

# DESIGN OF FUNCTIONALIZED POLYSILOXANE ADSORBENTS AND THEIR ENVIRONMENTAL APPLICATIONS

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**Abstract.** Here we consider the routes of synthesis (which is performed by use of sol-gel method) of a new class of sorbents, namely: polysiloxane xerogels functionalized with nitrogen-, oxygen-, phosphorus- and sulfur content ligand groups. Applying a number of physical methods (SEM, TEM, AFM, IR and Raman spectroscopy,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  CP/MAS NMR, EPR spectroscopy, ERS, thermal analysis) we established the structure of both: the xerogels and their surface. An influence of some factors on the structural-adsorption characteristics of such xerogels and their sorption properties is analyzed.

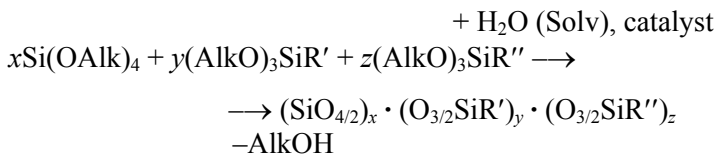
**Keywords:** Sol-gel method, functionalized polysiloxane xerogels, synthesis, structure, sorption properties.

## 1. Introduction

Modification of silicas surface by trifunctional silanes,  $\text{R}_3\text{SiR}'$  ( $\text{R} - \text{Cl}$  or  $\text{AlkO}$ ;  $\text{R}' - \text{functional group}$ )<sup>1-4</sup>; realization of hydrolytic polycondensation of alkoxy-silanes<sup>5-9</sup> (the sol-gel method<sup>10</sup>); accomplishment of hydrolytic polycondensation of alkoxy-silanes in the presence of surfactants (the template method)<sup>11</sup> – these are the most widely used approaches which are applied for synthesis of polysiloxane adsorbents that contain functional groups in their surface layer.

Here we consider the sol-gel method which recently had received wide practice. Usually, the most applied one is its variation which is based on reaction of joint hydrolytic polycondensation of alkoxy-silanes (Scheme 1). Introduction of water and catalyst (e.g.,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ) in the initial system leads to hydrolysis of alkoxy-silanes with a formation of silanol groups,  $\equiv\text{Si}-\text{OH}$ .

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Scheme 1

These groups start to interact with each other (or with alkoxy silyl groups,  $\text{Alk-O-Si}\equiv$ ) immediately, which leads to a creation of siloxane bounds ( $\equiv\text{Si-O-Si}\equiv$ ), causing occurrence of oligomers. The results of further condensation of these oligomers are the occurrence of polymers of a various structure. The growth of polymers conducts to occurrence of colloidal particles which consequently leads to occurrence of sol. The further integration of these particles and creation of aggregates causes transaction of sol into gel. The following treatment of formed gel (its ageing, washing, drying, etc.) results in a xerogel. The presence of trifunctional silanes  $(\text{AlkO})_3\text{SiR}'$  (functionalizing agents) in above-mentioned systems allows one to obtain xerogels (adsorbents) which contain necessary functional groups in their surface layer. Most of alkoxy silanes are liquids, which are mixed up together, however, nonaqueous solvents often are used during synthesis – as with the purpose to avoid the occurrence of interface phases during the gel formation, and with the purpose of rendering influence on porous structure parameters of the final products.

Application of the sol–gel method to synthesising functionalized polysiloxane adsorbents (FPA) offers a number of advantages over other methods. The main one of these advantages lies in the possibility of application of multicomponent systems. Firstly, it is possible to vary both nature and concentration of the structure-forming agent.<sup>12</sup> Tetraethoxysilane,  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (TEOS) is most often used as one. However, it is possible to use bis(trialkoxy)silanes,  $(\text{AlkO})_3\text{Si-B-Si}(\text{OAlk})_3$  (B – organic bridges)<sup>13–15</sup> and more complicated alkoxy silanes as structure-forming agents.<sup>16</sup> The combinations of structure-forming agents also can be used, including alkoxy compounds of other elements.<sup>17</sup> Secondly, it is possible to vary both composition and ratio of functionalizing agents.<sup>18</sup> In this case the application of one-stage process allows to prepare polysiloxane adsorbents which would contain simultaneously several functional groups with different nature.

It is meant, that character of these groups and the range of their ratios can be sufficiently wide. However, it is necessary to remember, that both nature and geometrical sizes of functional groups ( $\text{R}'$  и  $\text{R}''$ ) have, as a rule, an essential influence on a route of hydrolytic polycondensation reaction. As a result in such systems one can not observe gels' formation, or the formed gels would not be homogeneous, etc. It is noted, that the content of functional groups in xerogels can reach 6.0 mmol/g, which is about an order of magnitude greater than that attained in the situation with modified silicas.<sup>1–4</sup> It is noted also, that a wide

range in the choice of conditions which are acceptable for effecting the hydrolytic polycondensation reaction allows one to obtain final products – xerogels – with imperative properties. The above-stated relates, in the first place, to their structural-adsorption characteristics. Taking into account an existence of huge number of alkoxy silanes derivatives, it is possible to assert about the presence of significant prospect in search of new materials with unique properties. Therefore the fact of fast development of this chemistry area (especially last 10–15 years) does not cause surprise. The cycle of Slinyakova team's papers, which was devoted to research of organosilicon adsorbents (xerogels) with alkyl and aryl radicals in their surface layer,<sup>19</sup> was the base of such progress. Else in 1977 this team together with Voronkov's team also described a preparation of a xerogel with the use of hydrolytic polycondensation reaction of mercaptomethyltrimetoxysilane.<sup>20,21</sup> It was the start of papers series which concern S-containing silicon-organic sorption materials.<sup>22,23</sup> It is meant, that the nature of functional groups R' in the initial trialkoxysilanes (AlkO)<sub>3</sub>SiR' may be rather different. This short review was intended to consider the methods of synthesis, structure and sorption properties of xerogels containing complexing groups as functional one's.

## 2. Synthesis of Functionalized Polysiloxane Adsorbents

Else in 1966 3-aminopropyltriethoxysilane (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub> (APTES) was offered for producing of an aminocontaining xerogel.<sup>24</sup> Later such xerogels were obtained repeatedly and they are studied in details. The aim of numerous works<sup>25,26</sup> was to synthesis an adsorbent with a high content of amine groups. However, the influence of TEOS/APTES and other conditions on structural-adsorption characteristics of the final producers the ratio was not yet established. As it is known these characteristics have direct relation with functional groups accessibility. This gap was filled in.<sup>27–29</sup> Reaction of a concurrent hydrolytic polycondensation of TEOS and APTES at their molar ratio of 2:1 is used for synthesis of such xerogel; the alkaline medium was created after addition of water. Some synthesis were carried out by the use of nonaqueous solvents. The procedure made it possible to prepare xerogels with reproducible main characteristics and a content of [(SiO)<sub>2.6</sub>(O<sub>3/2</sub>Si(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>)H<sub>2</sub>O].<sup>27–29</sup> Depending on the synthesis conditions the content of amine groups varied in the interval from 2.8 to 4.2 mmol/g. The obtained xerogels have high hydrolytic and thermal stability, for example, the decomposition of their surface layer begins beyond 275°C.<sup>25,30</sup> The above-considered approach involved application of ethanol, which often allowed to avoid appearance of two phases during formation of gels and was employed for producing xerogels with such functional groups as ≡Si(CH<sub>2</sub>)<sub>3</sub>NHCH<sub>3</sub>, ≡Si(CH<sub>2</sub>)<sub>3</sub>NH(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>, ≡Si(CH<sub>2</sub>)<sub>3</sub>NC<sub>3</sub>H<sub>5</sub>N (imidazolyl), [≡Si(CH<sub>2</sub>)<sub>3</sub>]<sub>2</sub>NH.<sup>18,30</sup>

In the last case the formation of so-called “arched structures”  $\equiv\text{Si}(\text{CH}_2)_3\text{-NH-}(\text{CH}_2)_3\text{Si}\equiv$  expected, that obviously should have a high hydrolytic stability. The authors<sup>31–33</sup> described a synthesis of xerogels with ethylenediamine groups (and an additional vinyl groups<sup>33</sup>). These synthesis did not involve any solvent. The ratios of alkoxyxilanes  $\text{TEOS}/(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2/(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}=\text{CH}_2$  in the initial solutions were 1:1:1 and 4:1:1; a content of aminogroups in the final products was 1.8–2.8 mmol/g. However, no parameters of the xerogel porous structure of were presented. In<sup>6</sup> it was shown when the ratio of alkoxyxilanes of  $\text{TEOS}/(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2 = 2:1$  the formed xerogel was practically nonporous. This agrees with the data of Silva and Airolodi.<sup>34</sup>

Synthesis of xerogels with aniline group (or its derivatives) were presented in<sup>35–38</sup> (catalyst – HF, solvent – ethanol). Obtaining low-density xerogels that contain aminogroups of various nature was analyzed in,<sup>39</sup> and obtained monodispersed colloid particles which contain aminogroups were considered in.<sup>40</sup> Obtaining xerogel-anion-exchanger with functional group of  $\equiv\text{Si}(\text{CH}_2)_3\text{N}(\text{CH}_3)_3^+\text{Cl}^-$  composition was described in<sup>26,41</sup> (acid medium, solvent – alcohol), with 3-n-propyl-1-azonia-4-azabicyclo[2.2.2]octanechloride – in.<sup>42</sup>

Monocomponent systems were used to obtain xerogels that contain cyclam.<sup>43</sup> It was shown that parameters of their porous structure depend on a nature of catalyst, solvent, composition of hydrolysing groups [ $\text{Si}(\text{OEt})_3$  or  $\text{SiH}_3$ ] and a temperature of gel treatment. It is interesting, that hydrolytic polycondensation of the monomers with a ligand group  $-\text{NHC}(=\text{NH})\text{NH}_2$  was completed only in 70 h at 100°C, and in the situation of its symmetric analogue the corresponding polyalkylsilsesquioxane could not be obtained by this method. Therefore the hydrolytic co-polycondensation of that monomers with  $\text{TEOS}^{23}$  was used.

