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Modification of the Silica Particles Surface with Perfluoroalkylmethyloxiranes

T. I. Gorbunova[a], A. Ya. Zapevalov[a], I. V. Beketov[b], V. S. Gaviko[c], E. G. Vovkotrub[d], and V. I. Saloutin[a]

[a] *Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, ul. S. Kovalevskoi 22/Akademicheskaya 20, Yekaterinburg, 620990 Russia*
e-mail: gorbunova@ios.uran.ru

[b] *Institute of Electrophysics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

[c] *Institute of Physics of Metals, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

[d] *Institute of High-Temperature Electrochemistry, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia*

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Abstract—Silica particles have been prepared via the sol–gel process in the presence of perfluoropropyl- and perfluorobutylmethyloxiranes. Nanoparticles are formed in the presence of acidic catalyst. Under conditions of basic catalysis the attack of silanol group (formed in situ via hydrolysis of tetraethoxysilane) on the oxirane ring leads likely to the Si–O–C bond formation.

Keywords: sol–gel process, tetraethoxysilane, silica particle, surface modification, covalent binding, perfluoroalkylmethyloxirane

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Modern methods of modification of silica particles surface can be roughly divided into three groups. The first one includes methods related to occlusion of organic molecules with SiO_2 matrix formed via sol–gel process [1]. In the course of silica particles formation via hydrolysis and condensation of alkoxysilanes, the modifying compound is present in the reaction zone as well and can be therefore physically adsorbed. Occlusion methods give various materials used, for instance, in development of specific sensors capable of detection of chemical and biological agents [2]. Such materials suffer, however, from a serious drawback: when in contact with solvent, the organic molecules are rapidly leached from silica particles surface, and utilitarian properties of the latter deteriorate.

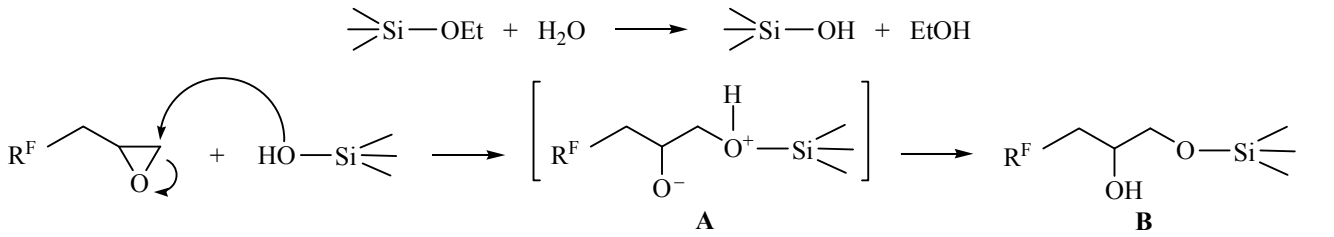
The second group of SiO_2 modification methods includes those based on sol–gel process in the presence of tetraethoxysilane and a functional silane bearing one to three non-hydrolyzable substituents [3]. Under such conditions, the surface of the formed silica particles is modified with the functional groups stable against hydrolysis. Materials based on such particles are known as Ormosil and have been used as sensors for biomolecules detection [3], lubricants [4], and anticorrosive coatings [5]. The co-hydrolysis methods are limited, as inertness of the functional groups against hydrolysis puts rigid requirements on the functionalized silane structure.

The last group of silica surface modification methods has been scarcely studied so far. It is based on covalent binding of the in situ formed hydrolyzed tetraalkoxysilane with organic molecules. Such functionalized organic compounds should contain the substituents capable of covalent bonding with silanol groups of hydrolyzed silane. In the modified material such substituents act as spacers between silicon atom and functional group of the organic molecule. The so prepared materials are promising for practical applications, as the modifier is not leached with solvent. One of the most interesting versions of the above-described process is silica modification with fluorine-containing groups; it can enhance the material resistance against thermal and mechanical actions, including those in corrosive media.

