Speciation of partly oxidized thiol-organosilica surface

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The paper describes conductometric quantitative determination of thiol- and sulfonic acid groups on organosilica surface with immobilized layer of partly-oxidized mercaptopropyl groups. A set of MCM-41 type samples containing 1 mmol g^{-1} of mercaptopropyl groups was oxidized with proportional quantitates of hydrogen peroxide and subsequently was characterized with different ratio of grafted mercaptopropyl and propylsulfonic acid groups. The data calculated from conductometric titration were approved by collation with corresponding XPS spectra, which demonstrate linear correlation of results of both technique. The described method was applied to reveal ambient oxidation of organo-silicas with immobilized thiol groups.

Н.В. ЗАЙЦЕВА, Н.Г. КОБИЛІНСЬКА, А. ВАЛКАРІУС, В.М. ЗАЙЦЕВ СЕЛЕКТИВНИЙ ХІМІЧНИЙ АНАЛІЗ ПОВЕРХНІ ЧАСТКОВО ОКИСЛЕНИХ ТІОЛВМІСНИХ ОРГАНОМІНЕРАЛЬНИХ МАТЕРІАЛІВ. *В статі обговорюється кількісне кондуктометричне визначення тіольних та сульфо-груп на поверхні кремній-органічного матеріалу з іммобілізованими частково окисленими тіолпропільними групами. Серія зразків, матеріалу типу MCM-41, з концентрацією тіолпропільних груп 1 ммоль/г була окислена пероксидом водню, що пропорційно збільшували, при приготуванні кожного зразка цієї серії. Синтезовані матеріали характеризуються різним співвідношенням меркапто- та сульфо-груп. Співставлення результатів одержаних методом кодуктометричного титрування з даними відповідних рентгенфотоелектроних спектрів демонструють лінійну корреляцію між результатами обох методів. Представлений метод кондуктометричного титруваннння застосовували для фіксування процесу окислення на повітрі тіольних груп іммобілізованих на поверхні органокремнеземів.*

Keywords: organo-silicas; immobilized layer characterization; thiol-silica; SH-silica; multifunctional layer; immobilized acid groups; MCM-41; solid conductometric titration.

Ключові слова: кремній-органічні матеріали; аналіз функіоналізованої поверхні шару; тіолвмісний кремнезем; SH-кремнезем; поліфунціональна повехня; іммобілізовані кислотні групи; MCM-41; твердофазне кондуктометричне титрування.

Silica-based organo-mineral hybrid materials having varieties of surface functionality, carrier's morphology and texture are efficiently applied in different fields of science. Typical example of such materials is mesoporous silica functionalized by alkylthiol-groups – thiol-functionalized hybrid (TFH) – either by direct co-condensation [1,2] or post-grafting [3,4] reactions. TFH is used as selective adsorbent for heavy metals removal [5,6,7], as a matrix for preparation of metallic nano-particles [8], immobilization of proteins [9] and enzymes [10], formation of electrodes [11]. Additionally, TFH is commonly used for preparation of silica with immobilized alkylsulfonic acid – sulfonic acid functionalized hybrid (SFH). The later one is widely used as ion-exchanger [12,13], solid acid catalyst [14,15,16] or solid electrolyte [17].

Because of wide application of TFH and its oxidized derivative SFH, composition of immobilized layer in native and oxidized state is thoroughly studied. Particularly it is demonstrated that, both TFH and SFH have poly-functional nature of immobilized layer and can contain mixtures of immobilized groups with different chemical composition. Thus, during sol-gel synthesis of TFH in alkaline aqueous solution, surface alkylthiol-groups can be partly oxidized by atmospheric oxygen [18,19] to disulfides.

Poly-functionality of SFH arises from incomplete oxidation of immobilized alkylthiol-groups on TFH into alkylsulfonic ones [20,21]. Often poly-functional nature of immobilized layer is not desirable since it may cause reduction of the material efficiency and bring unpredictable properties to the material. Native oxidation of TFH by atmospheric oxygen reduces the adsorbent capacity towards heavy metals (immobilized disulfides are much less active in metal binding than alkylthiol-groups [22]) and its selectivity (due to non-selective ion-exchange metal binding on alkylsulfonic-groups). Contrary, alkylthiol and

disulfide are undesirable on SFH surface since they deteriorate the acidity of the target material and are injurious for catalysis process (adsorption of catalytically active metals). In rare cases poly-functional nature of immobilized layer is beneficial.