The authors<sup>18,30,44</sup> described a synthesis of porous xerogels with a bifunctional surface layer composed of  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2/\text{CH}_3$  (or  $\text{C}_6\text{H}_5$ ). The ingredient ratio in the initial solution was 1:1:1. It allowed to keep relatively high content of 3-aminopropylgroups in the final products (3.0–3.7 mmol/g). A refusal to use of ethanol during synthesis of such xerogels leads to form two phases during gels formation.<sup>29</sup> Earlier<sup>41</sup> it was shown that an introduction of methyl groups increases mechanical strength of spheres of xerogels (0.2–1.5 mm) with amine groups.

Aminocontaining xerogels were obtained by  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3$  (BTESE),  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH})_2\text{Si}(\text{OC}_2\text{H}_5)_3$  (BTEST) and  $(\text{C}_2\text{H}_5\text{O})_3\text{SiC}_6\text{H}_4\text{Si}(\text{OC}_2\text{H}_5)_3$  (BTESB)<sup>13,14</sup> as structure-forming agents. The authors<sup>15</sup> studied the particularities which were observed in the case of the synthesis of xerogels with 3-aminopropyl groups and showed that in order to avoid nonhomogeneous gelation it was necessary to use ethanol, to effect a preliminary hydrolysis of structure-forming agent (with  $\text{F}^-$  as a catalyst), and to enlarge the time for gel ageing with the purpose to increase of polycondensation degree. The content of ligand groups in

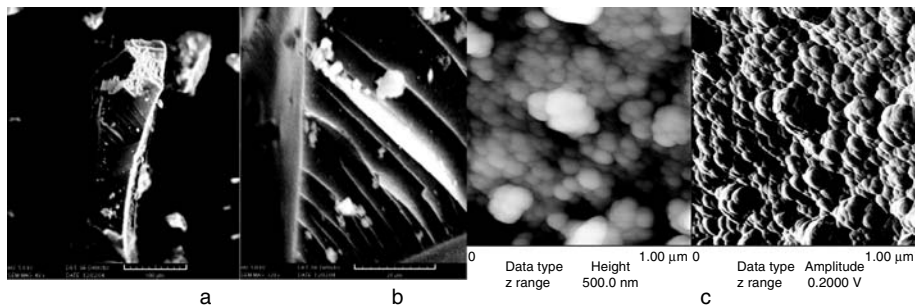


Figure 1. SEM (a – 480x; b – 3,200x) and AFM<sup>14</sup> micrographs of aminocontaining xerogel.

the prepared xerogels ranged from 1.0 to 2.6 mmol/g. According to SEM microphotographs (Figure 1a, b) the lamellar structure is characteristic feature for these xerogels. Their AFM micrographs are presented in Figure 1c. It is brought about by the existence of aggregates of primary particles (globules). Their size amounts to 30–65 nm.

Parish and co-workers<sup>32</sup> proposed several approaches to obtain xerogels which would contain  $\equiv\text{Si}(\text{CH}_2)_2$  or  $_3\text{PPh}_2$  groups (catalyst –  $(n\text{-Bu})_2\text{Sn}(\text{CH}_3\text{COO})_2$ , solvent – ethanol or toluene). Later these syntheses were reproduced in methanol.<sup>45</sup> The xerogels that contain additional groups (amine or thiol) were also described. Partial oxidation of P(III) atom was observed in all cases.<sup>45</sup> Obtaining xerogels with phosphine ligands was considered in details by Lindner.<sup>46</sup>

The systems with two and three components were used for synthesis of xerogels with (thio)urea groups (TEOS was a structure-forming agent; ethanol as a solvent;  $\text{F}^-/\text{Si} \sim 1/100$ ). The alkoxy silanes  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S}(\text{O}))\text{NHR}'''$ , where  $\text{R}''' = -\text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, -\text{C}_6\text{H}_5, -\text{CN}(\text{C}_6\text{H}_4), -(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$ , were involved as functionalizing agents.<sup>47</sup> Also the precursors forming arched structures are used.<sup>48</sup> When the TEOS/trifunctional silane ratio is 2:1 the surface of formed xerogels possessed hydrophobic properties, and the xerogel did not have porosity, while at a ratio of 4:1 (or 8:1) they showed hydrophilic properties and porous structure. The xerogel surface acquired hydrophilic properties also in the case of introduction of additional amine groups. The content of functional groups was 0.9–3.3 mmol/g. For xerogels with arched structure the first exoeffect was observed in the range 380–430°C.<sup>47,48</sup> Synthesis of xerogels with malonamide ligands were considered in.<sup>40</sup>

Unger and coworker<sup>50</sup> described the synthesis of xerogels using 1,2-epoxy-3-propoxypropyltriethoxysilane. Initially, polyethoxysiloxane was prepared from TEOS by acid hydrolysis. Homogeneity of the reaction medium in the second stage was maintained by adding of sodium or ammonium hydroxide, therefore the final product contained either 1,2-dihydroxyl-3-propoxypropyl or hydroxyl-amine functional groups.

Synthesis of xerogels with groups  $\equiv\text{Si}(\text{CH}_2)_3\text{SH}$  is usually performed by applying such catalysts as  $(n\text{-Bu})_2\text{Sn}(\text{CH}_3\text{COO})_2$ <sup>25,26</sup> or  $\text{HCl}$ .<sup>51,52</sup> However, according to the NMR spectroscopy data<sup>26,53</sup> the polysiloxane skeleton of these xerogels does not have any effective cross-linking. Besides that, the polymeric matrix composition includes tin.<sup>25</sup> Moreover, these systems are noted to have two phases, and the formed xerogel is practically non-porous.<sup>54</sup> These drawbacks could be avoided by using methanol as a solvent and  $\text{F}^-$  as a catalyst.<sup>54</sup> The xerogel obtained at  $\text{TEOS}/\text{MPTMS} = 2:1$  possessed an extended porous structure (the content of HS groups was equal to  $4.5 \text{ mmol g}^{-1}$ ).

The vary of alkoxy silanes ratio in the range of 5:1–1:1 allowed to obtain xerogels with thiol groups content from 1.9 to  $5.3 \text{ mmol/g}$ .<sup>55</sup> In the last case the sample consists of partly stick together particles of the spheric form (their size is 2.5–3.0  $\mu\text{m}$ , Figure 2). It is not typical for xerogels of this class. The xerogels which contain 3-mercaptopropyl groups were synthesized with the use of BTESE and BTESB as structure-forming agents; the content of functional groups was 1.0–2.7  $\text{mmol/g}$ .<sup>14,56</sup>

Obtainance of xerogel with a ligand group that contained sulphide, amine and thiol centers was considered in.<sup>57</sup> A comparative characteristic of sorbents with SH-groups is given in.<sup>52,58</sup>

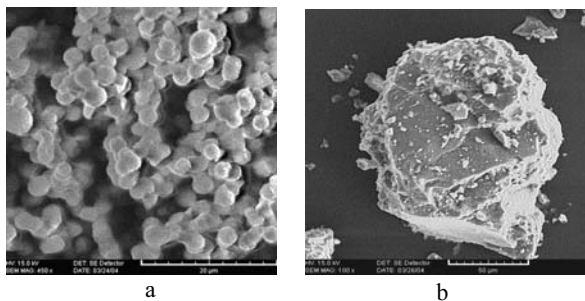
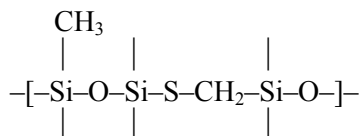


Figure 2. SEM microphotographs of HS-containing xerogels ( $\text{TEOS}/\text{MPTMS} = 1:1$  (a) and 3:1 (b)).<sup>55</sup>