Bearing a cycle capable of regioselective opening with nucleophilic agents [6], oxiranes are widely used

in organic synthesis. It is presumable that under certain conditions silanol group formed via tetraalkoxysilane hydrolysis can act as such a nucleophile; to the best of our knowledge, such reactions of oxiranes have not been described in the literature.

This study was aimed to investigate the interaction of tetraethoxysilane TEOS with perfluoroalkylmethyloxiranes under conditions of sol–gel process and to determine the type of surface modification of the so formed silica particles. Perfluoropropylmethyloxirane **Ia** and perfluorobutylmethyloxirane **Ib** were used as modifying oxiranes; they were prepared via cyclization of 2-iodo-4,4,5,5,6,6,6-heptafluorohexan-1-ol (**Ia**) and 2-iodo-4,4,5,5,6,6,7,7,7-nonafluoroheptan-1-ol (**Ib**) [7]. Main stages of the covalent bond formation at the interaction of TEOS with the oxiranes are schematically shown below.



$R^F = C_3F_7$ (**Ia**), C_4F_9 (**Ib**).

Firstly, silanol groups are formed via hydrolysis of TEOS. Hydrolysis of one ethoxy group is shown in the scheme for clarity; however, in the solvent excess and at heating all the ethoxy groups are hydrolyzed [8]. The second stage consists in the silanol oxygen attack on the secondary carbon atom of the oxirane and regioselective ring opening occurs to give the unstable intermediate **A**. The stabilization of this intermediate in the third stage under sol–gel process conditions is possible via two pathways. Proton from water or ethanol molecule can be attached to the alcoholate center on the intermediate, and proton from the onium oxygen is then simultaneously eliminated. Alteratively, the intermediate can be stabilized via the intramolecular rearrangement. Both pathways lead to the same product **B**.

The reagents ratios in the performed synthesis are collected in the table along with selected results of analysis of the so prepared products. Ethanol formed during TEOS hydrolysis could alter the substrates reactivity; therefore, ethanol was distilled off in the course of the syntheses. In all experiments, a low-boiling (bp 78–80°C) fraction was formed, its quantity was practically equal to the theoretical amount of ethanol to be released. Addition of the catalyst (HCl or NEt_3) significantly accelerated TEOS hydrolysis.

Samples 2–7 were white powders; samples 6 and 7 were looser: with the same initial charge of TEOS, their volume was 4–5 times that of the samples 2–5. Taking into account the determined specific surface area of the products (see the table) we suggested that samples 2–5 were nanoparticulate SiO_2 similar to the commercial Aerosil products. For example, Aerosil 300 (Evonik Industries) has S_{sp} of 300 ± 30 m^2/g and consists of about 7 nm particles, whereas the particles size of Aerosil 200 is of about 12 nm at S_{sp} of 200 ± 25 m^2/g [9–11].

Indeed, scanning electron microscopy showed that samples 1 and 7 were amorphous materials consisting of large particle agglomerates (Fig. 1). On the contrary, samples 3 and 5 consisted of the nanosized particles (Fig. 2).

The observed properties of samples 2–5 were surprising, because preparation on silica nanoparticles via the "wet" process without high-temperature annealing has not been reported in the literature so far. Evidently, hydrophobic oxiranes **I** adsorbed on the surface of silica particles formed under sol–gel process conditions, and thus protected the particles from agglomeration.

Even though the specific surface area of sample 7 was close to that of sample 1 (the latter being SiO_2 matrix formed in the absence of any epoxide), further studies showed that samples 6 and 7 were different from the reference sample 1. In particular, IR spectrum of sample 1 was identical to the published spectra of

