Kinetics and Catalysis, Vol. 41, No. 1, 2000, pp. 99–107. Translated from Kinetika i Kataliz, Vol. 41, No. 1, 2000, pp. 112–121.
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Synthesis and Investigation of Chemically Modified Silicas with the Island Structure of the Grafted Layer

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Received January 19, 1998

Abstract—Island structures on the chemically modified surface of silica are synthesized by the method of matrix prints. Dichlorosilicon phthalocyanine and copper naphthalocyanine were used as molecular templates. Two types of heterogeneous surfaces are prepared by this method: the islands of nonmodified silica on the trimethylsilylated silica (the first type) and the islands of aminopropyl silica on the esteric groups grafted on silica (the second type). The structure of the surfaces prepared is studied by ESR spectroscopy with the use of paramagnetic probes.

INTRODUCTION

Chemically modified porous silicas are successfully used as adsorbents, catalysts, supports, etc. [1–3]. The properties of modified surfaces are generally determined by the chemical nature of grafted molecules and their spatial arrangement at the surface layer. The preparation of modified surfaces with a controlled arrangement of the grafted layer, e.g., covalently bound, organized supramolecular structures, remains a challenging and still unsolved problem. The method of molecular (matrix) prints is one of the synthetic procedures that allows one to control the surface structure on a molecular level [4].

The first studies of the properties of mineral supports, including silica gels, prepared by the method of matrix prints were carried out in the 1930s [5, 6]. It has been shown that the presence of a template specially introduced at the stage of synthesis affects the pore size and adsorption properties of silicas [7, 8], the activity and selectivity of catalysts [9, 10] including stereospecific catalysts [11–14], and the efficiency of chromatographic sorbents [15–18].

Available data on the methods based on the use of molecular templates in the synthesis of organized surfaces have a common drawback: a low stability of the prints obtained. The prints formed can be sworn and disappeared due to the reconstruction of the surface of silica gel, e.g., during operation in an aqueous medium.

In this work, the method of matrix prints combined with chemical modification of the surface was applied. This allows one to prepare covalently grafted structures [4]. It was suggested that the prints fixed by chemical modification would exhibit hydrolytic, thermal, and other stabilities close to that of chemically modified silicas.

The idea of the method used is seen in Fig. 1 [19]. At the first stage, the molecules-templates are adsorbed on the silica surface at a coverage much less than a monolayer. The free surface is then chemically modified and finally the template is desorbed. Depending on the purpose of the study, the islands obtained can then be chemically modified by another dopant.

The goal of this work is the synthesis of an island structure by the method of matrix templates on the chemically modified surface of silica.

EXPERIMENTAL

1. Silica Supports

Aerosil Silochrom S-120 and aminopropyl-modified Silochrom S-120 prepared by treatment of S-120 with γ-aminopropyltriethoxysilane in toluene according to the procedure described in [3] were used.

2. Adsorption of Template Molecules

Adsorption was carried out from toluene solutions. A solution with a specified concentration (from 10^{-7} to 10^{-4} mol/l) was added to a weighed portion of a support and stored for several days (from 10 to 40). The amount of the adsorbed substance was estimated spectrophotometrically from a decrease in the absorption at the wavelengths of 750 nm (copper naphthalocyanine, NcCu) and 671 nm (dichlorosilicon phthalocyanine, $PcSiCl_2$).

3. Chemical Modification of Silica Containing NcCu and $PcSiCl_2$

Modification with chlorotrimethylsilane. A weighed portion (0.2–0.5 g) of Silochrom S-120 containing 1.7×10^{-7} mol/g of adsorbed NcCu was placed in a beaker with a porous bottom, and then the beaker was placed into a glass ampule containing a 10-fold excess of chlorotrimethylsilane with respect to the silanol groups on the surface of silica. The ampule was heated in an oven at 60°C for 2 h, and then the sample was kept for 4 h at 60°C and 2–6 Torr.