For instance, bisphenol-A is produced more effectively on catalyst surface that possess two types of functional groups on a single carrier [23]. Similarly, adsorption yield of Cr(VI) from wastewater increases from 40 to 100% for adsorbent having both alkylsulfonate and alkylthiol groups [18]. Consequently, in most cases immobilized layer of the real TFH and SFH samples consists from mixture of thiol-, disulfide- and sulfonic groups, and so can be abbreviate as TSFH.

Several methods were proposed to study composition of immobilized layer on TSFH. Most commonly concentration of immobilized thiols is calculated from results of elemental analysis of the adsorbent [24,25]. However, it is clear that the method is not selective and different S-containing groups cannot be distinguished. For selective determination of SH-groups the approaches based on chemical interaction with immobilized thiols were proposed.

These are iodometric titration [26], titration with Ellman's reagent [27], measurements of the adsorbents capacity towards mercury [24] or silver [28], esterification of thiol groups with Rhodamine B [29].

All the methods mentioned previously assume monofunctionality of the surface layer with immobilized SH-groups (which is questionable), and doesn't allow determine the level of polyfunctionallity (content of all group with different composition) in immobilized layer.

Similar, acid-base titration of SFH [30,31] doesn't reveal residual alkylthiols, presented in the immobilized layer. No single spectroscopic method proposes to determine immobilized layer composition. Particularly XPS is very useful to determine polyfunctional nature of immobilized layer, but cannot provide quantitative characteristics for thiols and sulphonic acid contents [32] similar to solid state NMR [25]. Both approaches are mostly used as comparative indicators.

One may suggest that any combination of the listed methods cannot be applied for an accurate analysis of a thiol-functionalized surface layer containing admixture of sulfonic acid groups and vice versa, as no reliable method of speciation based on the single technique of detection was proposed.

The present work was intended to develop simple, one-instrument method of thiol- and sulfonic group simultaneous determination on TSFH surface.

Direct and back conductometric titration is proposed for this to specify composition of immobilized layer on TFH, SFH and TSFH samples obtained by TFH oxidation with H_2O_2. The results of conductometric titrations were compared with elemental analysis, and XPS data of the same sample.

MATERIALS AND METHODS

Chemicals and Reagents

Analytical-grade chemicals were used for all solid sample preparations: tetraethoxysilane (TEOS, >98%, Merck), mercaptopropyltrimethoxysilane (MPTMS, 95%, Lancaster), cetyltrimethylammonium bromide (CTAB, 98%, Fluka), ammonia (28% aqueous, Prolabo), ethanol (95-96%, Merck), and HCl (37%, Prolabo). Silica with covalently attached groups of ethylsulfonic acid (SiO_2 – SO_3H) was synthesized by treating vinyl silica with sodium sulfite [33]. A Kieselgel Merck 60 silica gel (S_{sp} = 510 m^2/g, particles with sizes 0.063–0.2 mm) was used as the support. Ag(I) solutions were obtained from its nitrate salt ($AgNO_3$). They were prepared by diluting a stock solution of 0.10 M (in 0.1 M HNO_3) in distilled water. Their concentrations were checked with conductometric titration by using a certified standard solution of NaCl. All other reagents were analytical grade and all solutions were prepared with distilled water.

Preparation of Thiol-Functionalized Hybrid Materials (TFH)

The one-pot synthesis of TFH was conducted by using the reagents in such a proportion 1:0.41:11.8:65:175 (TEOS:MPTMS=9:1) / CTAB / ammonia / ethanol / water. To the mixture of water (65 mol), ethanol (175 mol) and ammonia (11.8 mol) a surfactant was added and stirred until its final dilution. A mixture of precursors was then injected into solution. Precipitate that occurred in 2 minutes was left stirring for 2 hours. Then it was filtered, washed with ethanol and water and dried under pressure (<10^{-2} bar) for 24 h. Template was removed from pores by refluxing the resulting solid with 1M HCl ethanol solution (1 g per 100 ml) during 24 hours. The derived material labeled as TFH was characterized by a well-defined hexagonal mesostructure (powder XRD d_{100} spacing of 33 Å), a specific surface area of 1598 m^2 g^{-1}, a total pore volume of 0.76 cm^3 g^{-1}, and a pore diameter of 20 Å.