The reagents ratio in the sol–gel synthesis and parameters of the products

Sample	Molar ratio of the reagents			Catalyst, μL	Oxirane conversion, %	Elemental analysis, found, wt %		Specific surface area S_{sp}, m^2/g
	$Si(OEt)_4$	H_2O	oxirane			C	H	
1[a]	1	11	0	HCl, 50	–	0.11[c]	2.64	3.1
2	1	11	4 (**Ia**)	HCl, 50	21	–	–	–
3	1	11	4 (**Ib**)	HCl, 50	18	10.61	1.60	280.0
4[b]	1	6	1.5 (**Ia**)	HCl, 50	53	–	–	–
5[b]	1	6	1.5 (**Ib**)	HCl, 50	50	13.33	2.49	210.0
6	1	6	1.1 (**Ia**)	NEt_3, 50	95	–	–	–
7	1	6	1.1 (**Ib**)	NEt_3, 50	94	8.33	1.98	1.9

[a] Reference sample: SiO_2 matrix with no oxirane added. [b] 2 mL of CCl_4 per 0.01 mol of $Si(OEt)_4$ as co-solvent. [c] Absent within the limits of the analysis accuracy.

amorphous SiO_2 [12–14], whereas spectra of all modified samples 2–7 contained weak additional signals assigned to vibrations of functional groups of the organic modifiers.

IR spectrum of sample 1 (Fig. 3a) contained a broad band at 3020–3650 cm^{-1} arising from overlapping of stretching vibration bands of silanol OH and of adsorbed water molecules [13]. In the cases of samples 4 and 5 (see example in Fig. 3b), that signal was weaker, thus supporting the suggested hydrophobization of SiO_2 surface due to adsorption of fluorinated oxiranes. Increasing of the oxiranes amount in the reaction mixture led to further weakening of the band (samples 2 and 3, see example in Fig. 3c).

IR spectrum of sample 1 showed no bands assigned to organic functional groups (Fig. 4a), whereas they were slightly seen in the spectra of samples 2–5. In the spectra of products 6 and 7 (see an example in Fig. 4c), absorption bands were clearly seen at 1133 and 1223 cm^{-1} assigned to C–O–C and C–F vibrations, respectively (cf. spectrum of oxirane **Ib** in Fig. 4b). Furthermore, spectra of samples 6 and 7 contained weak absorption bands assigned to C–H stretching vibrations (2981 cm^{-1}).

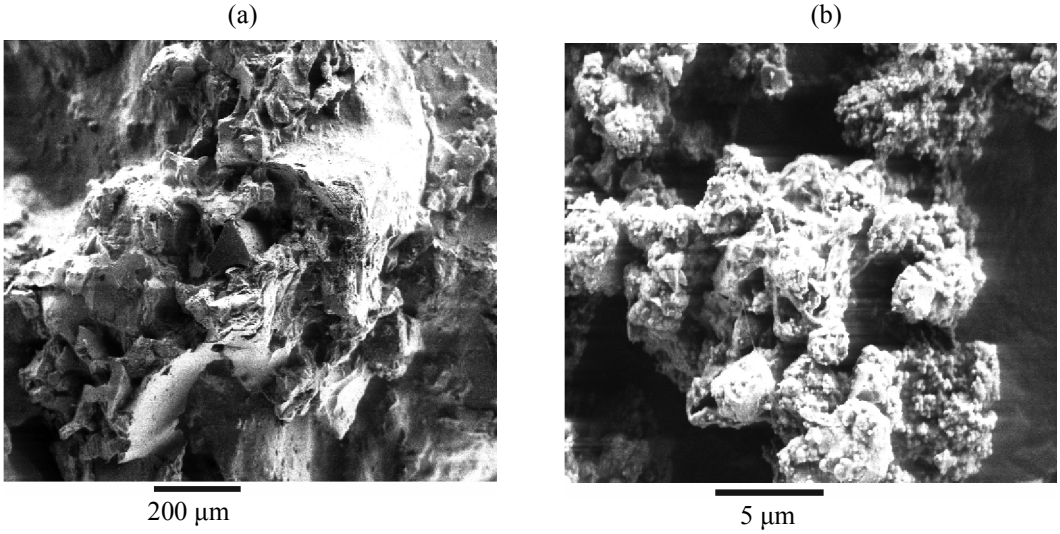


Fig. 1. Scanning electron microscopy images of samples (a) 1 and (b) 7.