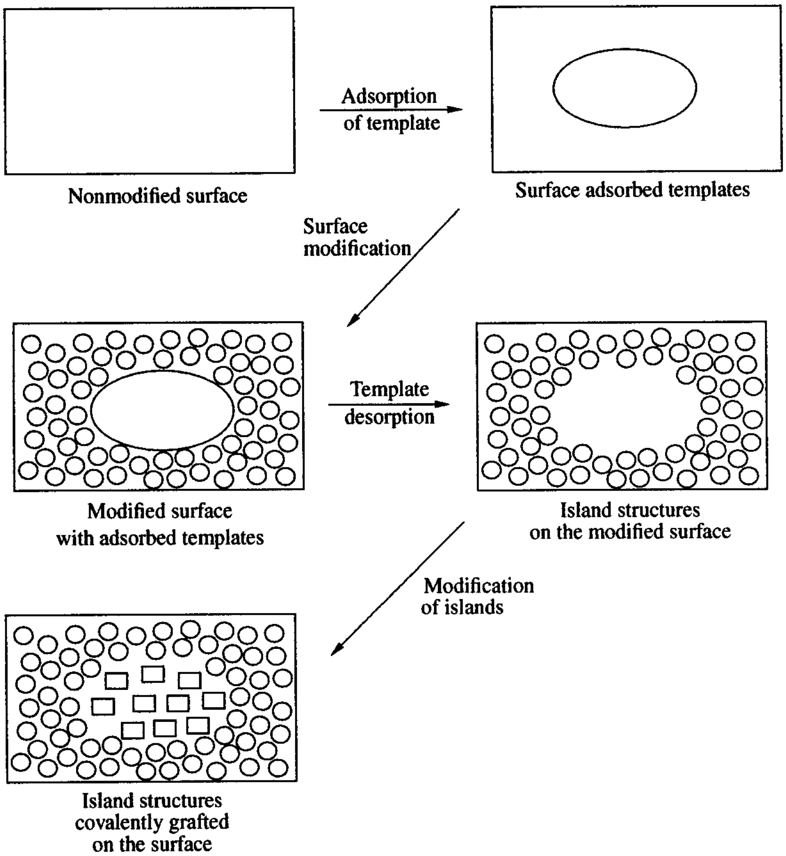


Fig. 1. Scheme of the formation of island structures covalently grafted on the surface by the method of matrix prints.

Modification with ethyl acrylate. A weighed portion (0.2–0.5 g) of aminopropylated Silochrom S-120 containing 5.7×10^{-7} mol/g $PcSiCl_2$ was placed in a beaker with a ground stopper, and 10 ml of isopropyl alcohol was added. Ethyl acrylate was added to a suspension in a 10-fold excess with respect to amino groups of the surface. The reaction mixture was periodically shaken during two days at room temperature. The support obtained was washed successively by isopropyl alcohol and diethyl ether, dried under vacuum of a water aspirator at room temperature to the powdered state and the absence of odor of solvents and ethyl acrylate.

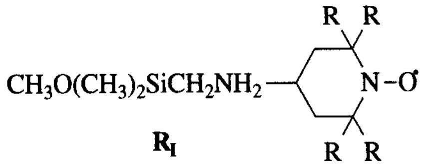
4. *Desorption of Template Molecules from the Surface*

To desorb NcCu from the surface of Silochrom S-120, the sample was treated with pivalic (trimethylacetic) chloroanhydride according to the following procedure.

A weighed portion (0.3 g) of the sample was washed with 30 ml of *n*-hexane, and 4-methylmorpholine (0.2 ml) and pivalic chloroanhydride (0.4 ml) were added. Then the sample was stored at room temperature for 2 h with periodic shaking. The support was separated from the solution and successively washed with toluene and mixtures $CH_3OH : H_2O$ (9 : 1, containing 1% of a 1 M solution of HCl), $CH_3OH : H_2O$ (9 : 1), $CH_3OH : H_2O$ (9 : 1, containing 1% of a 1 M solution of $NaHCO_3$), $CH_3OH : H_2O$ (9 : 1), CH_3OH, and $(C_2H_5)_2O$. The sample was dried under vacuum of a water aspirator at room temperature to the powdered state and the absence of an odor of solvents and 4-methylmorpholine.

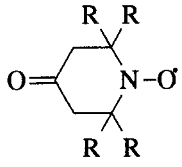
To remove $PcSiCl_2$ chemisorbed on the support, the sample was subjected to extraction with a small (3%) amount of glacial acetic acid during 12 h in a Soxhlet apparatus filled with toluene until $PcSiCl_2$ was completely transferred to the solution; this process was monitored by spectrophotometry.

5. *Treatment of Samples with R_I and R_{II} Radicals*



R

$\mathbf{R_I}$



, R = CH_3

$\mathbf{R_{II}}$

A weighed portion (70 g) of Silochrom S-120 containing the islands of nonmodified silica on trimethylsilylated silica was treated with a solution (10 ml, 1×10^{-4} mol/l) of nitroxyl radical R_I in toluene. The mixture was heated at 60°C for 4 h. The support was washed successively by toluene, methanol, and diethyl ether, dried under a vacuum of a water aspirator at room temperature to the powdered state and the absence of an odor of solvents.

A weighed portion (70 g) of aminopropylated Silochrom S-120 containing the islands of the aminated surface on the background of esteric groups was treated with a solution (10 ml, 1×10^{-4} mol/l) of nitroxyl radical R_{II} in toluene. The mixture was heated at 60°C for 4 h. The support was successively washed by toluene, methanol, and diethyl ether, dried under a vacuum of a water aspirator at room temperature to the powdered state and the absence of an odor of solvents.