Elemental analysis of the final product affirm the presence of 1 mmole of SH-goups per gram of the solid. The whole procedure was conducted under inert atmosphere (Ar).

Conversion of Thiol Groups into Sulfonic Acid Moieties

Preparation of TSFH-1.X series

To get oxidized material a typical procedure [32] involving H_2O_2 in a methanol-water mixture was used. 0.7 g of TFH was suspended in a mixture of aqueous 55% H_2O_2 and 35 mL of methanol. Different quantities of H_2O_2 (0, 0.19, 0.38, 1.15, 1.9 and 3.5 g) were also applied to get a series of samples with a diverse organic layer content (TSFH-1.X, where X=1-6 respectively). After 24 h of stirring, the solid particles were filtered and washed with water and ethanol. The wet materials were re-suspended in

50 mL of 0.1 M H_2SO_4 and stirred for another 4 h period, filtered again, washed with water and ethanol, and dried under vacuum (<10^{-2} bar) for 24 h. The most fully oxidized sample TSFH-1.6 was mesostructured, yet with a small lattice contraction (d_{100} at 30 Å), but its specific surface area fell down to 860 m^2 g^{-1} and the total pore volume to 0.42 cm^3 g^{-1} due to possible degradation of the long-range order in the material [32].

Preparation of TSFH-2.X series

Another sample was synthesized according to aforesaid procedure of TFM synthesis without taking care about oxidation by air oxygen. It was divided into three parts and titrated after different time of storing on air. Conductometric titration was performed on the samples being disposed on air during 1 day (TSFH-2.1), 2 weeks (TSFH-2.2) and 2 months (TSFH-2.3).

Methods

Conductometric titration

Electroconductivities of suspensions were measured by means of AC Conductivity Bridge R-5058 at operational frequency of 1000 Hz at room temperature. For acid-base conductometric titration, solutions of 0.011-0.024 M NaOH were used to titrate residual and bulk concentrations of sulfonic acid groups respectively. A batch of each sample (~0.15 g) was previously soaked in 25 ml of deionised water. In 24 h titration of equilibrated suspension was performed in the Arrenius cell. For back conductometric titration 0.1M NaCl solution was used to titrate excess of silver ions. The sample of TSFH (~0.15 g) was added to a mixture of 10 ml of 0.04 M $AgNO_3$ and 20 ml of deionised water with pH = 2. The suspension was kept without light access during 12 h to reach equilibrium and then filtrated. An aliquot of the solution was titrated in the Arrenius cell with NaCl. Solid desiccation under pressure (over P_2O_5) preceded all of the titration experiments.

Solid-phase analysis

X-ray photoelectron (XPS) spectra were obtained using an electron energy analyzer (VSW, MCD 5000) and an unmonochromatized MgK_α (1253.6 eV) source of photons. Powders were pressed at room temperature onto the adhesive side of a copper adhesive electrical tape. The binding energies were corrected on the basis of the standard value of C(1s) from contaminants at 284.6 eV. Narrow scanned spectra were used to obtain the chemical state information for sulfur.

RESULTS AND DISCUSSION

Two sets of silica (TSFH-n.X) with immobilized propylthiol groups were synthesized from corresponding silane by self-assemble co-condensation under procedure, leading to formation of MCM-41 type matrix [32]. The sets differ in concentration of bonded groups: the first one (TSFH-1.0) has 1 mmolg^{-1} of the functional group while the second one (TSFH-2.0) has only 0.5 mmolg^{-1}. Experimental samples (TSFH-n.X) were obtained from TSFH-n.0 by its oxidation with hydrogen peroxide in the conditions preserving the total loading of functional groups. To obtain samples having different degree of oxidation of the immobilized layer, concentrations of H_2O_2 was varied while time of treatment remained permanent. Oxidation of immobilized propylthiols with H_2O_2 leads to polyfunctional layer [20,21] of the adsorbent, that may also include unreacted propylthiol groups. Taking into account this fact and essential distinction in protolytic behavior of thiols and sulfonic acid groups, we assumed that conductometric acid-base titration can be used for determination of alkylsulphonic fragments on TSFH-n.X surface.