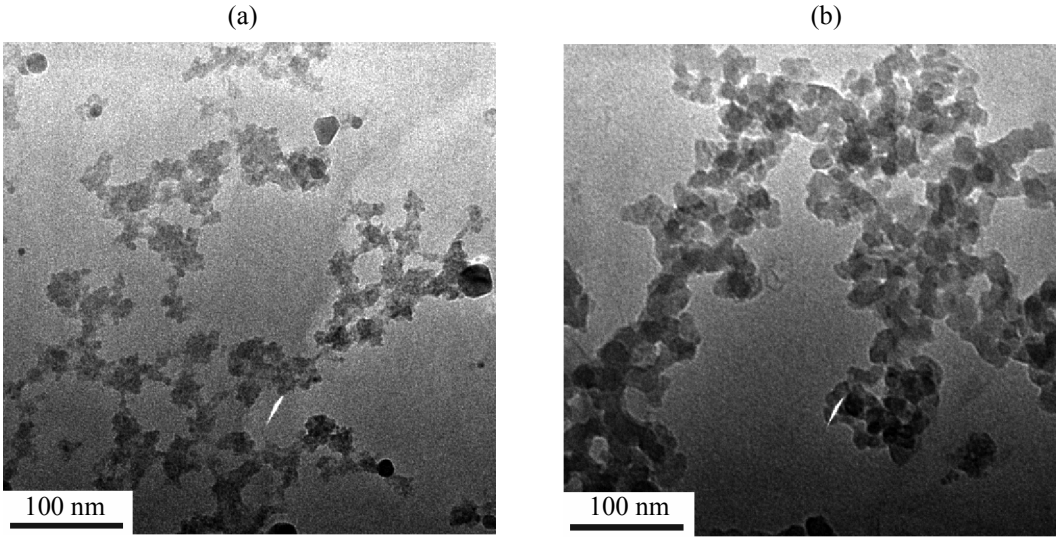


Fig. 2. Transmission electron microscopy images of samples (a) 3 and (b) 5.

Raman spectra of samples 6 and 7 (see example in Fig. 5) contained strong bands of C–H stretching vibrations at 2990 cm^{-1} as well.

X-ray diffraction pattern of sample 7 (Fig. 6) was qualitatively similar to that of ground commercial quartz glass containing 99.9% of amorphous SiO_2 [15]. The peak shift in the case of sample 7 (to 2θ 35.6°) as compared to the data reported in [15] (2θ 22.5°) evidenced that the oxirane-modified silica prepared in this work was not identical to amorphous SiO_2.

General view of X-ray photoelectron spectrum of the sample (Fig. 7) confirmed the presence of all the expected elements in the product: C, Si, F, and O. Furthermore, sample 7 contained admixtures of N and I. Evidently, nitrogen was introduced with the catalyst NEt_3, and iodine was contained in the residual 2-iodo-4,4,5,5,6,6,7,7,7-nonafluoroheptanol, precursor of oxirane **Ib** [7].

Atomic concentration of admixtures of N and I, according to the X-ray photoelectron spectroscopy data, was 1.4 and 1.2 mol %, respectively. Content of the main elements was as follows: Si 25.5, F 23.9, and O 26.5 mol %. Hence, the O : Si ratio in sample 7 was 1.23, in contrast to the unmodified silica particles (for example, the O : Si ratio was 2.50–2.70 in the cases of one crystalline and three amorphous silica samples [16]).

From the general view of the spectrum (Fig. 7), the binding energies in sample 7 were as follows: Si2*p* 103.3, O1*s* 532.6, and F1*s* 688.8 eV. Individual spectra of the main elements contained in sample 7 were recorded for detailed analysis (Fig. 8). The Si2*p* spectrum appeared as non-resolved in energy doublet of the Si2$p_{3/2}$ and Si2$p_{1/2}$ lines with binding energy of 103.3 eV. The value coincided with those determined in the cases of SiO_2 samples [16] and modified silica particles [17]. Hence, sample 7 contained either a single chemical form of silicon or its spectrally indistinguishable forms.