The authors<sup>18,54</sup> described also preparation of xerogels which contained a bifunctional surface layer of the SH/ $\text{NH}_2$  type (the structure-forming agent was TEOS).  $\text{MPTMS}/\text{APTES}$  ratio in an initial solution (3.0, 1.0 and 0.33 mol) determined the ratio of functional groups in the final products. Earlier synthesis of xerogels with thiol and amino groups were considered in.<sup>51</sup> Most of amino-groups in the obtained xerogel are protonated. The exception is a sample obtained at the ratio of  $\text{TEOS}/\text{MPTMS}/((\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}_2) = 4:1:3$ . The authors<sup>51</sup> suppose that most of aminogroups form hydrogen bond with thiol groups. This hinders their protonation in the acid medium. It is interesting that the treatment of these xerogels by 0.11 M  $\text{HCl}$  gives only 1–2% mass loss, during that time

when the same treatment of aminocontaining xerogels gives mass loss of 8–10%.<sup>26</sup>

The xerogels with an analogous surface layer were obtained using BTESE as a structure-forming agent.<sup>59</sup> MPTMS/APTES ratio in an initial solution was 1:1. The synthesis of xerogel that contain simultaneously CH<sub>3</sub>- and HSCH<sub>2</sub>- groups in its surface firstly was described in.<sup>60</sup> Co-polycondensation of these two alkoxy silanes in acetone leads to polymers that as the authors suppose<sup>60</sup> has the following structure of its chain:



The surface of this polymer has weaker acidic properties than the surface of xerogel which was synthesized using only (CH<sub>3</sub>O)<sub>3</sub>SiCH<sub>2</sub>SH.<sup>17</sup> Polysiloxane xerogels which contain 3-mercaptopropyl and methyl groups in the surface layer were obtained with ethanol used as a solvent and F<sup>-</sup> used as a catalyst.<sup>61</sup> The ratio of trifunctional silanes is varied from 1:2 to 2:1, and the ratio of TEOS/ (mix of trifunctional silanes) was 1:1 and 2:1. The content of HS groups in the xerogels obtained was 1.2–4.7 mmol/g. According to AFM these xerogels are composed of spheric particles. The mean size of these particles is close to 35–45 nm. The xerogels that contain *n*-propyl group instead methyl were synthesized in analogous conditions.<sup>62</sup> The content of HS groups in these xerogels was 1.2–3.5 mmol/g.

For the first time the xerogel with groups ≡Si(CH<sub>2</sub>)<sub>2</sub>COOH was synthesized in 1964<sup>63</sup> by the acid hydrolysis of (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>CN with following addition of TEOS. Obtained white product sorbed well the NHET<sub>2</sub> and Py. Later on this approach was considered in detail by the authors.<sup>64,65</sup> One of the salient features of the synthesized xerogels was that the content of carboxyl groups (according to the potentiometric titration data) was always lower than the content calculated from the element analysis data for carbon (1.8–3.7 mmol/g). Therefore, these groups may be partly incorporated in the polysiloxane matrix, or some part of them forms complex ethers. Synthesis of xerogels with ligand – EDTA analogue was described in.<sup>66</sup>

The hydrolytic polycondensation of (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> in boiling HCl (conc.) gives a fragile substance with a composition of [O<sub>3/2</sub>Si(CH<sub>2</sub>)<sub>2</sub>P(O)(OH)<sub>2</sub>]<sub>x</sub>.<sup>67</sup> The xerogels contained (thio)phosphineoxide groups were also prepared using (S<sub>2</sub>O=)P[C<sub>6</sub>H<sub>4</sub>Si(OPr<sup>i</sup>)<sub>3</sub>]<sub>3</sub>.<sup>68</sup> In this case the hydrolytic polycondensation was held in THF together with the presence of an excess of water, the catalyst was *n*-toluenesulfonic acid or HCl. In the last case the process resulted in formation of highly porous xerogels.

The system with two components TEOS/(C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>2</sub>P(O)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (DFTS) was used to obtain xerogels with P=O-groups (the ratio of components was 2:1–10:1; ethanol used as a solvent; F<sup>-</sup>/Si = 1/100 (mol)).<sup>69</sup> The content of functional groups in the obtained xerogels was 1.2–1.4 mmol/g. The samples which were synthesized at the alkoxy silanes' ratios of 6:1–10:1 had porosity.<sup>69</sup> At the same time the analogous xerogels which had HCl acid as the catalyst<sup>70</sup> were porous only at the ratios of alkoxy silanes equal 10:1. The acidic treatment of nonporous xerogels leads to formation of porous samples with ≡Si(CH<sub>2</sub>)<sub>2</sub>P(O)(OH)<sub>2</sub> functional group.<sup>71</sup> Its content was 2.6–3.5 mmol/g.

Also bis(trialkoxy)silanes (RO)<sub>3</sub>Si-B-Si(OR)<sub>3</sub> used for synthesizing P=O-containing xerogels.<sup>70</sup> However, in the case of B = -(CH<sub>2</sub>)<sub>2</sub>- (at a content of 80 mol%) and HCl as a catalyst these xerogels turned to be practically nonporous, and porous samples were obtained only in the case of conversion -P(O)(OEt)<sub>2</sub> → -P(O)(OH)<sub>2</sub>. In<sup>72</sup> it was shown that gelation of alkoxy silane (EtO)<sub>3</sub>SiCH<sub>2</sub>CH [PO(OEt)<sub>2</sub>]CH<sub>2</sub>CH<sub>2</sub>Si(OEt)<sub>3</sub> in the medium of 1 M HCl (with THF as a solvent) for 11 days led to the transpiration of monolithic sample whose boiling in concentrated HCl yielded a xerogel with -P(O)(OH)<sub>2</sub> groups. Xerogels which contained amide derivatives of phosphonic and thiophosphonic acids, ≡Si(CH<sub>2</sub>)<sub>3</sub>NHP(O,S)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> were obtained by application three components systems (TEOS was a structure-forming agent).<sup>73</sup> 3-mercaptopropyl and 3-aminopropyl groups were used in addition to P=O-groups. The general content of functional groups were reaching 3.6 mmol/g.

Ethoxysilyl derivatives<sup>74</sup> of α- and β-cyclodextrines were used for preparing xerogels with these macrocyclic molecules (DMF (or DMF/water) used as a solvent, F<sup>-</sup>/Si = 1/100 (mol)).<sup>75</sup> The content of functional groups was 0.1, 0.5 and 1.0 mmol/g.

### 3. Structure of Functionalized Polysiloxane Adsorbents

The research of the FPA structure have some difficulties as FPA are the amorphous compounds. Therefore it is necessary to apply a number of physical methods which allow to obtain the reliable information about FPA's structure on the globular and molecular levels. There is also difficulties in the studying of the composition and structure of FPA surface layer, particularly, when this layer is polyfunctional. In this chapter the authors consider the possibilities which some physical methods give.

#### 3.1. VIBRATIONAL SPECTROSCOPY

The vibrational spectroscopy, especially IR spectroscopy, is known to be a traditional technique used for FPA investigation. Its wide application makes it



possible to ascertain that the obtained adsorptive materials contain (a) siloxane bonds and introduced functional groups (and/or products of their transformation during the course of synthesis), (b) silanol groups (and/or alkoxy silane groups), (c) water and/or nonaqueous solvents used during synthesis. Finally, the vibrational spectroscopy data often gives possibility to make conclusions about the participation of functional groups in hydrogen bond formation.

Here we considered IR spectra of some xerogels which are typical for functionalized polysiloxane adsorbents. Thus, the most intensive adsorption band with a high-frequency shoulder is observed in the region  $1,000\text{--}1,200\text{ cm}^{-1}$  of IR spectra of the xerogels with  $\equiv\text{Si}(\text{CH}_2)_3\text{SH}/\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$  bifunctional surface layer<sup>54</sup> (Figure 3) consistent with the presence of a three-dimensional siloxane framework ( $\equiv\text{Si-O-Si}\equiv$ ). The presence of propyl chains in the IR spectra is indicated by a group of adsorption bands of weak intensity in the region  $1,300\text{--}1,500\text{ cm}^{-1}$  and two (sometimes – three) adsorption bands of medium intensity in the region  $2,800\text{--}3,000\text{ cm}^{-1}$ . Last one is characterized by stretching vibrations of  $\nu_{\text{s,as}}(\text{CH})$ . In the IR spectrum of xerogel with thiol groups (Figure 3B) at  $2,565\text{ cm}^{-1}$  is legibly fixed the adsorption band which refers to  $\nu(\text{SH})$ . The reduction of part of MPTMS in a starting solution results into the decrease of its intensity and which becomes invisible in the IR spectra of xerogels C and D (Figure 3). However, Raman spectra of these xerogels<sup>6</sup> have the line in  $2,570\text{--}2,580\text{ cm}^{-1}$  region, assigned to  $\nu(\text{SH})$ ,<sup>76</sup> irrespectively to a ratio in surface layer of thiol and amino groups. Besides in Raman spectra of samples C and D at higher than  $3,250\text{ cm}^{-1}$  weak lines are observed and assigned to  $\nu_{\text{s,as}}(\text{NH})$  vibrations of amino groups. As all the samples contain water, the adsorption band of medium intensity is observed in the region  $1,625\text{--}1,640\text{ cm}^{-1}$ , and it correspond to vibrations of  $\delta(\text{H}_2\text{O})$ . Other wide intensive band is presented at higher  $3,100\text{ cm}^{-1}$  in all IR spectra, assigned to  $\nu(\text{OH})$  of adsorbed water. On its background for samples C, D, E and F at  $\sim 3,300$  and  $\sim 3,370\text{ cm}^{-1}$  there are two additional low intensive adsorption bands which can be referred to  $\nu_{\text{s,as}}(\text{NH})$  of amino groups (Figure 3). Besides in the IR spectra of samples C-F there are weak adsorption bands at  $1,585\text{--}1,595$  and  $1,540\text{--}1,555\text{ cm}^{-1}$  which intensity increases from the sample C to F, that is at increasing of amino groups in surface layer. Such bands are absent in the IR spectrum of xerogel B. Occurrence of these bands is caused by deformation vibrations of amino group  $\delta(\text{NH}_2)$ .