Conductometric titration can also be used for quantitative determination of propylthiol group on the same adsorbent, but with another approach. It is known that immobilized –SH groups can strongly bound silver ions from solution [28,34]. This adsorption process can easily be monitored by back-conductometric titration of silver excess in solution with NaCl, for example [35]. None of immobilized fragments on TSFH except –SH is able to bound silver in acid condition, so the proposed approach can be used for selective determination of –SH residuals on TSFH.

The features of a direct acid-base titration were first studied for the material (SiO_2-SO_3H) characterized with monofunctionalized layer of sulfonic acid groups [33] to be safe from overlapping of deprotonation of thiol-groups.

Similarly to neutralization of strong acid in solution, the curve of conductometric titration of SiO_2-SO_3H in aqueous suspension is V-shaped (Fig. 1). At the same time the conductivity of aqueous suspension of SBA in selected range increases in linear proportion to quantity of added alkali.

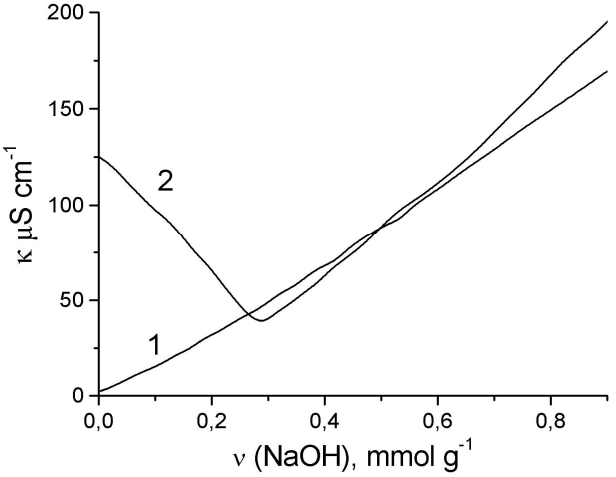

Fig. 1. Curves of conductometric titration of unmodified SBA (*1*) and SiO_2 with covalently attached groups of ethylsulfonic acid (*2*)

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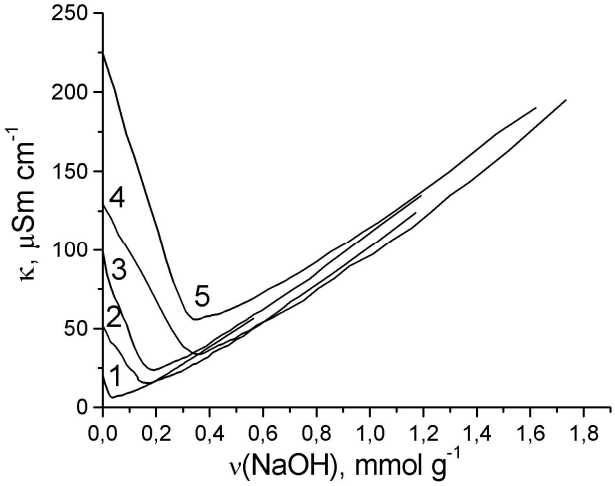

Fig.2. Curves of direct conductometric titration of differently oxidized samples: TSFH-1.1 (*1*), TSFH-1.2 (*2*), TSFH-1.3 (*3*), TSFH-1.4 (*4*), TSFH-1.5 (*5*)

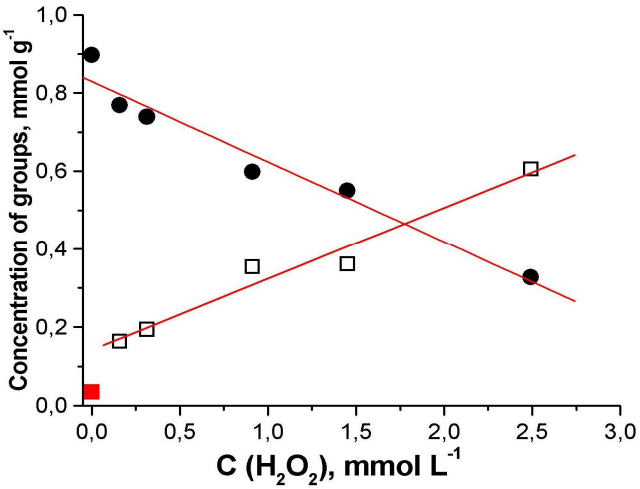

Fig 3. Correlation of thiol (solid circles) and sulfonic acid concentrations (hollow squares) with quantity of oxidizing agent used during the synthesis

Similarly to silanols, immobilized propylthiol groups shall not affect to smooth increase of suspension conductivity [39]. Indeed, acid-base titration of TSFH-1.0 demonstrates no inflexion on conductometric curve, similar to titration of SBA (see later discussions). This observation is typical for neutralization of weak acid with $pK_a \geq 6$ in solution and was also expected for immobilized mercaptopropyl groups. So the concentration of bonded $-SO_3H$ groups was determined from the position of V-type minimum on the titration curve as 0.28 mmol g^{-1}.