In contrast to silicon, the C1*s* spectrum pointed at co-existence of several non-equivalent chemical states of carbon. The two lines with the highest binding energy were assigned to the $>CF_2$ and $–CF_3$ bonds [17], whereas the low-energy lines corresponded to the $>CH_2$ bonds [18, 19]. The two lines of intermediate energy (including the strongest one) could likely be assigned to carbon atoms adjacent to hydrogen and oxygen [18, 19]. Noteworthily, the low-energy lines assigned to the $>CH_2$ groups could be additionally enhanced due to hydrocarbons adsorption from surrounding air onto the sample 7 surface.

According to the O1*s* spectrum, practically all oxygen atoms in sample 7 existed in the same chemical form, the fact not fully understandable. Even if the silica surface was not covalently modified, at least two signals should have been present in the O1*s* spectrum: that of SiO_2 oxygen and that of the physically adsorbed oxirane **Ib** oxygen; that assumption was in line with the view of C1*s* spectrum.Yet, the only oxygen signal, corresponding to the silica oxygen [20], was found in the O1*s* spectrum.

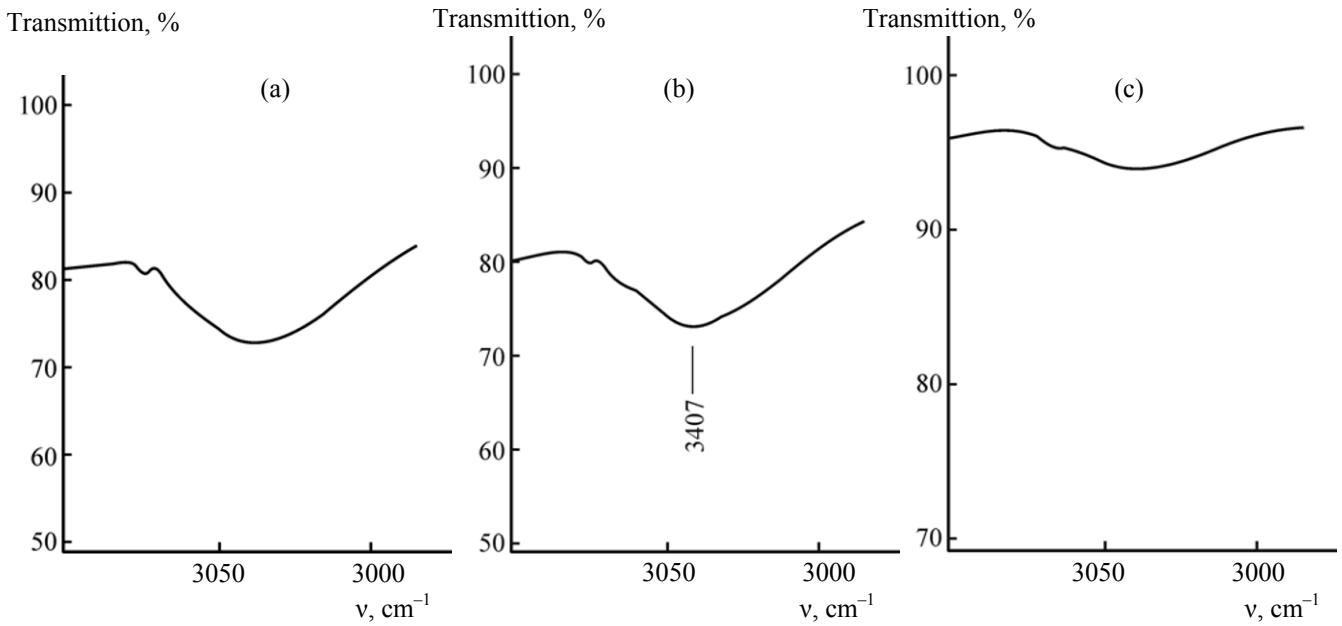


Fig. 3. IR spectra of samples (a) 1, (b) 5, and (c) 3. The samples preparation for the analysis was identical.

