

Bifunctional Mesoporous Phosphorus/Sulfur-Containing Silicas: Synthesis and Properties

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Abstract: Template method was used to obtain SBA-15 type mesoporous silica with monofunctional surface layer containing phosphonic acid groups [$\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OH})_2$] and with bifunctional surface layer of phosphonic acid and thiol groups [$\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OH})_2/\equiv\text{Si}(\text{CH}_2)_3\text{SH}$]. Comparison of mono- and bifunctional samples was carried out using a variety of physical and chemical methods. There was analyzed the effect of additional functional groups on the structural parameters of the samples and the effect of pH on the physical and chemical characteristics of the materials. It was shown that addition of SH groups influences the morphology and the spatial order of the porous structure of the samples.

Keywords: SBA-15; Functionalized mesoporous silica; Phosphonic groups; Thiol groups

1 Introduction

Many existing silica sorbents possess high sorption capacity and well developed porous structure. However, one more important issue to consider is their selectivity to certain ions or compounds. In such cases, the matrix functionality of the sorbents usually results from corresponding alkoxy silanes used during synthesis. Depending on the tasks, the formation of the active surface could be influenced by the variation of the reagents nature or ratio. The simultaneous presence in the surface layer of the functional groups of different nature and structure (e.g. with acidic and basic properties or significantly different in geometrical dimensions) can determine specific structure of the surface layer. The mutual influence of functional groups in the surface layer, which may cause the synergy effects, should also be considered. Such two groups can be activated by different reagents, for example electrophilic and nucleophilic agents. Or they can be successively activated by one reagent. One group can activate and increase the ability of the product to catalyze the reaction, for example, by changing nucleophilicity of the other group. Finally, the surface groups may act in concert, stabilizing the transition state through several weak interactions. Any of these strategies can be used to design synthetic catalyst, with the advantages of multifunctional cooperativity [1]. Studying bifunctional xerogels, it was determined [2-4] that the parameters of the porous structure are largely defined by the geometry of the introduced functional groups, molar ratio of the

trifunctional silanes, the acidity of the reaction media, and the nature of catalyst of the hydrolytic polycondensation reaction. These conclusions allowed conducting targeted synthesis of the xerogels with multifunctional surface layers [5].

Pluronic P123 (surfactant) was used as a template for the synthesis of the functionalized silica with hexagonal structure in acidic conditions. Such materials possess uniform pore sizes, high surface area, thermal and hydrothermal stability. A large variety of organic groups (mercaptopropyl, cyanopropyl, chloropropyl, diethylphosphatopropyl and propyl imidazoline), with high concentrations (up to 25 mol %) were introduced using the template method [6]. Isotherms of N_2 adsorption and desorption by such materials belong to the type IV, which is characteristic of mesoporous materials (narrow pore size distribution, high specific surface area ($600\text{-}1000\text{ m}^2\text{g}^{-1}$), and hexagonal structure). It was shown, that the organic groups introduced into the surface pores of these materials are readily available and can be subjected to further chemical transformations without deteriorating the ordered structure. This is important because such transformations allow introducing a wide variety of chemical groups, thus greatly increasing the potential of such materials. The introduction of two or more functional groups during the one-step synthesis is also possible, although the location of the functional groups is not controlled and they can be randomly distributed in the product. Analysis of the previous publications on ordered organosilicas containing two different functional groups: phenyl and aminopropyl,

phenyl and mercaptopropyl, phenyl and allyl, methyl and aminopropyl groups [7] showed that the concentration of the functionalized alkoxysilanes should not exceed 20%; therefore, the content of organic groups should be in the range 1 – 5 mmol/g. Working with two-component (considering alkoxysilanes) systems, we managed to synthesize partially ordered materials with ~ 30% the content of alkoxysilanes in the reaction mixture [8, 9].