Considering the different nature of  $-\text{SH}$  and  $-\text{NH}_2$  groups, it is possible to assume the protonation of amino groups. In other words, in such xerogels the surface layer can have salt character of type  $[\equiv\text{Si}(\text{CH}_2)_3\text{NH}_3]^+[\equiv\text{Si}(\text{CH}_2)_3\text{S}]^-$ . However the line correspond to  $\nu(\text{SH})$  in Raman spectrum is conserved even at dominating quantity of amino groups in surface layer (sample E).<sup>76</sup> Moreover the adsorption bands which correspond to stretching vibrations of  $\nu_{\text{s,as}}(\text{NH})$  and deformation vibrations  $\delta(\text{NH}_2)$  of unprotonated amino groups are observed in the

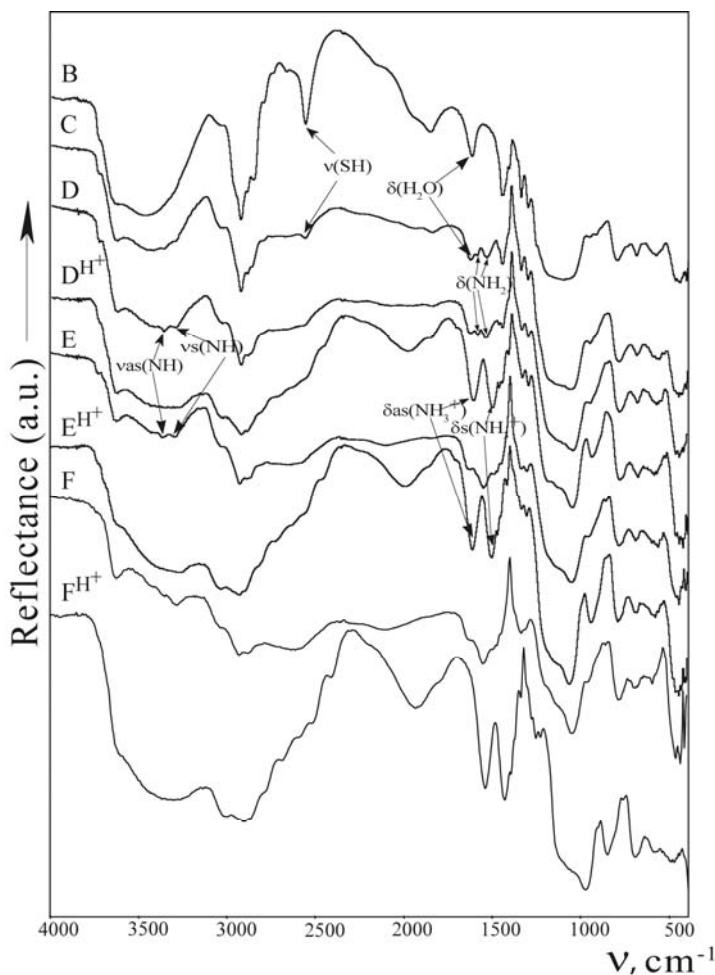


Figure 3. IR reflection spectra of xerogels containing HS-group (B); bifunctional surface layer with the ratio of  $-\text{SH}/-\text{NH}_2 = 3.2$  (C), 1.1 (D) and 0.4 (E); amino group (F); the xerogels treated by 0.1 M HCl solution ( $\text{D}^{\text{H}^+}$ ,  $\text{E}^{\text{H}^+}$  and  $\text{F}^{\text{H}^+}$ ).

IR spectra of xerogels C and D (Figure 3) (Worth mentioning that these figures have excess of thiol groups in relation to amino groups in their surface layer). The similar situation was observed for the polymers which were obtained by reaction of hydrolytic polycondensation of mixtures MPTMS/APTES at the ratios 1:1 and 4:1.<sup>77</sup> If the alkylammonium cation was formed in samples B–D, several typical adsorption bands would have been observed in their IR spectra in the region  $2,500\text{--}2,800\text{ cm}^{-1}$  and the band of medium intensity at  $\sim 2,000\text{ cm}^{-1}$ .<sup>76</sup> However these adsorption bands are not registered in the IR spectra for these samples (Figure 3). They are observed in the IR spectra of

samples D, E and F only after their treatment by 0.1 M HCl solution (Figure 3). Moreover two intensive adsorption bands at  $\sim 1,500$  and  $\sim 1,610$   $\text{cm}^{-1}$  which are referred to  $\delta_s(\text{NH}_3^+)$  и  $\delta_{as}(\text{NH}_3^+)$  correspondingly (last adsorption band is masked by less intensive adsorption band of  $\delta(\text{H}_2\text{O})$  located in the same region) appear in the IR spectra of such samples (Figure 3). Similar adsorption bands were observed in the IR spectra of intercalate APTES/Zr( $\text{HPO}_4$ )<sub>2</sub> which contained protonated products of the APTES condensation.<sup>78</sup> Thus, the amino groups in the surface layer of the initial FPA are non-protonated but are involved in the hydrogen bond formation. The weak adsorption band  $\delta(\text{NH}_2)$  at  $1,600$   $\text{cm}^{-1}$  is recorded in the IR spectrum of individual APTES. This band was assigned to a hydrogen bond between amino groups.<sup>6</sup> In the IR spectra of xerogels C–F there is low intensive adsorption band in this region (see above) which often splitted in two components and shifted in low-frequency area on  $7\text{--}69$   $\text{cm}^{-1}$  (Figure 3). This fact may indicate the formation in xerogels of hydrogen bond of different nature than in APTES. Probably, the mentioned hydrogen bonds differ a little in nature. Similar observations have been made for bifunctional xerogels which were synthesized using BTESE as a structure forming agent.<sup>59</sup>

The application of IR spectroscopy aiming to study xerogels which synthesis involved participation of bis(trialkoxysilanes)<sup>13–15</sup> enabled one to reveal the presence of  $\equiv\text{Si}\text{--B}\text{--Si}\equiv$  bridges, noncondensed silanol groups of two types (their absorption bands  $\nu(\text{OH})$  are observed at  $\sim 3,730$  and  $\sim 3,650$   $\text{cm}^{-1}$ ) and some nonhydrolyzed  $\equiv\text{Si}\text{--OC}_2\text{H}_5$  groups. This provides evidence for particularities of a polymeric skeleton structure of such sorbents.

If in a surface layer of xerogels appear functional groups that are more complex in their composition (for instance,  $\equiv\text{Si}(\text{CH}_2)_2\text{NHC}(\text{O},\text{S})\text{NHR}''''$  or  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$ ), the IR spectra of the xerogels also becomes more complex. However, the presence of typical absorption intensive bands in the region  $1,400\text{--}1,700$   $\text{cm}^{-1}$  (one in the case of thiourea groups and two in the case of urea groups) allows one to detect easily the presence of  $\text{--NH}\text{--C}(\text{O} \text{ or } \text{S})\text{--NH}\text{--}$  fragments in the xerogel surface layer.<sup>47</sup> In the case of IR spectra of xerogels which contained  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  groups, the most intense absorption band exhibits the second shoulder at  $\sim 1,210$   $\text{cm}^{-1}$  corresponding to  $\nu(\text{P}=\text{O})$ . This band is observed at  $1,241$   $\text{cm}^{-1}$  for individual DFTS. Hence, the shift of this band in a low frequency region testifies to the presence of phosphoryl groups in the hydrogen bond formation.<sup>69</sup> The same situation is observed in the case of xerogels with such groups as  $\equiv\text{Si}(\text{CH}_2)_2\text{NHP}(\text{O})(\text{OC}_2\text{H}_5)_2$ .<sup>73</sup>

The absence of absorption bands  $\nu(\text{C}\equiv\text{N})$  in the region  $2,200\text{--}2,300$   $\text{cm}^{-1}$  of the IR spectra for carboxyl-containing xerogels gives evidence for the complete saponification of nitrile groups.<sup>79</sup> At the same time in these spectra an intense band of absorption appears in the region  $1,720\text{--}1,730$   $\text{cm}^{-1}$ . This is a typical

feature of COOH groups which are connected with OH groups by hydrogen bonds.<sup>76</sup> Moreover, another band appears at  $\sim 1,645\text{ cm}^{-1}$ , which provides evidence to formation of some carboxyl groups of ester bonds. This process is due to the interaction of carboxyl group with either silanol groups<sup>4</sup> or with ethanol.

