 4:1, sample **1**) is given below. To the solution of 0.04 mol of BTESE in 15 cm^3 of ethanol a solution of NH_4F (0.9×10^{-3} mol in 0.135 mol of water) was added. After 5 min, to this mixture 0.01 mol of MPTMS in 15 cm^3 of ethanol was added. Transparent gel formed in a few minutes and opalescence was observed. After 30 days, the gel was pounded and dried in a vacuum at 20/50/105 °C for 2 h at each temperature.

‡ The IR spectra were recorded on a Nexus FT-IR spectrometer. The samples were mixed with KBr (1:30). Solid-state NMR spectra were obtained on a Bruker DSX 350 spectrometer. Structure-adsorptive characteristics were calculated from low-temperature nitrogen adsorption isotherms (using an ASAP–2405N instrument). Before adsorption measurements, each sample was degassed at 120 °C in a vacuum. Specific surface area was determined by the BET method,[5] and the effective pore diameter, by the BJH method.[5] The surface morphology of the samples was characterised by AFM using a Nanoscope III scanning force microscope (tapping mode).

Table 1 Synthetic conditions and characteristics of xerogels.

Sample	Components	Initial ratio of alkoxysilanes and aging time (days)	Concentration of thiol groups/ mmol g^{-1}	Structure-adsorptive characteristics			Characteristic absorption bands in the IR spectra/cm^{-1}
				S_{sp}/m^2 g^{-1}	V_s/cm^3 g^{-1}	d/nm	
1	BTESE/MPTMS	4:1 (30)	1.9[a] (1.6)[b]	834	0.543	2.8	3726 ν(OH), 3662 ν(OH)$_{H_2O}$, 2977, 2922, 2884 ν(CH), 2573 ν(SH), 1416 ω(CH$_2$), 1269 δ(CH$_2$),1034 ν(SiOSi)
2	BTESE/MPTMS	2:1 (30)	2.5 (2.8)	630	0.418	3.0	3645 ν(OH)$_{H_2O}$, 2974, 2927, 2893 ν(CH), 2569 ν(SH), 1416 ω(CH$_2$), 1269 δ(CH), 1030 ν(SiOSi)
3	BTESB/MPTMS	4:1 (14)	1.0 (1.3)	968	0.601	3.6	3723 ν(OH), 3643 ν(OH)$_{H_2O}$, 3064, 3006 ν(CH)$_{Ph}$, 2978, 2932, 2897 ν(CH), 2573 ν(SH), 1066 ν(SiOSi)
4	BTESB/MPTMS	2:1 (14)	2.7 (2.2)	932	0.684	3.0	3729 ν(OH), 3648 ν(OH)$_{H_2O}$, 3058, 3009 ν(CH)$_{Ph}$, 2977, 2931, 2892 ν(CH), 2572 ν(SH), 1056 ν(SiOSi)
5	BTESB/MPTMS	2:1 (30)	2.1 (2.2)	698	0.424	2.8	3727 ν(OH), 3626 ν(OH)$_{H_2O}$, 3061, 3012 ν(CH)$_{Ph}$, 2978, 2935, 2900 ν(CH), 2570 ν(SH), 1072 ν(SiOSi)

[a]From titration data. [b]Theoretical concentration of functional groups.

samples are presented in Table 1. All parameters were calculated using the above isotherms.

An increase in the relative concentration of a structure-forming agent (in case of the –C_2H_4– spacer) in initial solution leads to an increase in the value of S_{sp}. This was not observed in case of a phenylene spacer. However, an increase in the aging time of gels (compare, for example, samples **4** and **5** in Table 1) significantly decreases the specific surface area but does almost not affect the pore size. Therefore, these factors (the nature and rigidity of the spacer, the ratio between reacting alkoxysilanes, and the gel aging time) may be used for the modification of structure-adsorptive characteristics of this class of adsorbents. The use of BPS as structure-forming agents leads to materials with specific surface areas two or three times higher than that of xerogels synthesised conventionally from tetraethoxysilane.[6]

AFM‡ data show that the structures of all of the functionalised BPS xerogels probably consist of separated aggregates (Figure 2). The size of such aggregates is about 30 nm. These species (by TEM data not given here) consist of small particles (globules). An analogous situation was observed earlier in BPS xerogels with phenylene spacers.[7]

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