According to recent publications, bifunctional mesoporous silicas (BFS) outperform the conventional monofunctional materials as catalysts. Recently, the main attention has focused on the combination of organic functional groups. Immobilized organic amines (basic) were used with silanol groups of the substrate (acidic) [10] for bifunctional catalysis. Functional amino groups were also immobilized together with thiol groups [11, 12]. Dufaud and Davis [3] reported the synthesis of bifunctional materials with thiol and sulfonic groups to verify the nature of the cooperative effect, studying the interactions of sulfonic / sulfonic or thiol- / sulfonic groups [1, 3, 5, 13]. They studied the effect of the distance between two functional groups that can condense. In addition, there was also studied the bifunctional catalysis with various active centers on different substrates [14-17].

Zeidan et al. received bifunctional SBA-15 with sulfonic and amino groups that were highly efficient catalysts in aldol reactions compared with monofunctional materials with sulfonic or amino groups [4]. The difference in catalytic properties is most likely due to the different hydrophobicity of phosphonic and thiol-modified materials. However, the activity of thiol groups may increase due to the cooperation with phosphonic groups. The interaction of sulfonic acid and thiol groups was investigated in [3]. It appeared that the activity and selectivity of the catalysts is largely dependent on the distance between two groups, and the best catalytic properties are shown by materials with sulfonic acid and thiol groups in the vicinity. Hydrophilicity of phosphonic groups and hydrophobicity of thiol groups are favorable factors in solving environmental issues of water purification.

Acid groups are often used as cation exchangers. Thiol groups can be converted to sulfonic, which are used in the fuel cells due to their high acid strength (pKA), which provides high proton (ionic) conductivity [18].

As for the phosphonic acid groups, they can be used in membrane fuel cells at normal and high temperatures, due to their amphoteric nature and ability to transport protons even in anhydrous conditions according to the Grotthuss mechanism [19].

Therefore, the purpose of this work is to develop a methodology and to synthesize mesoporous materials with the prospect of their application in sorption of ions of rare earth elements and heavy metals. The next stage of this

research will be the oxidation of thiol groups to sulfonic acid groups to use them in fine organic catalysis.

2 Experimental

2.1 Materials

Sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (SMS, Sigma, USA); diethylphosphatoethyltriethoxysilane, $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ (DPTS, 95%, Gelest, USA); 3-mercaptopropyltrimethoxysilane $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{SH}$ (MPTMS, 95%, Aldrich, USA), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) Pluronic P123 block copolymer, $(\text{EO}_{20}\text{RO}_{70}\text{EO}_{20})$, 99%, BASF, USA); concentrated acetic acid, CH_3COOH (99.7%, Aldrich, USA); concentrated hydrochloric acid (37.6%, Fisher Scientific), ethanol (absolute).

2.2. Preparation Techniques

Monofunctional (with phosphonic acid residues) and bifunctional (phosphonic acid/thiol groups) were synthesized according to the techniques presented below. Letters P and S in the samples acronyms stand for phosphonic acid and thiol groups, H and A refer to hydrochloric and acetic acid.

PSH (SMS / DPTS / MPTMS = 10:1:1 (mol.)). 0.25 cm^3 of DPTS were pre-hydrolyzed in 7.36 cm^3 of concentrated HCl acid at 80°C for 6 hours using reflux condenser and oil bath; afterwards, the mixture was cooled down to the room temperature. 0.15 cm^3 MPTMS and the solution of template (0.8 g of Pluronic P123 in 13 cm^3 of water) were added to the solution of DPTS. Separately, 1.7 g of sodium metasilicate were dissolved in 5 cm^3 of water, and added to the reaction mixture. Then, the resulting suspension was left on the oil bath for 2 h at 40°C. Finally, the mixture was subjected to hydrothermal treatment for 2 h at 80°C. The resulting precipitate was filtered and air-dried for a day. Polymeric template was removed by boiling the sample in acidified ethanol (30 cm^3 per 1 g of mesophase) for 3h. The procedure was repeated three times. The final sample was filtered, dried under vacuum at 50°C for 3 days.