The F1*s* spectrum signal was substantially broadened, but the line shape evidenced the only chemical form of fluorine in sample 7. Indeed, in contrast to the case of the carbon C1*s* spectrum, the CF_2 and CF_3 were expected to be spectrally indistinguishable in the F1*s* spectrum.

The ambiguity in X-ray photoelectron spectra interpretation could result from the low content of organic fragments in the sample as compared to the unmodified silica, complicating the observation of modified particles. Besides, the spectral results could be distorted by the shielding of the modified particles signal with the internal volume of SiO_2. However, the collected results allowed suggesting that sample 7 was amorphous SiO_2 with its surface covalently modified with substrate **B** (see the reactions scheme above).

To conclude, we demonstrated that depending on the reaction conditions the sol–gel preparation of silica particles in the presence of perfluoroalkylmethyloxiranes could result in two types of products. Under the acidic catalysis conditions the surface of the prepared SiO_2 was modified with perfluoroalkylmethyloxiranes via physical adsorption; in that case the silica particles were nanosized, as aggregation of hydrophobic particles was unfavorable. Under the basic catalysis conditions, large silica particles were formed, and their surface was modified with perfluoroalkylmethyloxiranes via the covalent bonding.

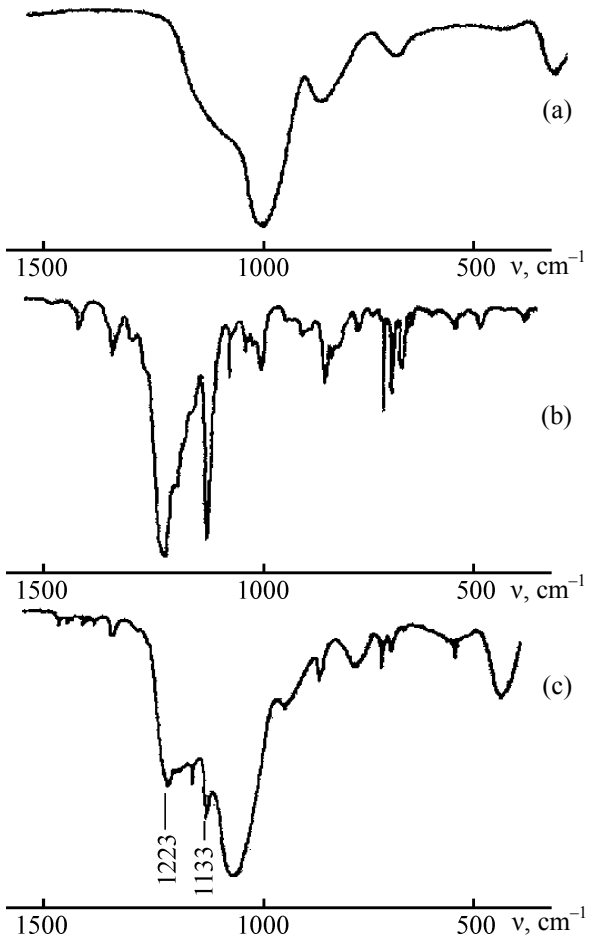


Fig. 4. IR spectra of sample (a) 1, (b) oxirane **Ib**, and (c) sample 7.