### 3.2. SOLID-STATE NMR SPECTROSCOPY

It is noted that  $^{13}\text{C}$  CP/MAS NMR spectroscopy is used to study mostly FPA, but its results have as a rule qualitative character. Here is considered spectra of some xerogels with mono ( $-\text{SH}$  or  $-\text{NH}_2$ ) and bifunctional ( $-\text{SH}/-\text{NH}_2$ ) surface layer (Figure 4). Assignment of signals which are observed in those solid-state NMR spectra are represented in Table 1. This fact supports in.<sup>51</sup>

The peculiarity of these spectra is a signal overlap of the central carbon atom of propyl chains and the C atom which is connected with SH-group of the same chain.<sup>26,51</sup> It is known that the chemical's shift value of the central carbon atom of propyl radical  $\equiv\text{Si}-\text{C}[\text{CH}_2]\text{C}-\text{NH}_2$  in the  $^{13}\text{C}$  CP/MAS NMR spectrum points out the status of amino groups. Thus, this resonance line is present at  $\sim 28$  ppm in the  $^{13}\text{C}$  CP/MAS NMR spectrum for individual APTES which have a hydrogen bond between amino groups while in the case of protonation of 3-aminopropyl groups grafted to  $\text{SiO}_2$  surface this line shifted into the strong field region and is seen at 21–22 ppm.<sup>80</sup>

Considering a signal location of the central carbon atom of 3-aminopropyl chain in the  $^{13}\text{C}$  CP/MAS NMR spectrum of sample D (Figure 4 and Table 1), it is necessary to make a conclusion about protoning  $\text{NH}_2$ -groups of this xerogel. Thus the protoning of  $\text{NH}_2$ -groups can be as a result of interaction of this group either with a proton of thiol group or with a proton of silanol group. However it contradicts with the conclusions which were made on the basis of vibration spectroscopy data. Therefore, if the 3-aminopropyl group is not protonated in xerogel D then it takes part in a hydrogen bond. This is due to shift in signal of the central carbon atom of propyl chains in the region of stronger fields (20–23 ppm). Thus, there is resonance at  $\sim 28$  ppm of individual APTES in the  $^{13}\text{C}$  CP/MAS NMR spectrum while at protoning of graft 3-aminopropyl groups to surface  $\text{SiO}_2$  it is moved in the region of stronger fields (21–22 ppm). It is clear that the hydrogen bond characters in the sample D differs from the one which is realized in initial APTES. It is evident that 3-aminopropyl group in a surface of the sample D (and also C and E) forms hydrogen bond with a silanol group. Water molecules which are located in the surface layer of these xerogels<sup>54</sup> also form hydrogen bond, for example, like this type  $[\equiv\text{Si}(\text{CH}_2)_3\text{H}_2\text{N} \cdots \text{H}_2\text{O} \cdots \text{HOSi}\equiv]$ . Therefore, a signal from the central carbon atom of propyl chains will be located in the same region (20–23 ppm) of  $^{13}\text{C}$  CP/MAS NMR spectrum – as well as in the case of protonation of the aminogroup, which is found in the xerogel surface

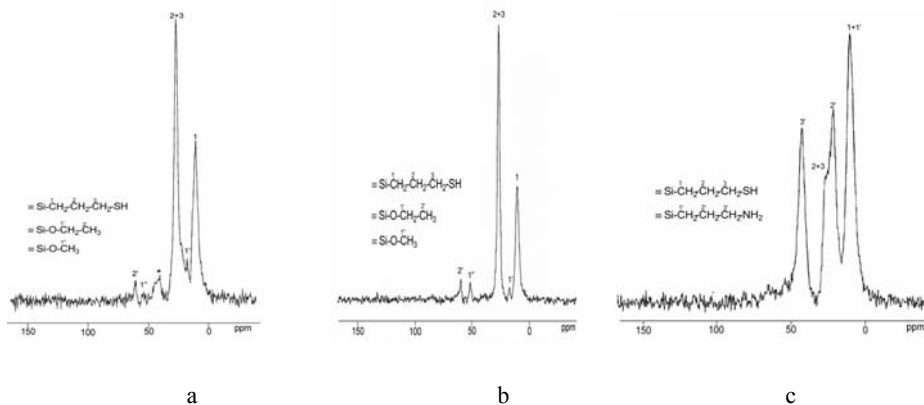


Figure 4.  $^{13}\text{C}$  CP/MAS NMR spectra of samples A, B and D.

TABLE 1. Summary of  $^{13}\text{C}$  CP/MAS NMR data for A, B, D and F xerogels.

Signals assignment	Chemical shifts (ppm)			
	Sample A	Sample B	Sample D	Sample E <sup>81</sup>
$\equiv\text{Si}\underline{\text{C}}\text{H}_2\text{CH}_2\text{CH}_2(\text{SH or NH}_2)$	10.9	10.8	10.0	10.4
$\equiv\text{SiO}\underline{\text{C}}\text{H}_2\text{CH}_3$	17.7	17.7	—	—
$\equiv\text{SiCH}_2\underline{\text{C}}\text{H}_2\text{CH}_2\text{NH}_2$	—	—	21.2	22.1; 25.5 (sh)
$\equiv\text{SiCH}_2\underline{\text{C}}\text{H}_2\text{CH}_2\text{SH}$	27.2	27.1	27.0	—
$\equiv\text{SiCH}_2\underline{\text{C}}\text{H}_2\text{CH}_2\text{NH}_2$	—	—	41.9	42.9
$\equiv\text{SiO}\underline{\text{C}}\text{H}_3$	~52	51.4	—	—
$\equiv\text{SiOCH}_2\underline{\text{C}}\text{H}_3$	60.4	59.7	—	—

layer, and same is in the case of its formation of hydrogen bond with a silanol group (with participation of water molecule).

The suggested hypothesis about surface layer structure in such bifunctional xerogels correlates and is supported by the results of studying  $^{13}\text{C}$  CP/MAS NMR and  $^1\text{H}$  MAS NMR spectra of sample F.<sup>13</sup> Thus, a signal from the central carbon atom of propyl chains is found in the same region (21–23 ppm) in  $^{13}\text{C}$  CP/MAS NMR spectrum of this sample obtained before and after its treatment by HCl solution (Figure 5). This signal is moved to weak fields in the  $^{13}\text{C}$  CP/MAS NMR spectrum when the initial xerogel are heated in a oven (Figure 5). This is in that region where the signal from the central carbon atom of individual APTES is located. In other words, removing of water from surface layer during the heating of the sample results into removing of a bridge between amino and silanol groups, the role of which carried out water molecule, and to form a new hydrogen bond between only amino groups.

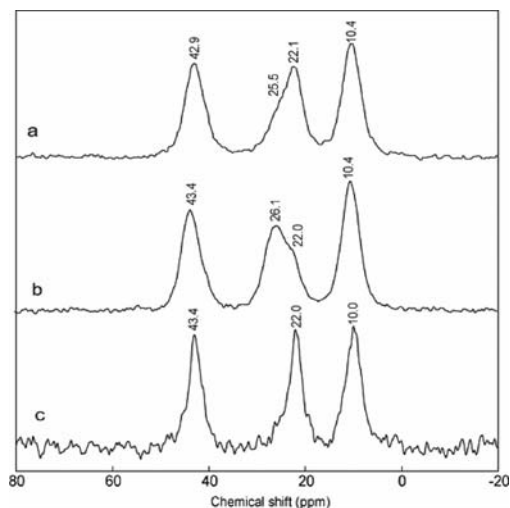


Figure 5.  $^{13}\text{C}$  CP/MAS NMR spectra of initial xerogel E (a), dried in oven (b) and treated by 0.1M HCl (c).

Otherwise, there is a reorganization of surface layer in the xerogel. Therefore, the state of surface layer in such xerogels depends on a drying condition of the samples. This conclusion is supported by the results of works<sup>26,52,82</sup> for which long drying of xerogels in vacuum is characterised: according to  $^{13}\text{C}$  CP/MAS NMR spectroscopy data amino groups in the surface layer of these samples take part at hydrogen bond the character of which is similar to one in individual APTES.