Diffuse-reflectance spectra were recorded using a Spektroton colorimeter (Khimavtomatika, Chirchik, Uzbekistan) in Teflon cuvettes of 6 mm in depth with a cylinder hole with a diameter of 16 mm. The absorption spectra of solutions and suspensions in the visible range were recorded on a Specord UV-VIS spectrophotometer in glass cuvettes.

ESR spectra were recorded on a Varian E-3 (X-band) spectrometer at room temperature and at 77 K. The number of spins (N) in the sample was estimated by comparison with a standard (a weighed $CuCl_2 \cdot 2H_2O$ single crystal) at room temperature.

The concentration of paramagnetic centers (C, molecule/nm^2) on the surface was calculated according to the formula

$$C = N/S_{sp},$$

where S_{sp} is the specific surface area (BET) of silica measured by benzene adsorption.

The average distance between paramagnetic centers was evaluated from dipole–dipole broadening of the ESR spectra according to a model dependence described in [20, 21]. The $A_{\parallel}$ parameter was estimated from the distance between the external lines in the ESR spectrum [22].

Titration of the surface amino groups of aminopropylated silica was carried out by the inverse titration of excess HCl by alkali (NaOH) according to a conventional procedure [3].

The elemental analysis for carbon, hydrogen, and nitrogen was carried out in the Laboratory of organic microanalysis of the A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. The content of grafted groups was calculated according to the formula

$$n = P \times 10^6 / S_{sp}(A \times 10^3 - MP),$$

where n is the content of grafted groups in the sample, (µmol/m^2), P is the content of the element being determined (%), S_{sp} is the specific surface area of the sample (m^2/g), A is the atomic weight of the element (g/mol), and M is the corrected molecular weight of the grafted group (g/mol).

RESULTS AND DISCUSSION

1. Nonmodified Silochrom–Copper Naphthalocyanine System

The adsorption isotherm of NcCu on aminopropylated Silochrom was measured (Fig. 2) and the statistical treatment of data was carried out [23]. The isotherm was approximated by a sigmoid $y = a + b/–\exp((x - c)/d)$ with the parameters $a = 2.9 \times 10^{-8}$, $b = 1.38 \times 10^{-5}$, $c = 3.18 \times 10^{-5}$, and $d = 9.41 \times 10^{-6}$. The S-shape of the isotherm provides evidence that the interactions between the adsorbate molecules are stronger than the interactions of the adsorbate–adsorbent type [24]. Hence, association of the NcCu molecules on the surface of aminated Silochrom is possible. This makes the aminopropylated Silochrom–adsorbed NcCu system hardly suitable to prepare the island structures.

The statistical treatment of the adsorption isotherm of NcCu on the nonmodified Silochrom (Fig. 3) was also carried out [23]. The curve was approximated by the Langmuir isotherm $y = ax/(1 + bx)$ with parameters $a = 0.33$ and $b = 47739$.

Calculation performed for the isotherms shows that on the aminated surface, 1 molecule of NcCu occupies 12.8 nm^2. This value exceeds the crystallographic radius of the molecule calculated from the angles and bond lengths. On the nonmodified surface, 1 molecule of NcCu occupies 25 nm^2. These data confirm the hypothesis that NcCu molecules are not closely packed on the surface.

The kinetics of adsorption was also studied. The data are presented in Fig. 4. As can be seen, a long time is required to achieve the equilibrium.

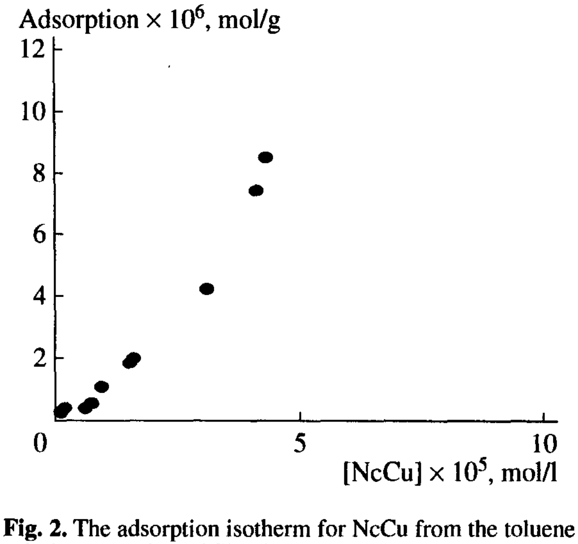


Fig. 2. The adsorption isotherm for NcCu from the toluene solution on aminated Silochrom.