This number is in good agreement with the concentration calculated for the same material discussed in [33]. Sharp V-type minimum on the curve of acid-base titration of SiO_2-SO_3H and weak interference with other immobilized groups as well as with silica matrix suggest that conductometry is applicable for quantitative determination of acidic group loading on TSFH. The approach was verified on TSFH-1.X samples, obtained from the same initial THF but differently treated with H_2O_2.

Similar to SiO_2-SO_3H, all TSFH-1.X samples demonstrate V-type shape titration curves (Fig.2) indicating the presence of propylsulfonic acid on the surface. Similarly to SiO_2-SO_3H we assign position of V-type minimum on TSFH-1.X titration curves to concentration of immobilized acid. The results presented on Fig. 3 indicate that concentration of immobilized acidic groups for different TSFH-1.X samples, which were determined form the position of the curve minimum, depends on concentration of the applied oxidizing agent.

Particularly it is linear in the range of H_2O_2 concentrations from 0.2 to 2.5 mmol L^{-1}. So, from the titration results it can be suggested that the transformation degree of immobilized thiols to sulfonic acid grows proportionally to the increasing of hydrogen peroxide concentration in the reaction mixture.

The curve of conductometric titration of TSFH-1.1 (a sample that was not treated with H_2O_2, but was stored on air) also exhibits a small V-shaped minimum, which corresponds to 30 μmol g^{-1} of $-SO_3H$ (Fig. 3, solid square).

The origin of sulfonic acid groups presented at the TFH surface is concerned with spontaneous oxidation on air and will be discussed hereafter.

Back-conductometric titration of the Ag^+ excess with NaCl was performed to quantify immobilized propylthiol groups on TSFH-1.X samples. The general reaction that takes place at the surface site under Ag^+ treatment can be presented by next equation:

$$\overline{SiO_2-(CH_2)_3-SH}+Ag^+ \Rightarrow \overline{SiO_2-(CH_2)_3-SAg}+H^+$$

In order to minimize the influence of silica surface silanols and immobilized alkyl-sulfonic groups, reaction was performed in acidic medium [36]. It was stated that in the proposed conditions a nonspecific bounding of silver ions didn't exceed the value of detection error.

The results of –SH group determination on different samples of TSFH-1.X by conductometric titration, are presented on Fig. 3. It can be seen that the concentration of immobilized propylthiols linearly decreases with increasing of H_2O_2 concentration in the range 0.2 - 2.5 mmol L^{-1}.

Nevertheless, correlation between concentration of H_2O_2 in solution and transformation of –SH to $-SO_3H$ is limited. Complete transformation of –SH to $-SO_3H$ is newer reached neither in this research nor in other known sources [2,32,37].

Indeed, from Table 1, where the compositions of immobilized layer for different samples of TSFH-1.X are summarized, it can be seen that maximum degree of –SH to $-SO_3H$ group transformation (ω_H+) for selected conditions is 65%. The results obtained from conductometric titration of TSFH-1.X agreed with the data received from elemental analysis of TSFH-1.X samples (see Table 1).