The use of  $^{31}\text{P}$  CP/MAS NMR spectroscopy allowed to reveal transformation of  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  functional groups in the surface layer of xerogels after they were treated by boiling conc. HCl.<sup>69,83</sup> Thus,  $^{31}\text{P}$  CP/MAS NMR spectrum of the initial xerogel contains a single intense symmetric signal within the region from 10 to 40 ppm (Figure 6a). The location of this signal is close to the one of phosphorus atom signal of the initial DFTS (32.9<sup>84</sup> or 34.5 ppm<sup>70</sup>). The appearance of an additional signal at 23–24 ppm in the  $^{31}\text{P}$  CP/MAS NMR spectrum was observed after the treatment of the initial xerogel by conc. HCl and its drying in vacuum (Figure 6b). This signal gives evidence to the formation of  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OH})\text{OSi}\equiv$  product during the drying in vacuum at 120°C. The difference between the two signals is  $\sim 9$  ppm, therefore, two types of functional groups are presented on the surface: those which take part in the hydrogen bonds formation,  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OH})_2$ , and those which are involved in the  $\equiv\text{Si}\text{--O}\text{--P}(\text{O})(\text{OH})\text{--}$  bond formation.<sup>69,83</sup> The appearance of an additional signal in the  $^{31}\text{P}$  CP/MAS NMR spectra of bifunctional xerogels most likely is due to formation of similar bridges,  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)\text{OSi}\equiv$ , by the part of phosphorus containing groups.<sup>73</sup>

Solid-state NMR spectroscopy was found very useful for studying xerogels with complex functional groups, for instance, cyclodextrins (CD).<sup>75</sup> In  $^{13}\text{C}$  CP/MAS NMR spectrum of the xerogel which were functionalized by  $\alpha$ -CD with ethoxysilyl groups are presented by signals on CD fragment as  $\equiv\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{O}$ - spacer.

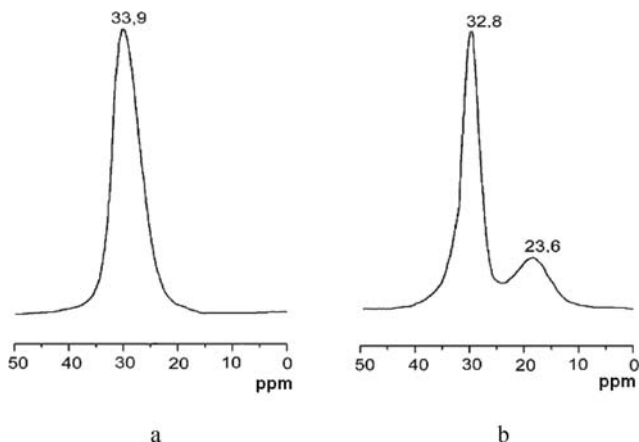


Figure 6.  $^{31}\text{P}$  CP/MAS NMR spectra of the xerogels containing  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$  groups: before (a) and after (b) the treatment of conc. HCl.

$^{29}\text{Si}$  CP/MAS NMR spectra can furnish valuable information about local surroundings of the silicon atoms. These spectra of functionalized polysiloxane xerogels contain, as a rule, two sets of resonance signals in the spectrum interval from  $-110$  to  $-50$  ppm relating to different structural units (Figure 7). In the first region there are three signals at about  $-110$ ,  $-100$ , and  $-90$  ppm that are related to  $(\equiv\text{SiO})_4\text{Si}$  ( $\text{Q}^4$ ),  $(\equiv\text{SiO})_3\text{Si}(\text{OAlk})$  ( $\text{Q}^3$ ) and  $(\equiv\text{SiO})_2\text{Si}(\text{OAlk})_2$  ( $\text{Q}^2$ ), respectively (Alk = H, Me or Et).<sup>85</sup> The second region also contains one signal at  $-66$  ppm with a shoulder at  $-57$  ppm, that are related to the structural units  $(\equiv\text{SiO})_3\text{SiR}'$  ( $\text{T}^3$ ) and  $(\equiv\text{SiO})_2(\text{AlkO})\text{SiR}'$  ( $\text{T}^2$ ).  $^{29}\text{Si}$  CP/MAS NMR spectra of xerogels which contain 3-mercaptopropyl and methyl groups in their surface layer presented in Figure 7 as example.<sup>61</sup> The absence of signals from structural units  $\text{T}^0$ ,  $\text{T}^1$  and  $\text{Q}^0$ ,  $\text{Q}^1$  type in the considered spectra testifies about a high degree of course of hydrolytic polycondensation reaction. The analysis of  $^{29}\text{Si}$  DP/MAS NMR spectra of these xerogels showed that, in all samples, the content of structural units of  $\text{T}^3$  type [ $(\equiv\text{SiO})_3\text{SiCH}_3$  and  $(\equiv\text{SiO})_3\text{Si}(\text{CH}_2)_3\text{SH}$ ] is significantly higher than structural units of  $\text{T}^2$  type [ $(\equiv\text{SiO})_2\text{Si}(\text{OR})\text{CH}_3$  и  $(\equiv\text{SiO})_2\text{Si}(\text{OR})(\text{CH}_2)_3\text{SH}$ , R = H,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ ]. Thus, the  $\text{T}^3/\text{T}^2$  ratio for sample **2TMM** equals to 4.8. Therefore, these xerogels should be characterized by a sufficiently high hydrolytic stability of the surface layer. Note that the use of

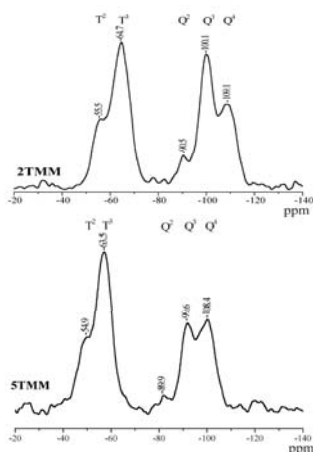


Figure 7.  $^{29}\text{Si}$  CP/MAS NMR spectra of xerogels with HS-groups: TEOS/MPTMS/MTES ratio was equal to 4:1:1 (**2TMM**) and 2:1:1 (**5TMM**).<sup>61</sup>

other catalysts<sup>53</sup> for preparing xerogels with thiol groups results in the formation of a significant number of structural units of  $\text{T}^2$  type in their surface layer.

Introduction of *n*-propyl groups instead of methyl groups are conduct to occurrence easy hydrolyzed structural units of  $\text{T}^1$  type in  $^{29}\text{Si}$  CP/MAS NMR spectra of these samples, i.e. structural units, which are connected with polysiloxane framework by only one siloxane bond. Moreover, if in a content of the xerogel with methyl groups structural units of  $\text{T}^3$  type prevail appreciably above  $\text{T}^2$ , then in a content of the xerogel with propyl groups their contents are about identical. Therefore, the significant degree of incompleteness of the polycondensation process is typical for the last-mentioned xerogel due to influence of the geometrical size of functional group on this process. It is interesting, that replacement of amino group in the xerogel with  $\equiv\text{Si}(\text{CH}_2)_2\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2/\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$  in surface layer of thiol group also conducts to occurrence of a signal from structural units of  $\text{T}^1$  type<sup>73</sup> in  $^{29}\text{Si}$  CP/MAS NMR spectrum. Apparently, it reflects the influence of pH from environment on a degree of polycondensation in such xerogels.

The analysis of the  $^{29}\text{Si}$  CP/MAS NMR spectra of xerogels which were obtained by the use of BTESE/APTES/MPTMS system (Figure 8) leads to the conclusion that in alkoxy silanes during the reaction of hydrolytic polycondensation the  $\equiv\text{Si}-\text{C}$  bond is stabile.<sup>59</sup> The absence of any signals in the region of  $-90$  to  $-110$  ppm confirms such statement. Secondly, only one wide and asymmetric resonance signal is present in the range of  $-43$  to  $-75$  ppm in the  $^{29}\text{Si}$  CP/MAS NMR spectra of these xerogels (Figure 8). A deconvolution of this signal gives five components that corresponds with  $\text{T}^1$ ,  $\text{T}^2$  and  $\text{T}^3$  structural



units. For BTESE these signals correspond with the following products of its hydrolysis and condensation:  $(\equiv\text{SiO})_2(\text{RO})\text{SiC}_2\text{H}_4-$  ( $-55.7$  ppm;  $\text{T}^2$ ) and  $(\equiv\text{SiO})_3\text{SiC}_2\text{H}_4-$  ( $-64.1$  ppm;  $\text{T}^3$ ), where R is  $\text{C}_2\text{H}_5$  or OH [20]. From the last three signals the first one (at  $-46.6$  ppm) has been attributed to the  $\text{T}^1$  structural unit of MPTMS, and the rest of two (at  $-60.0$  and  $-69.5$  ppm) has been attributed consecutively to the  $\text{T}^2$  and  $\text{T}^3$  structural units of APTES and MPTMS.<sup>6,53</sup> Therefore, solid-state NMR spectroscopy application allows to make identification of the nature of functional groups in the surface layer of xerogels. It also reveals the transformation of these groups during the course of xerogels synthesis and allows to establish structural units' type, which form both xerogels and their surface layer. This spectroscopy application allows to fix the participation of functional groups in hydrogen bond formation and other interactions.