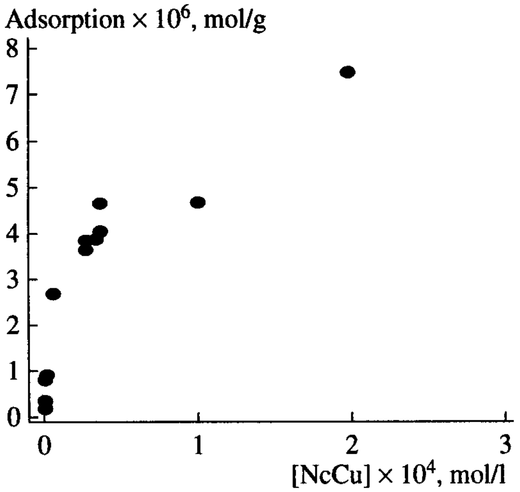


Fig. 3. The adsorption isotherm for NcCu from the toluene solution on nonmodified Silochrom.

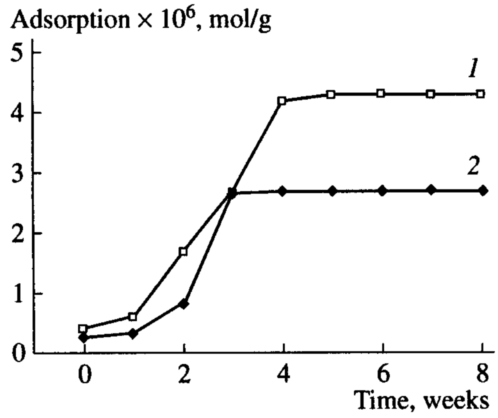


Fig. 4. The NcCu adsorption as a function of time for (*1*) aminated and (*2*) nonmodified Silochrom samples at [NuCu] = 3×10^{-5} (*1*) and 5×10^{-6} mol/l (*2*).

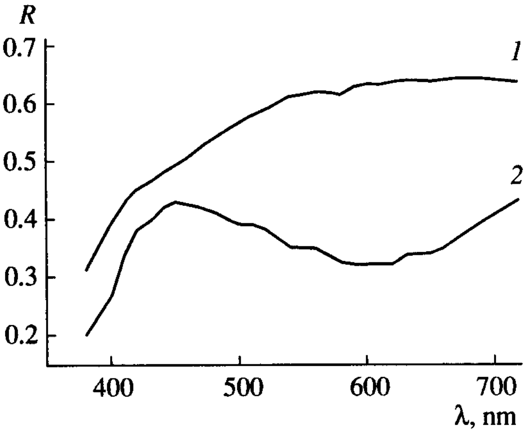


Fig. 5. Diffuse-reflectance spectra of the samples of (*1*) nonmodified and (*2*) aminated Silochrom containing adsorbed NcCu.

The samples which adsorb less than 1×10^{-6} mol/g (the initial section of the adsorption isotherm) were used for further modification.

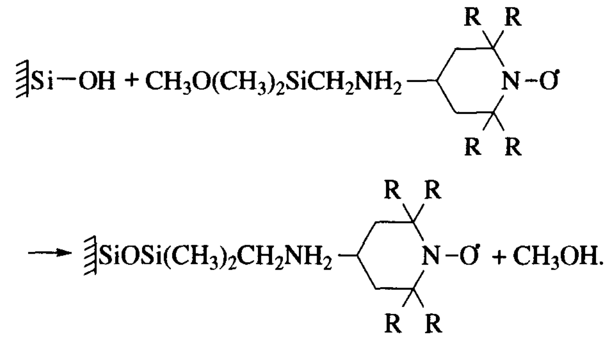
The reflection spectra of the samples of Silochrom containing adsorbed NcCu are shown in Fig. 5. The spectra of NcCu adsorbed on nonmodified Silochrom and on aminated Silochrom differ from each other. The color of the samples also changes after adsorption, and the colorimetric data confirm this fact. It was assumed that the change in color is connected with the protonation of the azo-bridges in the NcCu molecule by the most strong silanol groups on the surface. To verify this assumption, we studied the spectra of the samples containing NcCu adsorbed on aminopropylated Silochrom, which contains a considerable number of blocked acid sites. Comparison of the absorption spectra for the suspensions and a solution of NcCu in toluene presented in Fig. 6 confirms that the change in the NcCu spectrum after adsorption on Silochrom (a decrease in the absorption at 450 and 580 nm) is caused by the protonation of NcCu by the silanol groups on the surface.

The ESR spectrum of adsorbed NcCu is shown in Fig. 7. It is identical to the spectrum of polycrystalline NcCu [25]. However, because of the low content of adsorbed NcCu in the sample, the intensity of the spectra was low, and the spectra were not used in the further study.

The principle of the method of chemical modification of the samples containing adsorbed NcCu is presented in Scheme 1.