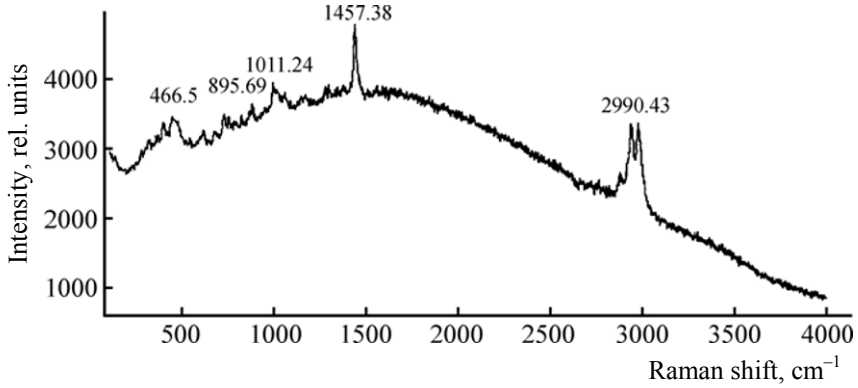


Fig. 5. Raman spectrum of sample 7.

EXPERIMENTAL

Elemental analysis was performed using the CHN PE 2400 (Perkin-Elmer) automated analyzer. IR spectra were recorded on a Spectrum One (Perkin-Elmer) spectrophotometer. Raman spectra were recorded on a U1000 (Renishaw) spectrometer at the irradiation with the He–Ne laser (λ = 632.8 nm). Specific surface area was determined with the Micromeritics Tristar automated sorption device; the results were processed via the BET equation. The samples morphology was studied using the LEO 982 (Karl Zeiss) (scanning electron microscopy) and the JEM 2100 (JEOL) (transmission electron microscopy) instruments. X-ray diffraction studies were performed with the DRON-6 automated diffractometer (CrK_α monochtomatic radiation).

X-ray photoelectron spectra were recorded using the VG ESCALAB MK II electron spectrometer. The analyzer chamber pressure was 10^{-8} Pa during the operation (up to 10^{-6} Pa during the spectra recording); MgK_α radiation (1256.3 eV) was used as the excitation source. The scanning step was 0.1 eV, the spectrometer was calibrated using the Au4*f*7/2 line (84 eV), the sample charge was estimated from the C1*s* spectrum (284.5 eV) arising from natural hydrocarbon admixtures on the surface. Qualitative analysis of the sample was performed using the general view spectrum (0–1000 eV with step of 0.5 eV). The sample surface with respect to the analyzer axis was at Θ = 90°, the surface layer of 3–4 nm thickness was accessible under those conditions.

SiO_2 particles preparation *(general procedure).* After mixing all required components at room temperature (see the mixtures composition in the Table, the mixing order did not affect the results), the mixtures were heated and refluxed under stirring; the low-boiling products were simultaneously distilled off. Then, the excess of oxirane **Ia** or **Ib** and CCl_4 (samples 4 and 5, see table) were distilled off. After the reaction

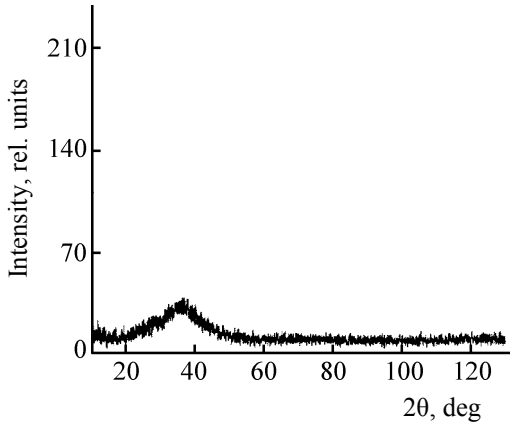


Fig. 6. X-ray diffraction pattern of sample 7.

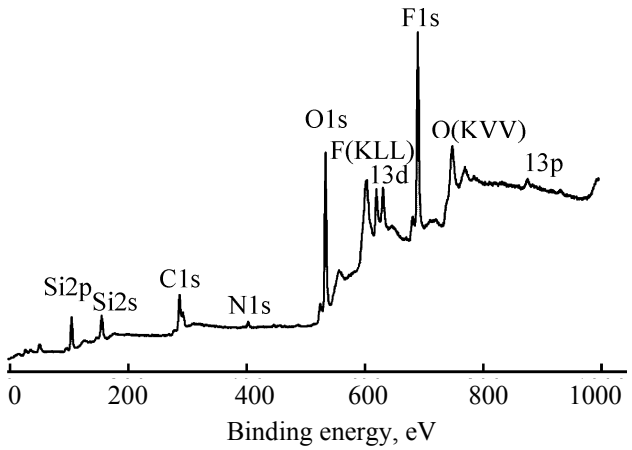


Fig. 7. General view of the X-ray photoelectron spectrum of sample 7.