PH (SMS / DPTS = 10:1 (mol.)) – was obtained using technique [8]

PSA (SMS / DPTS / MPTMS = 15:1:1 (mol.)). 0.13 cm^3 DPTS were pre-hydrolyzed in 3.68 cm^3 of concentrated acetic acid at 80°C for 6 hours using reflux condenser and oil bath; afterwards, the mixture was cooled down to the room temperature. 0.08 cm^3 MPTMS and the solution of template (0.8 g of Pluronic P123 in 13 cm^3 of water) were added to the solution of DPTS. Separately, 2.7 g of sodium silicate were dissolved in 10 cm^3 of water, and added to the reaction mixture. Then, the resulting suspension was left on oil bath for 2 h at 40°C. Finally, the mixture was exposed to

microwave treatment for 2 h at 40°C with stirring and 10 h at 100°C without stirring). The resulting precipitate was glutinous and grayish. It was filtered and air-dried for a day. The template removing and sample drying procedures were similar to PSH sample.

PA (SMS / DPTS = 10:1 (mol.)) – was obtained using technique [9].

2.3 Measurements

The small angle XRD patterns were recorded over a range of $0.50 < 2\theta / ^\circ < 2.5$ on a PANalytical X'Pert Pro Multi-Purpose Diffractometer (MPD) with $\text{CuK}\alpha$ radiation (0.1540 nm) using an operating voltage of 40 kV and 40 mA, 20s step time and 0.01 step size. Microscope glass slides were used as sample supports. All materials were manually ground prior to the XRD analysis and the measurements were performed at room temperature.

For morphology investigation and elemental composition determination, a Hitachi TM-3000 scanning electron microscope (SEM) supplied with an EDS detector was used. TEM photomicrographs were taken on a transmission electron microscope JEM-1230 (JEOL, Japan).

IR reflectance spectra in the region of $4000\text{--}400\text{ cm}^{-1}$ were recorded on a spectrometer Thermo Nicolet Nexus FTIR, using the "SMART Collector" accessory with a resolution of 8 cm^{-1} . Samples were mixed with KBr (Aldrich) in a ratio of 1:20.

The textural properties of the synthesized samples were evaluated from the nitrogen adsorption and desorption isotherms measured with ASAP 2010 volumetric analyzer manufactured by Micrometrics, Inc. (Norcross, GA). Adsorption isotherms were measured at $-196\text{ }^\circ\text{C}$ in the interval of relative pressures from 10^{-6} to 0.995 using ultra high purity nitrogen from Praxair Distribution Company (Danbury, CT, USA). Before analysis, samples were degassed under vacuum for 2 h at $110\text{ }^\circ\text{C}$ until the residual pressure dropped to 6 or less μmHg . The Brunauer–Emmett–Teller (BET) [20] surface area was evaluated using adsorption data in p/p_0 range of 0.05–0.2, whereas the single-point total pore volume was estimated at p/p_0 0.98 [21]. Pore-size distribution curves together with the maximum pore diameters (d_{m_c}) were determined by Kruk–Jaroniec–Sayari (KJS) method [22] based on the Barrett–Joyner–Halenda (BJH) algorithm [23].

3 Results and Discussion

The determination of the BFS structure is a challenging task. To begin with, the choice of physical methods suitable for the identification of the surface layer especially in the case of low content of functional groups can be problematic. Secondly, BFS are rather complex objects; therefore, it is necessary to use a set of physical techniques that would

clearly establish the composition of the obtained materials and provide reliable information about their structure on globular and molecular levels. There is a set of commonly used methods to study polysiloxane materials, including the elemental analysis, thermogravimetry, infrared and Raman spectroscopy, solid-state NMR spectroscopy, electron microscopy, and AFM. If the materials belong to SBA-15 type, it is appropriate to use adsorption method and XRD. The comparison of data provided by all these methods of analysis can give an idea about the structure and physicochemical properties of the synthesized materials. On the example of monofunctional phosphorus-containing materials, we determined [8, 9], that the conditions of mesophase treatment have no decisive role in the formation of the structure, and the samples treated at higher pH values possess slightly worse structural parameters. Therefore, we compared monofunctional phosphorus-containing silica materials with bifunctional samples with phosphorus-containing and thiol groups. It was expected that thiol groups would enhance the sorption properties of materials. The resulting SBA-15 samples featured fine-structured powders. According to SEM images (Fig.1.) BFS based on metasilicates are composed of spherical particles (more or less uniform in size), glued together in agglomerates. The primary particles of BFS are smaller than of their monofunctional analogues. Whereas, the size of the former is 1.2–1.3 μm , the particles of PH are larger than $\sim 2\mu\text{m}$. The MPTMS presence in the reaction mixture affects the pH, speeding up the condensation process and resulting in the formation of smaller particles.