Sample **I** for which the adsorption of NcCu, *G*, was equal to 1.7×10^{-7} mol/g (this corresponds to 1.02×10^{-3} group/nm^2) was treated with chlorotrimethylsilane from the gaseous phase (1). As a result, sample **II** with the carbon content of 1.16% (the surface concentration of trimethylsilyl groups is equal to 1.9 group/nm^2) was obtained. Taking into account that the maximum possible density of trimethylsilyl groups grafted in the course of synthesis from the gaseous phase is equal to 2.3 group/nm^2 [26], one can conclude that a significant portion of the surface in sample **II** is covered by trimethylsilyl groups. At the following stage (2), the sample was treated with pivalic chloroanhydride, and sample **III** was obtained. NcCu was completely desorbed and transferred into the solution, which was confirmed by spectrophotometry. Treatment of sample **III** with water resulted in the hydrolysis of pivaloesteric groups and the formation of sample **IV**, which contained the islands of nonmodified silica at the background of the trimethylsilylated surface.

To study the structure of the surface of sample **IV**, the method of paramagnetic probe molecules using nitroxyl radicals was employed. Sample **IV** was treated with an excess of nitroxyl radical containing the organosilicon group (R_I) according to the following reaction:

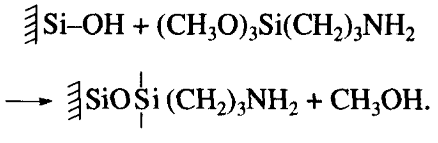


The radical R_I contains a methoxysilyl group, which can react with silanol groups on the surface and does not interact with the surface that has already been modified. As a result, sample **V** was obtained at stage (4). ESR spectra of samples **V** and **VI** prepared by the treatment of Silochrom with radical R_I under the conditions of uniform statistical distribution of the probe molecules on the surface are presented in Fig. 8. Table 1 shows the comparison of the parameters of these spectra. As can be seen, when the surface concentrations of the grafted radical are equal in both samples, the distribution of a tracer on the surface is considerably different: a significant deviation from the uniform statistical distribution is observed for sample **V**. Since the same radical was used for testing similar surfaces with comparable concentrations and was grafted according to the same procedure, we suggest that the dipole–dipole interaction mainly contributes to the broadening of the spectra along with the own line width, the polarity of the environment, etc. This approach has been described in a series of works on the estimation of the local concentration and distribution of nitroxyl radicals in solid matrices [20, 21, 27]. As the distribution of the grafted radical in this case is determined by the distribution of the sections of nonmodified silica, we suppose that the data of Table 1 confirms the island nature of the surface of sample **IV**.

The adsorption capacity of sample **IV** toward a solution of NcCu in toluene was also studied. The findings were compared with those for sample **VII** prepared by the treatment of Silochrom with an excess of chlorotrimethylsilane (2.1 group/nm^2). The results are shown in Table 2. The capacity of sample **IV** with respect to NcCu at the equilibrium concentration, which is at least twice lower, is 12% greater than exhaustively trimethylsilylated sample **VII**.

2. *Aminopropylated Silochrom–PcSiCl$_2$ System*

Aminopropylated Silochrom was used as the original support. It was prepared according to the following reaction:



$$\equiv Si–OH + (CH_3O)_3Si(CH_2)_3NH_2$$

$$\longrightarrow \equiv SiO\overset{|}{\underset{|}{Si}}(CH_2)_3NH_2 + CH_3OH.$$

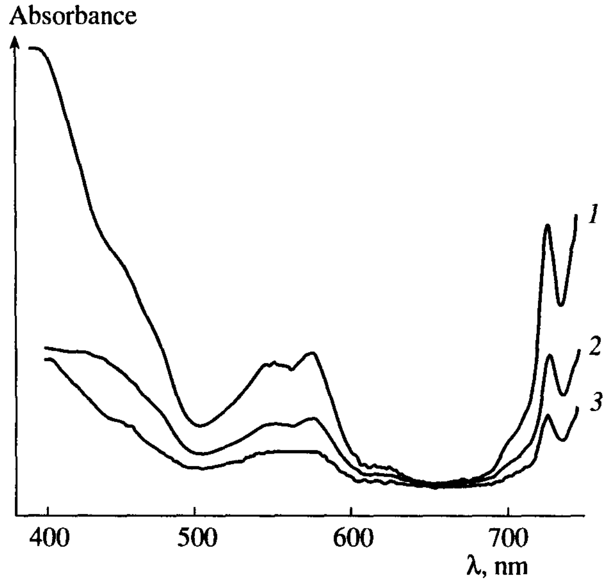


Fig. 6. Absorption spectra of (*1*) a toluene solution of NcCu and (*2*) glycerol suspensions of aminopropylated Silochrom and (*3*) Silochrom both containing adsorbed NcCu.