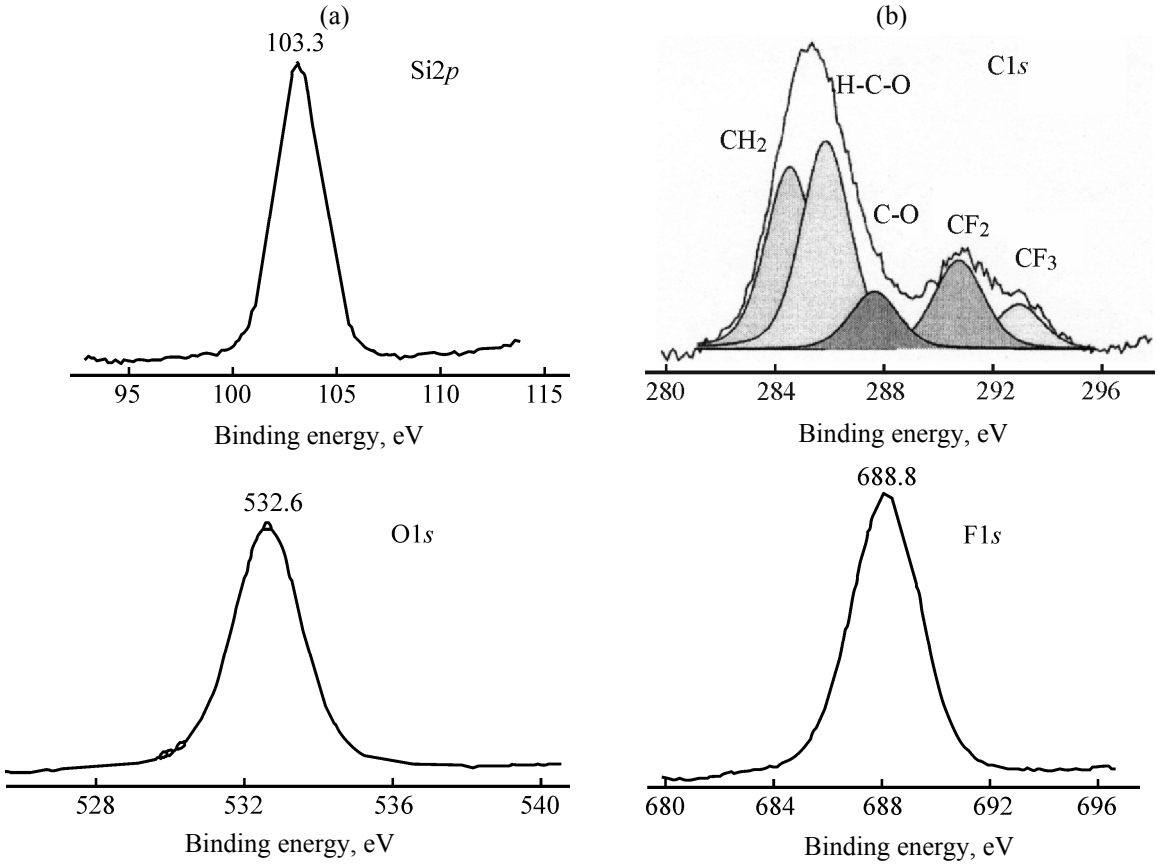


Fig. 8. Detailed view of the X-ray photoelectron spectrum of sample 7.

completion the products were maintained at 90–120°C and 5 mmHg. The samples 1–7 were white powders.

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