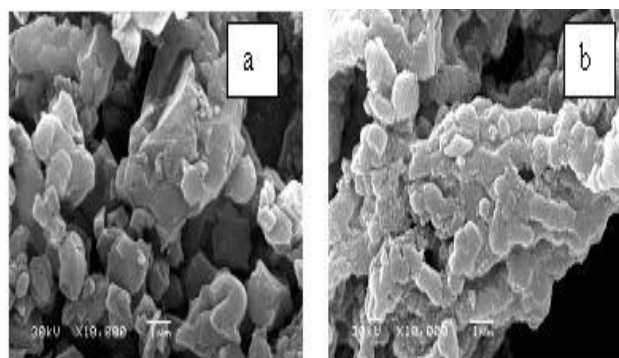


Fig 1. SEM images of samples PSH (a), PH (b).

The structural characterization of phosphorus and sulfur containing silica mesostructures was performed using small angle X-ray diffraction in the 2θ range from 0.5 to 2 degrees (Fig.2).

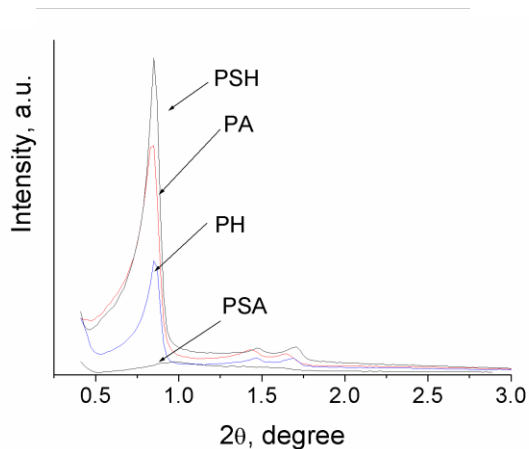


Fig 2. Powder XRD patterns of functional SBA-15 type mesoporous silica.

The XRD patterns of the samples PSH, PH, PA contain three well-defined reflexes: (100) $\sim 0.8^\circ$, (110) $\sim 1.5^\circ$ and

and indicating that the derived materials are well-ordered. These patterns are typical for mesoporous SBA-15 type materials (p6m symmetry group). The reflex at 0.8° of the XRD pattern of the sample PSA is very small, indicating the amorphous structure. Typically, researchers add MPTMS after the formation of siloxane network from TEOS molecules. In this case, the natures of functionalizing silane or pH have no impact on the structure formation, and the sample has clearly ordered hexagonal structure, e.g. [24]. The data obtained by XRD analysis were confirmed using TEM study. TEM images of most samples (Fig. 3) clearly indicated the presence of hexagonal mesopore ordering. The distances between the centers of the pores for samples PH and PSH were 8.7 and 7.1 nm, respectively. It is obvious that the presence of groups, various in nature, leads to the formation of structures with narrowed pores. Perhaps this could be the evidence that the groups are located on the surface and thus affect the sorption volume of the samples.