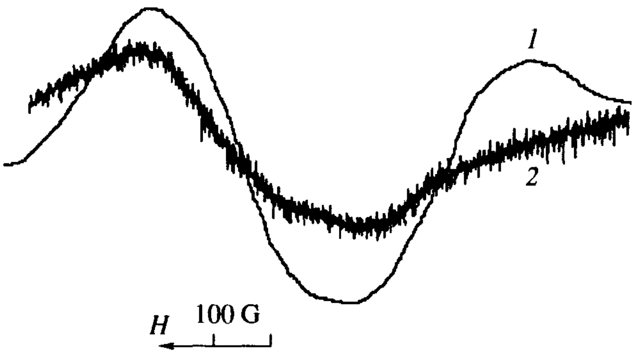


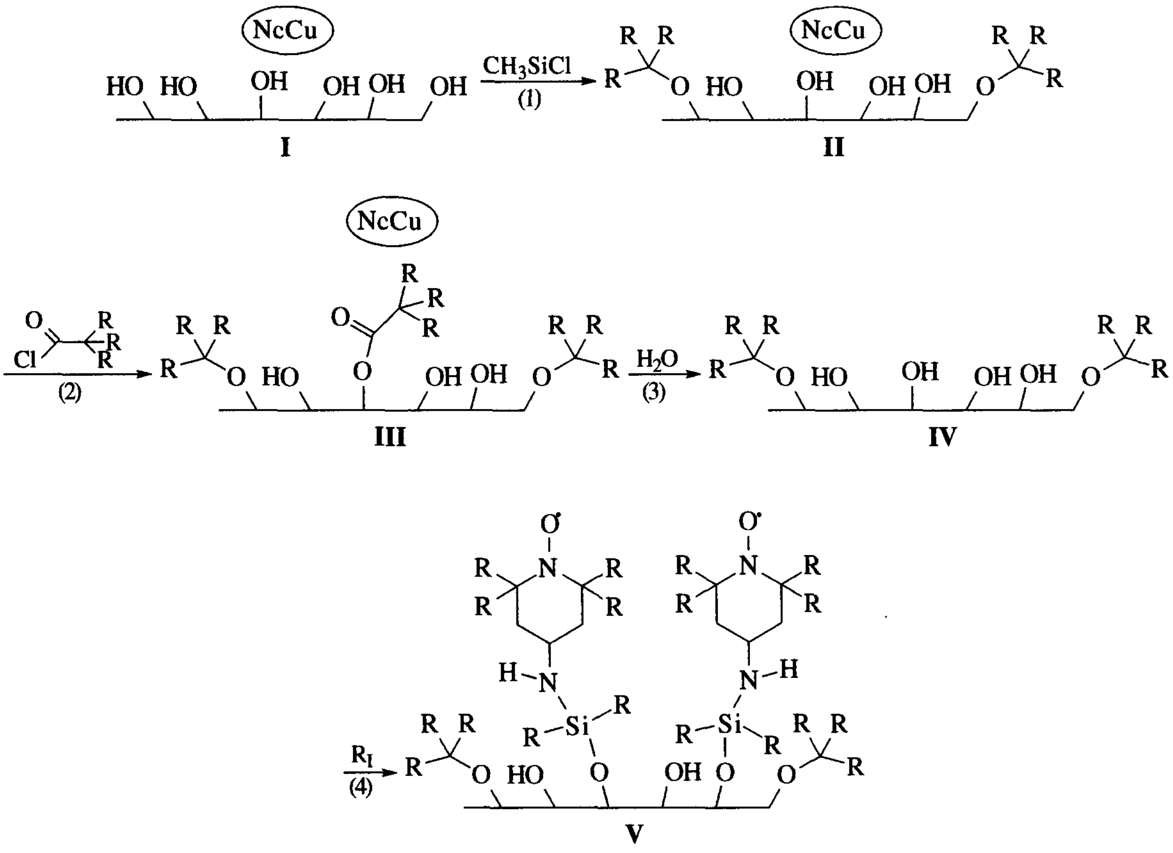
Fig. 7. ESR spectra of (*1*) NcCu and (*2*) NcCu adsorbed on Silochrom (8.5 × 10^{-6} mol/g).

As follows from the analysis data (Table 3), the density of the grafted aminopropyl groups is 1.6–2.1 group/nm^2, which corresponds to 1–1.5 layers of the modifying agent.