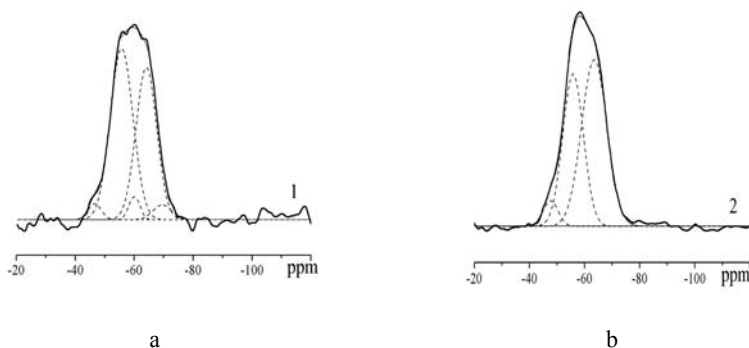


Figure 8.  $^{29}\text{Si}$  CP/MAS NMR spectrum of the xerogel obtained with the use of BTESE/APTES/MPTMS systems (4:1:1 and 8:1:1 (mol)).<sup>59</sup>

### 3.3. METAL MICROPROBE TECHNIQUE

The topography of FPA surface presents an undoubtful interest. For its establishment the authors<sup>86-88</sup> employed the metal microprobe technique: composition and structure of complexes coordination bundle, which forms during sorption of copper(II) ions by amine-containing xerogels from acetonitrile solutions, were identified by electron reflection spectroscopy (ERS) and EPR spectroscopy. It was found that irrespective of degree of surface coverage by the metal on the surface there is the proceeded formation of complexes of one and the same composition ( $\text{CuO}_2\text{N}_2$ ) only. That means that at the equatorial plane of a coordination polyhedron of copper (II) there were two nitrogen atoms. However, the increase of copper(II) content on the surface of xerogels often leads to reduction, firstly, of geometry uniformity of formed complexes and, secondly,

to reduction of a number of the isolated paramagnetic centers, for which the superfine structure is typical. It encounters on an idea that the surface in such xerogels has quite complex character. The similar conclusion also has been made during the study of copper(II) complexes by ERS and EPR spectroscopy. This complexes are formed on the surface of bifunctional xerogels (-SH/-NH<sub>2</sub>) during the sorption of copper(II) ions from their acidified water solutions.<sup>89</sup> The signals form and the calculated values of spectra parameters<sup>89</sup> are typical for tetragonal complexes of copper(II) with a coordination environment [2N, 2O].<sup>90</sup> The analysis of ERS and EPR spectroscopy data which was received during the study of Cu<sup>2+</sup> ions complexation with aminogroups on the surface of FBPS<sup>91</sup> also results in a conclusion that complexes form coordination bundle with [CuO<sub>2</sub>N<sub>2</sub>].

The comparison of EPR spectra parameters for copper(II) complexes, which are formed on the surface of aminocontaining xerogels, leads to following conclusion: two nitrogen atoms are always included in the coordination sphere of copper(II) ion – irrelevant to the nature of structuring agents, to the nature of amine groupings, to functionality of the surface layer, to structural-adsorption characteristics of the sorbent as well as to the nature of the solvent which was used for the sorption. Moreover, all of the Cu(II) complexes, which were identified on the surface of different aminocontaining silicas,<sup>6</sup> have the same composition of a coordination polyhedron, CuN<sub>2</sub>O<sub>2</sub>. All these was determined from the analis EPR spectra parameters.<sup>6</sup> It gave grounds to conclude about a specific and, probably, similar distribution of complexing groups in the surface layer of those silicas. One can not exclude that this is due to exist in that layer – at least, in the case of xerogels – oligomers with the aminopropyl groupings.

## 4. Adsorption Properties of Functionalized Polysiloxane Xerogels

### 4.1. SOME FACTORS CONTRIBUTING TO STRUCTURAL-ADSORPTION CHARACTERISTICS OF FUNCTIONALIZED POLYSILOXANE XEROGELS

Early in<sup>6</sup> on the example of amine-containing xerogels, which were obtained using of two-component system of TEOS/APTES, it was shown that (1) all of the obtained samples are classified as mesoporous adsorbents (for the majority of them their values of  $S_{sp}$ , sorption volume  $V_s$ , and size  $d$  fall within the interval 92–315 m<sup>2</sup> g<sup>-1</sup>, 0.12–1.38 cm<sup>3</sup> g<sup>-1</sup>, 3.7–17.7 nm, respectively); (2) in all cases the introduction of a nonaqueous solvent results in a decrease of  $S_{sp}$  and  $V_s$  and an increase of  $d$ ; (3) with decrease of TEOS/APTES ratio the porosity of samples decreases substantially (at a ratio of 1:1 the xerogel becomes practically nonporous); (4) a similar effect is exerted by a decrease in the amount

of water taken for the hydrolysis; (5) drying of liogels at atmospheric pressure leads to large-pored sorbents; (6) washing of xerogels with water (before repeated vacuum drying) results in a fine-pored adsorbents while washing with abundant amounts of water considerably increases sizes of pores. Relative increase of geometric sizes of the functional group leads to practically nonporous xerogels.

These conclusions were confirmed and expanded in future by studying xerogels with functional groups of other nature. Thus, the increase of TEOS's loading in an initial solution caused the increase in  $S_{sp}$  of the xerogels which contained (thio)urea,<sup>47</sup> thiol,<sup>61</sup> phosphoryl<sup>69</sup> and propionic acid<sup>6,65</sup> groups. However, it should be mentioned that formation of porous structures was observed only for the systems with TEOS/trifunctional silane molar ratio which was higher than 1:1 in case of the HS-groups,<sup>61</sup> 2:1 in case of  $-NHC(O,S)NHR'''$  groups<sup>47,48</sup> or 4:1 in case of the  $-P(O)(OC_2H_5)_2$  groups.<sup>69</sup> Geometric sizes of the mentioned functional groups increases with the same sequence. An influence of the contain of functional groups on structural-adsorption characteristics is clearly seen on samples of xerogels with calixarene or cyclodextrine groups.<sup>75,92</sup>

It was shown by the example of TEOS/(MPTMS + MTES) system that the change in molar ratio of trifunctional silanes in the initial solution from 2:1 to 1:2 leads to the formation of xerogels with the developed porous structure. Thus, at TEOS/trifunctional silanes ratio of 2:1  $S_{sp}$  raised from 408 to 678 m<sup>2</sup>/g and at the molar ratio of 1:1 it raised from 44 to 394 m<sup>2</sup>/g. Simultaneously, the tendency to the increase of other parameters, namely  $V_s$  and  $d$ , was observed.<sup>55</sup> Similar tendencies were defined also for the xerogels with a bifunctional surface layer of NH<sub>2</sub>/CH<sub>3</sub> (or C<sub>6</sub>H<sub>5</sub>) composition.<sup>28,29</sup> By the example of amine-containing xerogels<sup>6</sup> it was shown with using of TEM that such distinctions were determined by sizes of globules and their packed structure.

In the case of the bridged polysilsesquioxane xerogels which were functionalized by amine and thiol groups, their high values of  $S_{sp}$  attract attention, namely from 510 to 840 m<sup>2</sup>/g for xerogels with ethylene bridges and from 650 to 970 m<sup>2</sup>/g for xerogels with phenylene bridges.<sup>13-15</sup> The type of isotherms of these xerogels depends, on the first place, from the nature of functional groups (amine or thiol groups). In the first case the isotherms for xerogels with ethylene bridges are S-shaped and have a distinct hysteresis loop (in contrast to xerogels with phenylene bridges) while isotherms in the second case are more likely to be Langmuir isotherms (Figure 9). This difference is brought about by the nature of a medium that is created by these groups during the synthesis. It was shown<sup>13-15</sup> that the parameters of the porous structure of such xerogels were substantially affected by the nature of a spacer, relative size of the functional group, ratio of reacting alkoxysilanes, and gel ageing time.

Thus, taking into account the mentioned above factors, it is possible to obtain polysiloxane xerogels with controlled porosity, surface layer composition and loading of functional groups.