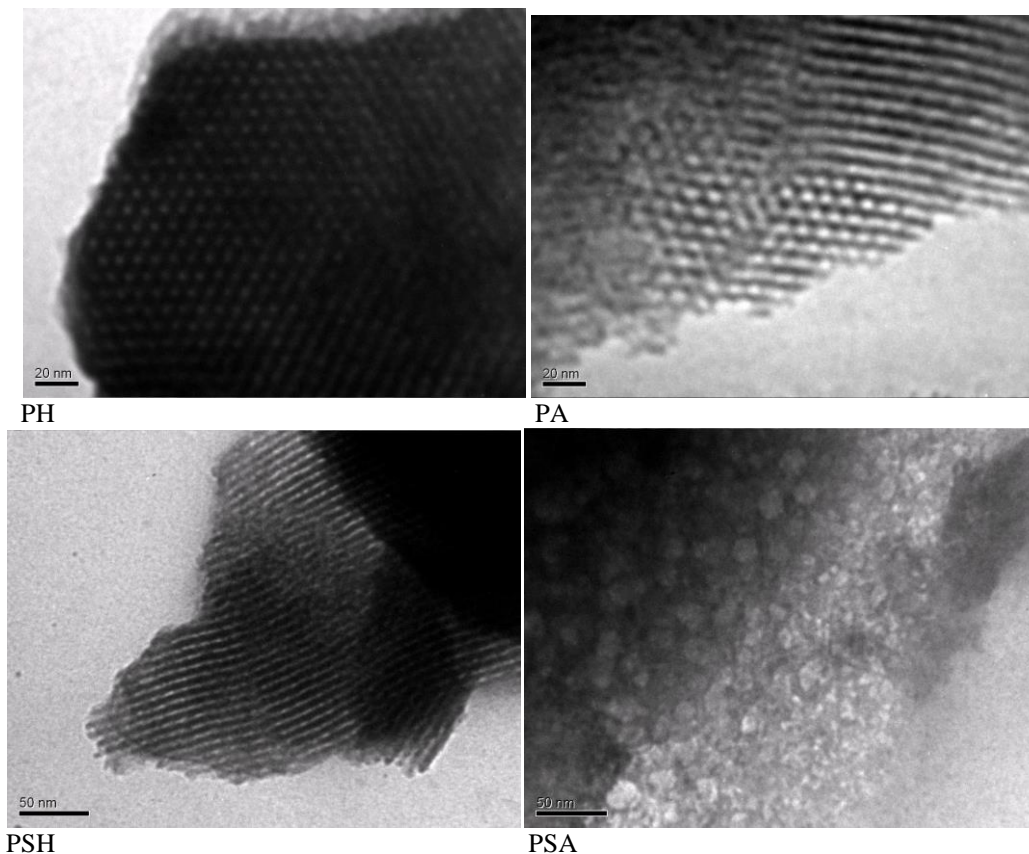


Fig 3. TEM images of the synthesized BFS and their monofunctional analogues.

(200) $\sim 1.7^\circ$, corresponding to the hexagonal structure

quite interesting. It should be mentioned that the

replacement of hydrochloric acid with other catalysts or the change in the pH of the reaction medium in the range of 3-5 could lead to the formation of materials with disordered porosity [9, 25-29]. Brinker [28] and Hook [29] established that the rate of TEOS hydrolysis at pH below 4 is higher than its polymerization rate. The same is true for metasilicate samples. Perhaps the increase in pH accelerates polymerization and slows down the hydrolysis. Thus, hydrolyzed silicate molecules gather around the micelles, leading to the formation of worm-like structures. Earlier, Imai et al. also showed that the change of pH could lead to the same processes [30]. That is why TEM image of the PSA sample showed no ordered structure (Fig. 3). Its structure was similar to the so-called nanofoams. This study suggested that the formation of BFS structures was influenced not only by the composition of the reagents and method of synthesis, but also by the choice of the catalyst and the acidity of the medium. This phenomenon was not observed for PA monofunctional analog, most likely due to the higher content of phosphonic groups and more significant influence on the pH of the reaction medium. Almost all samples, even after drying under vacuum at 100-120°C contain adsorbed water. This water, in addition to absorption bands at 1620-1640 cm^{-1} in the IR spectra (Fig. 4), has extended and often high-intensity absorption band above 3000 cm^{-1} , which masks all absorption bands of functional groups of organosilicas that are in this area in the infrared spectra.