Data on the adsorption of $PcSiCl_2$ is presented in Fig. 9. In the aminopropylated Silochrom–$PcSiCl_2$ sys-

Table 1. Comparative analysis of ESR spectra of supports **V** and **VI**

Parameter of ESR spectrum	Sample **V**	Sample **VI**
Average surface concentration of paramagnetic centers, group/nm^2	$(5 \pm 0.2) \times 10^{-3}$	$(5 \pm 0.2) \times 10^{-3}$
I_1/I_2	≈0.6	≈0.4
Average effective distance estimated from the I_1/I_2 parameter	≈3 nm	≈15 nm
Change in the signal with increasing power	No change	Changed
$A_\parallel$ (polarity of the environment of a tracer)	33 G	38 G



$R = CH_3$

Scheme 1.

tem, the chemical interaction of the template with the support surface occurs according to the reaction

$$\| \mathrm{SiOSi(CH_2)_3NH_2} + \mathrm{PcSiCl_2}$$

$$\longrightarrow \| \mathrm{SiOSi(CH_2)_3NHPcSiCl} + \mathrm{HCl}.$$

Table 2. Adsorption of NcCu on samples **IV** and **VII**

Sample	Adsorption, mol/g	Equilibrium concentration of NcCu in the solution, mol/l
IV	3.57×10^{-7}	7.7×10^{-7}
VII	3.17×10^{-7}	1.82×10^{-6}

Table 3. Characteristics of the original supports

Sample	V_{pore}, cm^3/g	d_{pore}, nm	S_{sp}, m^2/g	Density of the amino groups, group/nm^2	
				A	B
S-120	0.86	350	105	–	–
S-120 treated with γ-Aminopropyltriethoxysilane	0.86	350	105	2.14	1.58

Note: V_{pore} and S_{sp} were determined from N_2 adsorption. The density of amino groups was estimated by titration (A) and elemental analysis (B).

The adsorption isotherm belongs to those describing the chemisorption of an adsorbate [24]. Statistical processing of the data [23] resulted in the following parameters of the function $y = ax/(1 + bx) + c$: $a = 3.15$, $b = 126912$, and $c = 9.39 \times 10^{-7}$. This corresponds to the situation when one $PcSiCl_2$ molecule occupies the area of 33 nm^2 in the monolayer.

The adsorption isotherm on nonmodified Silochrom also belongs to the isotherms describing the chemisorption of adsorbate [24]. In this case, the following reaction on the surface occurs:

$$\| \mathrm{SiOH} + \mathrm{PcSiCl_2} \longrightarrow \| \mathrm{SiOPcSiCl} + \mathrm{HCl}.$$

Statistical processing of the data [23] showed that the isotherm is described by the equation $y = ax/(1 + bx) + c$ with parameters $a = 8.08$; $b = 2.16 \times 10^6$; and $c = 1.48 \times 10^{-6}$. One $PcSiCl_2$ molecule occupies 6.8 nm^2 in the monolayer.

The spectra of glycerol suspensions of aminopropylated Silochrom and nonmodified Silochrom, as well as the spectrum of the toluene solution of $PcSiCl_2$, were studied, and they proved to be identical (Fig. 10). Thus, the adsorbate did not undergo changes that would cause a shift of the absorption bands in the visible region of the spectrum [28].