Table 1. Concentrations of different sulfur groups in TSFH-n.X series

Sample	$C(H_2O_2)$, mmol L^{-1}	$C(-SO_3H)$, mmol g^{-1}	$C(-SH)$, mmol g^{-1}	ΣC_L, mmol g^{-1}	ΣC_L[c], mmol g^{-1}	ω_H+, %
TSFH-1.0	0	0	0.931	0.931		0
TSFH-1.1	0[a]	0.035	0.898	0.933		4
TSFH-1.2	0.16	0.164	0.769[b]	-		18
TSFH-1.3	0.31	0.194	0.739[b]	-	1.06	21
TSFH-1.4	0.91	0.354	0.599	0.953		37
TSFH-1.5	1.45	0.361	0.550	0.911		40
TSFH-1.6	2.49	0.606	0.327[b]	-		65
TSFH-2.1						3
TSFH-2.2	0[a]	0.015±0.003	0.572±0.024	0.587±0.027	0.63	2
TSFH-2.3						2

a - oxidation on air, **b** - the values were calculated from the total concentration of sulfur bearing groups, **c** - concentration determined by elemental analysis

Table 2. Data from the XPS spectra

Sample	Height (*h*) of the peak, cm		S(VI)/S(II), %		Results of conductometric determination		
	S(II)	S(VI)			C(SH), mmol/g	$C(SO_3H)$, mmol/g	ω_H+, %
TSFH-1.6	1.7	2.6	60	68[a]	0.33	0.61	65
TSFH-1.5	2.1	1.9	48	65[a]	0.55	0.36	40
TSFH-1.4	2.4	1.5	38	48[a]	0.60	0.35	37
TSFH-1.3	4.4	1.6	26	40[a]	0.74	0.19	21

[a]Mass concentration according to the quantification report of XPS spectra analyzer

The S ($2p_{1/2}$) peak area was constrained to be one half of the area from major S($2p_{3/2}$) band. For TSFH-1.0 sample the energy of the major band in the doublet is observed at 163.3±0.1 eV (Fig. 4a) and it is typically attributed to S(II) in mono- or poly-sulfide species [38].

This position remains constant for the whole TSFH-1.X set, while the peak area decreases with increasing of oxidation rate of the immobilized layer. For oxidized TSFH-1.X samples together with doublet at 165 eV another asymmetric peak at higher energy is observed (Fig. 4).

Indeed, for all TSFH-n.X samples overall concentration of –SH and $–SO_3H$ groups (ΣC_L), determined from conductometric titration is about equal to the concentration of immobilized groups determined from elemental analysis on sulfur

In this regard, all TSFH-1.X samples, synthesized by TFH treatment with hydrogen peroxide are polyfunctional and contain at least two types of immobilized groups: propylthiol and sulfonic acid.

As an alternative approach for corroboration of the stated results of titration we have used XPS data of the series. XPS spectra (S_{2p} core level) of TSFH-1.X series were fitted using doublets $2p_{1/2}$ and $2p_{3/2}$ separated by a spin-orbit splitting of 1.2 eV. Intensity of this peak is growing with increasing of oxidation degree of the immobilized layer, Fig.4.

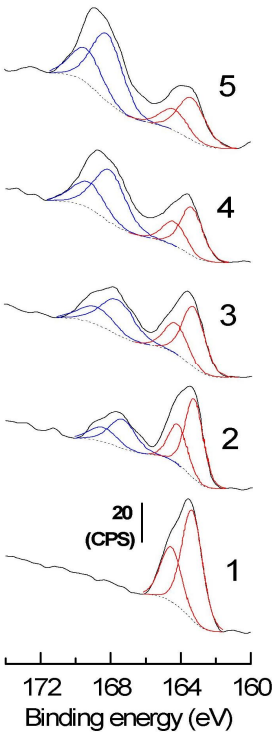

Fig. 4. XPS spectra (S_{2p} core level) of TFH (*1*), TSFH-1.3 (*2*), TSFH-1.4 (*3*), TSFH-1.5 (*4*), TSFH-1.6 (*5*)

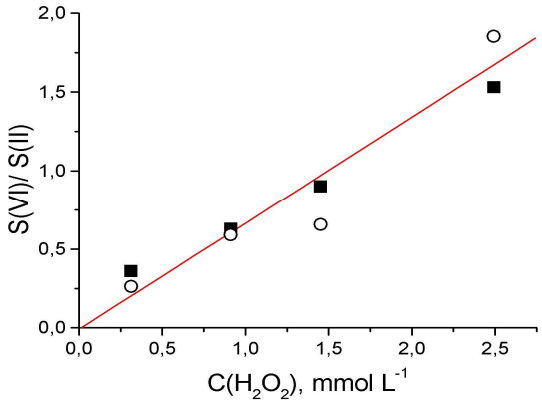

Fig.5 Correlation of $–SO_3H$ to –SH ratio, calculated from conductometric titration curves (hollow circles) and heights of XPS peaks (solid squares), with concentration of added H_2O_2