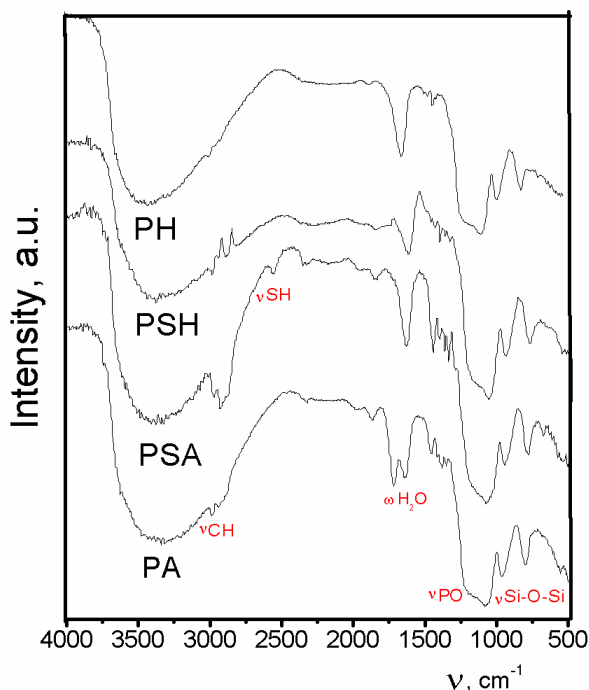


Fig 4. IR spectra of the synthesized samples.

The presence of sorbed water in the surface layer of synthesized materials is reflected in the absorption bands at $\sim 1630 \text{ cm}^{-1}$ and above 3100 cm^{-1} [31]. The low-intensity absorption band at $\sim 2565 \text{ cm}^{-1}$ relating to the $\nu(\text{SH})$ (Fig. 4) is identified for the samples synthesized using MPTMS in their IR spectra (PSA). Therefore, it is difficult to identify for the sample PSH because of weak intensity [31]. The presence of fluctuations of the silica network in the IR spectra ($1000 - 1200 \text{ cm}^{-1}$) is characteristic for the three-dimensional framework of the siloxane bonds ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$). IR spectra analysis confirms the softness of the synthesis conditions in the presence of acetic acid that cannot provide the ordered structure.

It was interesting that in the spectrum of sample PA, except for the absorption band at 1641 cm^{-1} , there is absorption band of medium intensity at 1723 cm^{-1} (Fig. 4). These absorption bands are characteristic of stretching vibrations of $-\text{COOH}$ groups from acetic acid physically adsorbed by the sample. But these bands were absent in bifunctional PSA sample obtained in the same conditions. Perhaps, hydrophobicity of the thiol groups prevented the adsorption of acetic acid by the surface groups. We supposed that the connection between the initial composition of the reaction solution and structural-adsorption properties of BFS would be more complex than for monofunctional silica (PH, PA). This is primarily due to the interaction of functional groups of different nature in the initial solution, changing the acidity of the medium, that certainly influences the BFS structure formation and, consequently, the parameters of their porous structure. On the other hand, even if the functional groups are of the same nature, they are expected to form hydrogen bonding affecting the topography of their location in the surface layer. However, in this case, although indirect, the effect of this interaction on structural and adsorption properties of the final products could be possible. Fig. 5a presents low temperature isotherms of nitrogen adsorption-desorption by BFS that have developed porous structure (Table 1) and distribution pores by sizes confirms this, too (Fig. 5b). However, a significant difference in the shape of isotherms witnesses of the impact of pH of the reaction mixture of trifunctional silanes in the initial solution on the parameters of the porous structure of silica. BFS isotherms obtained using concentrated hydrochloric acid (PSH) belong to the type IV according to the IUPAC classification [23] and have hysteresis loops in the range of relative pressures from $\sim 0.6 - 0.8$. The loop of sample PSA is very narrow and its shape is not typical for SBA-15 type samples.