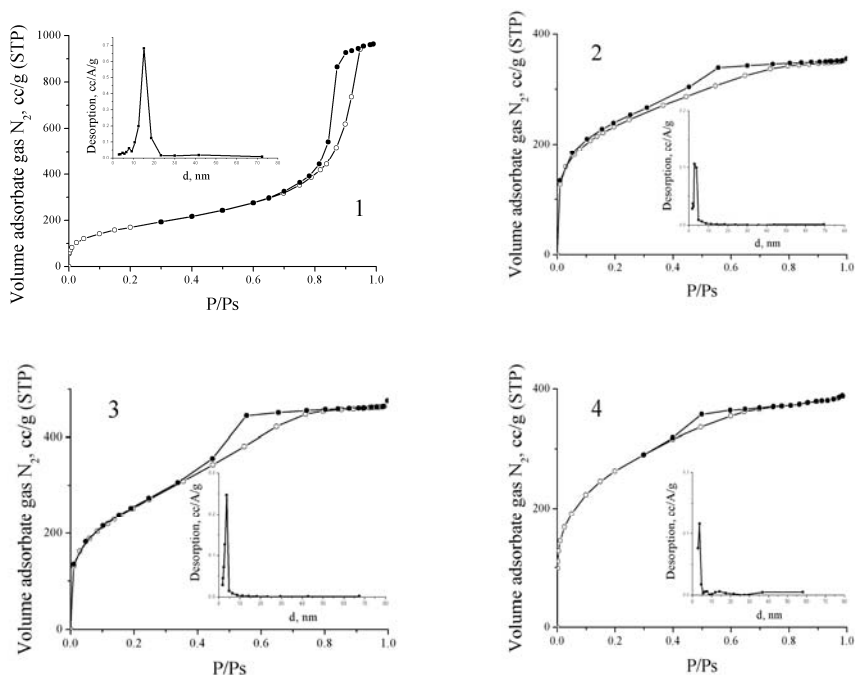


Figure 9. Isotherms of  $N_2$  adsorption/desorption and PSDs for the xerogels synthesized using the following systems: (1)  $-C_2H_4/-NH_2=4:1$ ; (2)  $-C_2H_4/-SH=4:1$ ; (3)  $-C_6H_4/-NH_2=4:1$ ; (4)  $-C_6H_4/-NH_2=4:1$ .<sup>13-15</sup>

#### 4.2. ADSORPTION PROPERTIES OF FPA

Parish and co-workers<sup>25</sup> studying in 1989 adsorption of Ni(II), Co(II), Cu(II) and Zn(II) by aminocontaining xerogels showed that an equilibrium in such systems is reached at least in 15 h. Xerogels with  $PPH_2$  groups<sup>32</sup> absorb metal ions (Co and Ni(II)) from their ethanol solution slower. It is noted that time of equilibrium attainment depends on particle sizes. The other authors<sup>35</sup> pointed out that the equilibrium attainment at adsorption of metal ions during 20–30 min. However even at optimal sorption conditions a part of xerogels' functional groups does not take part in complex formation.<sup>25,32,33,93</sup> This data is confirmed by HCl acid adsorption by aminocontaining xerogels.<sup>94</sup> However, as it was shown for the Cu(II) adsorption from the acetonitrile solutions, that almost all the amino-groups are accessible for metal ions (adsorption time was 48 h).<sup>86,88</sup> In acid medium these xerogels absorb copper ions best of all that is in agreement with data.<sup>95</sup>

It was shown that a separation of Ni(II) and Cu(II) is possible for xerogels with bifunctional surface layer (ethylenediamine and vinyl groups).<sup>33</sup> In<sup>96</sup> attention has been given to sorption of microquantities of Au(III) from acidic solutions by xerogels which surface layers contain thiourea and thiourea/amine groups. It has been found that the maximum degree of extraction of Au(III) is typical for the sorbent with a bifunctional surface layer. It is interesting that an increase of solution temperature (up to 50°C) causes the significant decreases in the time of an attainment of sorption equilibrium (up to 5 min) and at the same time increases the degree of gold extraction. The xerogels with thiourea- and aminogroups in their surface layer also have a high efficiency in sorbing mercury(II) from acidic solutions.<sup>97</sup>

Hg(II) ions could be effectively extracted from their acidic solutions by xerogels with monofunctional surface layer containing thiol groups.<sup>98</sup> Good extraction of mentioned ions from their acidic solutions (pH ~ 2) was achieved also for the xerogels that contain 3-mercaptopropyl and alkyl groups. The influence of surface layer's composition and pore structures' parameters of such xerogels on their complexing properties towards Hg(II) was studied in details.<sup>99</sup> Using the model of chemical reactions,<sup>100</sup> it was possible to calculate the constants of stability for the complexes which are formed on the surface of considered xerogels. The analysis of obtained data shows, that complexes stability decreases at the increasing of surface concentration of 3-mercaptopropyl groups in these xerogels. Moreover, the bordered concentration of functional groups was revealed. The complexes with compositions 1:1 and 1:2 are formed above this concentration. In conclusion, the authors considered the values of static sorption capacity (SSC) for such adsorbents. One can assume, that gradual increase of 3-mercaptopropyl groups concentration should lead to systematic increase of xerogels SSC. However, this dependence has the maximum for the xerogels with thiol groups concentration near 3.0–3.8 mmol/g (Figure 10). Further increase of 3-mercaptopropyl groups concentration leads to SSC decrease. This fact is due to complexes' formation with composition 1:2 in the surface of these sorbents. It should be pointed out, that highest SSC (620 mg Hg<sup>2+</sup>/g), which was achieved, is comparable with SSC for the best organic cation-exchangers which are used for the Hg(II) extraction.<sup>101</sup> Hence, presented results give evidence, that synthesized xerogels with 3-mercaptopropyl groups could be used for the extraction of Hg(II) from aqueous solutions.

In this case the surface concentration of thiol groups strongly influences on both: stability and composition of the complexes which are formed on the surface of such polysiloxane sorbents. Since the surface concentration of functional groups is determined as a ratio of functional groups quantity to adsorbent surface area, then porous structure parameters of xerogels strongly influences their sorption properties.

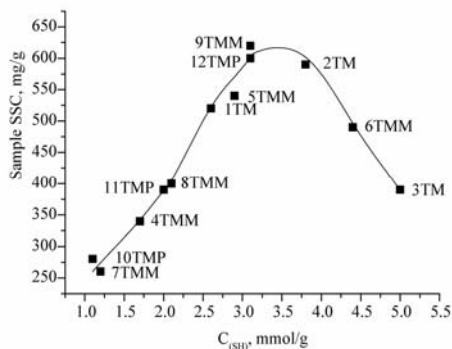


Figure 10. Dependence of SSC sorbents from 3-mercaptopropyl groups concentration.<sup>99</sup>

It was found that FBPS xerogels which were functionalized by 3-mercaptopropyl groups have a high efficiency in sorbing Ag(I) ions.<sup>102</sup> It should be mentioned that functionalized xerogels were used mostly to study sorption of 3d-metals.<sup>35,57,95</sup> However recently a range of investigated metals has been extended such as: (Hg(II)<sup>52,58,95,103</sup>; Ca(II)<sup>66</sup>; Zn(II)<sup>66</sup>; Cd(II)<sup>52,66</sup>; Pb(II)<sup>52</sup>; Pd(II)<sup>66</sup>; UO<sub>2</sub>(II)<sup>104</sup>; Ln(III),<sup>105</sup> Am(III), Pu(IV)<sup>49,105</sup>). It was shown,<sup>92</sup> that xerogels with calixarene groups could adsorb Cs(I) ions from acidic aqueous solutions (1 M HNO<sub>3</sub>). The adsorption equilibrium in the system is reached less than in 1 h. It was determined that the increase of functional groups' content leads to the increase of Cs(I) sorption degree. However, no more than 10–40% of functional groups takes part in Cs(I) extraction process.<sup>92</sup>

Finally it should be noted that sol-gel method has a great potential at synthesis of sorbents “with memory” for metal ions<sup>106</sup> or for their analytical determination.<sup>107,108</sup>

## 5. Conclusions

In this paper we have discussed the preparation routes of polysiloxane xerogels which contain functional groups of different nature in their surface layer and which are capable to complexation. Significant influence on structural-adsorption characteristics of formed xerogels with a monofunctional surface layer has the nature and the geometrical sizes of functional groups, the nature of structure-forming agent as well as the synthetic conditions.

The preparation paths of polysiloxane xerogels with a bifunctionalized surface layer has also been discussed. In this case the ratio of alkoxy-silanes and nature of additional functional groups influence significantly on surface hydrophobicity degree of such materials as well as their porosity.

Physical method data testify about presence of structural units with the same nature on the surface of functionalized polysiloxane xerogels and about the similar character of surface structure.

Taking into account the presented results on sorption of metal ions as well as the results obtained by other authors,<sup>22,23,106–109</sup> it is as possible to assert the significant perspectives of the usage of functionalized polysiloxane xerogels in sorptive technology.

## Acknowledgment

The author would like to acknowledge the partial financial support of NATO for this work (Grant SFP–978006) and also to thank Professor A. Dabrowsky, Dr. B. Alonso and Dr. M. Barchak for NMR spectra and productive discussion.

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