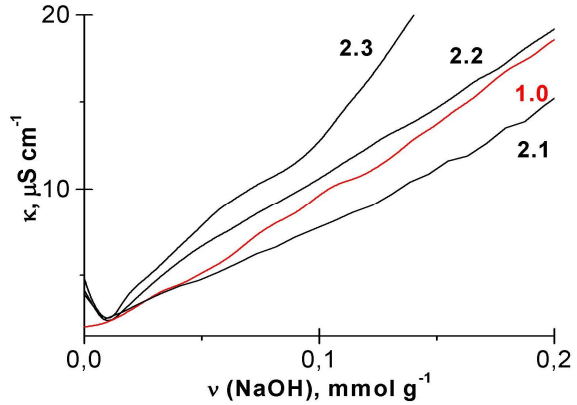

Fig.6 Curves of conductometric titration of TSFH-1.0 (*a*), TSFH-2.1 (*b*), TSFH-2.2 (*c*) and TSFH-2.3 (*d*) with NaOH

The later pick is shifted for 5 eV to higher binding energy in respect to the position of S(II) one, and attributed to S(VI) sulfur species in alkylsulphonic fragments [38]. Consequently, XPS data confirms formation of alkylsulfonic acid species on the TSFH-1.X surface.

Similar to the results of conductometric titration, XPS data denote incomplete transformation of propylthiol into propulsulfonic groups under H_2O_2 treatment: spectrum of TSFH-1.6 sample that was obtained in highest concentration of H_2O_2 is still characterized with both S(II) and S(VI) bands, Fig.4.

The XPS data cannot be used directly for quantitative determination of concentration of bonded species because of unavailability of the standards, but the ratio of intensities (*h*) for different XPS peaks correlates with the concentration ratio for corresponded fragments. Table 2 summarized the results obtained form XPS spectra of different TSFH-1.X samples together with data obtained from their conductometric titration.

Better correlation between S(VI)/S(II) ratio and ω_{H}+, % is observed for data obtained from the peak intensities but not from mass concentration according to the quantification report of XPS spectra analyzer.

Both the ratio of S(VI) to S(II) peak intensities in XPS spectra of TSFH-1.X and concentrations of $-SO_3H$ to -SH found from conductometric measurements are in linear correlation with the quantity of oxidizing agent used for TSFH-1.X synthesis, Fig.5.

The proposed conductometric technique was used to determine composition of immobilized layer on TSFH-2.x samples obtained from TSFH-2.0 by its oxidation on air. Figure 6 shows the curves of conductometric titration with an alkali of TSFH-2.X samples disposed on air during different periods of time. As it can be seen from the figure, a typical minimum for sulfonic acid groups is observed at each titration curve. The results for all the curves are in close agreement, stating the presence of 15 μmol g^{-1} of sulfo groups and 572 μmol g^{-1} of mercaptopropyl groups. Comparison of these curves with the curve of the sample, which was kept in atmosphere of argon, shows that disposition of thiol groups on air provokes insignificant oxidation, which doesn't increase with prolongation of the contact

CONCLUSIONS

The proposed single instrumental method is applicable for detection of thiol and sulfonic acid groups simultaneously present at the surface of silica-based mesoporous organo-mineral materials containing up to 1 mmol g^{-1} of propylthiol groups and 15-600 μmol g^{-1} of sulfonic acid groups.

Reliability of the obtained results is confirmed by the repeatable coincidence of the total concentration of thiol and sulfonic acid groups calculated by conductometric titration, which in turn agrees with the data of elemental analysis. It is demonstrated that thiol and sulfonic acid groups are present at the surfaces of all studied samples except the one that was synthesized in conditions of inert atmosphere.

The concentrations of strong acid moieties calculated from conductometric titration curves were found to be in linear proportion to the quantity of added oxidant, which prove the transformation of one groups into others.

But still, in agreement with the XPS data, the proposed method of titration proves incomplete transformation of thiols to sulfonic acid (65%), even at 100-fold molar excess of oxidant.

At the same time it is also shown that thiol-functionalized materials synthesized on air contain small concentrations of sulfonic acid groups (up to 3% of the total concentration of sulfur-containing groups) and are not susceptible to further oxidation by being disposed on air in room conditions during 2 months.

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