Notes: 1) S_{BET} - Specific surface area calculated from adsorption data in relative pressure range 0.05-0.20; 2) V_{sp} - Single point pore volume calculated at $P/P_0 = 0.98$; 3) d_{me} - Pore width calculated at the maximum of PSD curve using improved KJS method [22]; 4) a_0 - The distance between the centers of the pores from TEM, 5) h_w - The thickness of the pore walls from TEM.

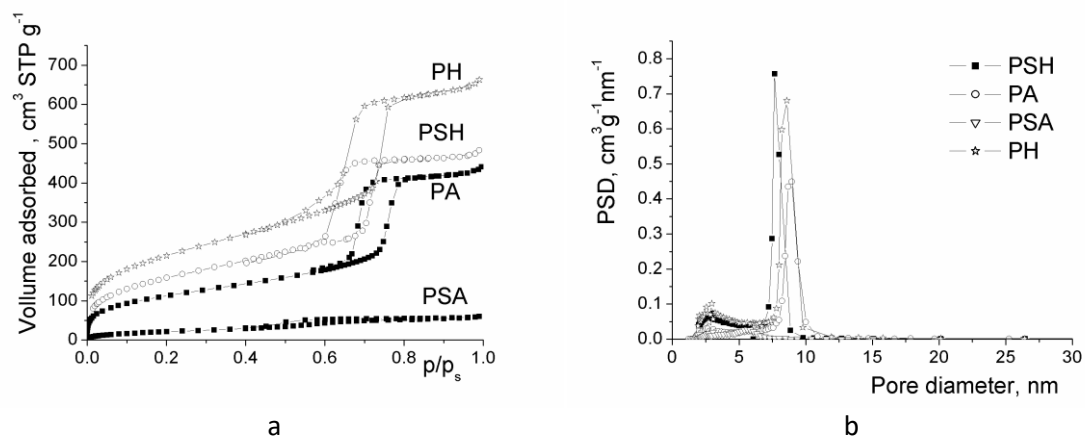


Fig 5. Isotherms of nitrogen adsorption and desorption (a) and pore size distribution curves (KJS) (b).

Table 1. Structural and adsorption properties of the synthesized bi- and monofunctional silicas

Sample	Ratio of SMS/trifunctional silanes	¹ S _{BET} , m ² g ⁻¹	² V _{sp} , cm ³ g ⁻¹	³ d _{me} , nm	⁴ a ₀ , nm	⁵ h _w , nm
PH	10:1(DPTS)	789	1.01	8.6	12.5	2.0
PSH	10:1(0.5 DPTS+0.5 MPTMS)	588	0.74	7.7	12.0	2.1
PA	10:1 (DPTS)	417	0.66	8.9	12.1	2.2
PSA	15:1(0.5 DPTS+0.5 MPTMS)	80	0.09	5.6	-	-

However, it could be concluded, that the presence of mercaptopropyl groups together with phosphor-containing groups can deteriorate the three-dimensional structure. The obvious fact is, that the introduction of higher amount of functional groups and soft synthesis conditions change micelle-forming process, and the resulting materials possess disordered structure and low specific surface area (PSA). That is why we could not recommend this technique (PSA) for the industrial production and use as adsorbents or catalysts.

4 Conclusions

One-pot synthesis can be used to produce bifunctional materials with different hydrophilic / hydrophobic surface functional groups with the prospect of further use as heterogeneous catalysts or sorbents, as possessing developed surface area, ordered structure, and high concentration of functional groups. The technique of template synthesis (using template P123) allowed obtaining mesoporous materials of SBA-15 type with thiol and phosphonic groups in the surface layer (S_{BET} = 417-789 m²g⁻¹, V_{sp} = 0.66-1.01 cm³g⁻¹, d_{me} = 7.7-8.9 nm). They have highly developed porous structure typical for SBA-15 type silica.

This method of synthesis allows introducing thiol group preserving the structural parameters typical for SBA-15.

The use of acetic acid instead of concentrated hydrochloric acid causes a decrease in the specific surface area, pore sorption volume and diameter. The method of synthesis of BFS using hydrochloric acid as catalyst can be recommended for the synthesis of highly efficient sorbents.

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