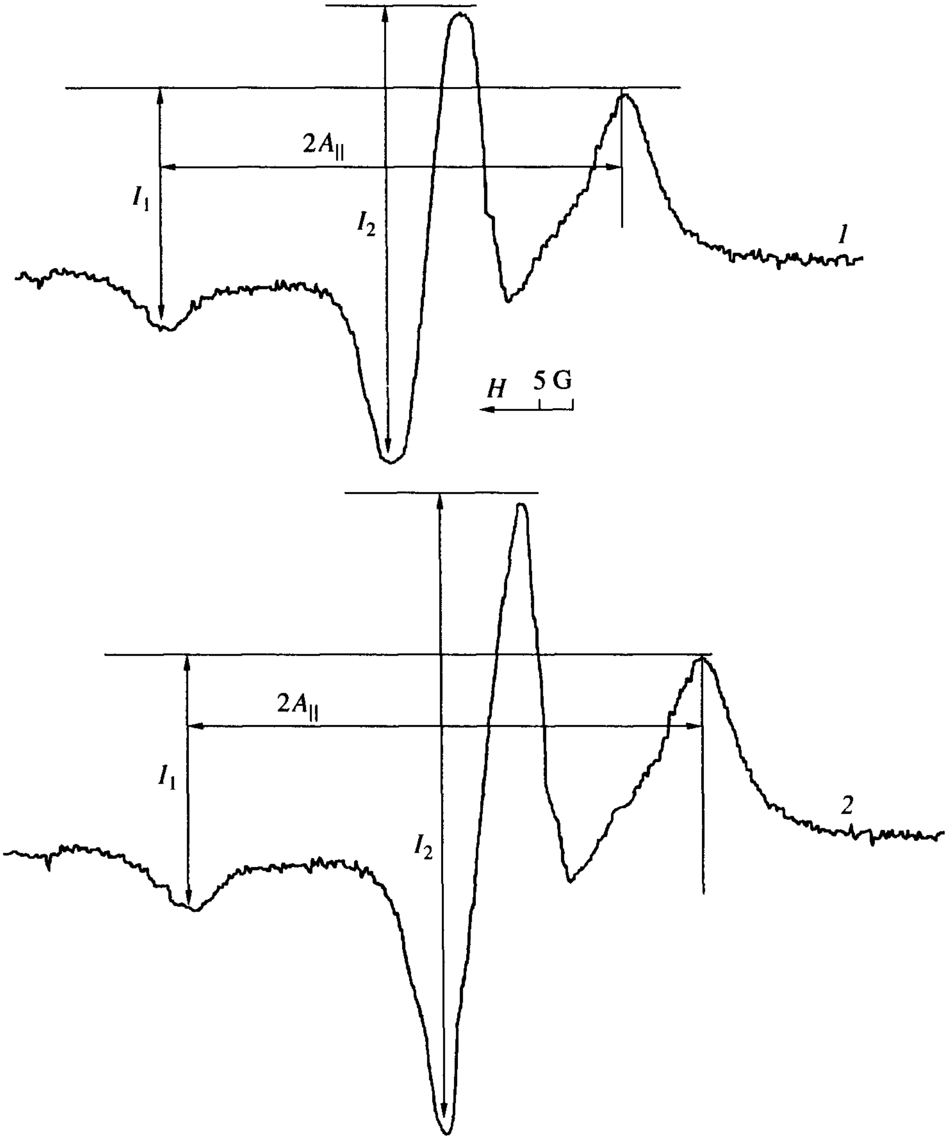


Fig. 8. ESR spectra (20°C) of samples (*1*) **V** and (*2*) **VI**.

The principle of modifying the samples containing chemisorbed silicon phthalocyanine is presented in Scheme 2. Sample **VIII** containing chemisorbed $PcSiCl_2$ that is characterized by the adsorption $G = 5.7 \times 10^{-7}$ mol/g (4.3×10^{-3} group/nm^2) was treated with ethyl acrylate (reaction (5)). Elemental analysis of the prepared sample **IX** showed the carbon content equal to 4.66% corresponding to the surface concentration of the esteric groups of 3.07 group/nm^2. Hence, the ethyl acrylate groups compactly cover the support surface that does not contain adsorbed silicon phthalocyanine. An insignificant desorption of $PcSiCl_2$ into a solution occurred during the treatment of the support with ethyl acrylate, and finally the concentration of chemisorbed $PcSiCl_2$ was equal to 5.2×10^{-7} mol/g. After the treatment of the sample with ethyl acrylate, the desorption of silicon phthalocyanine from the surface was carried

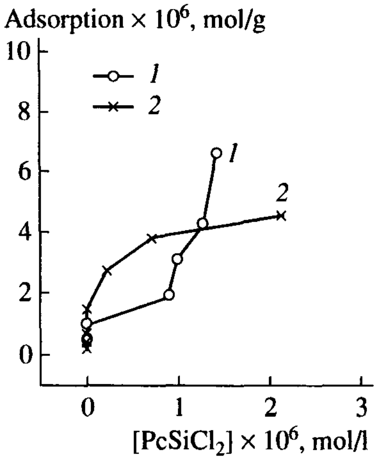


Fig. 9. Adsorption isotherms for $PcSiCl_2$ from the toluene solution on (*1*) aminated and (*2*) nonmodified Silochrom samples.

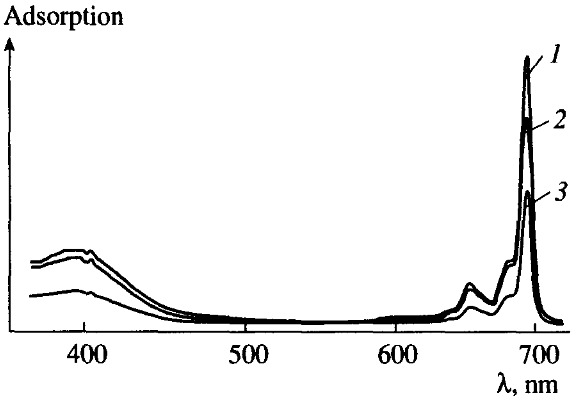
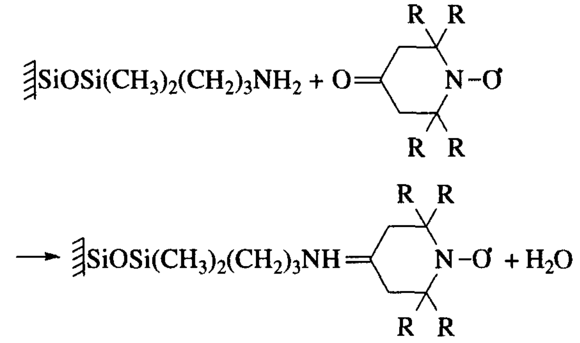


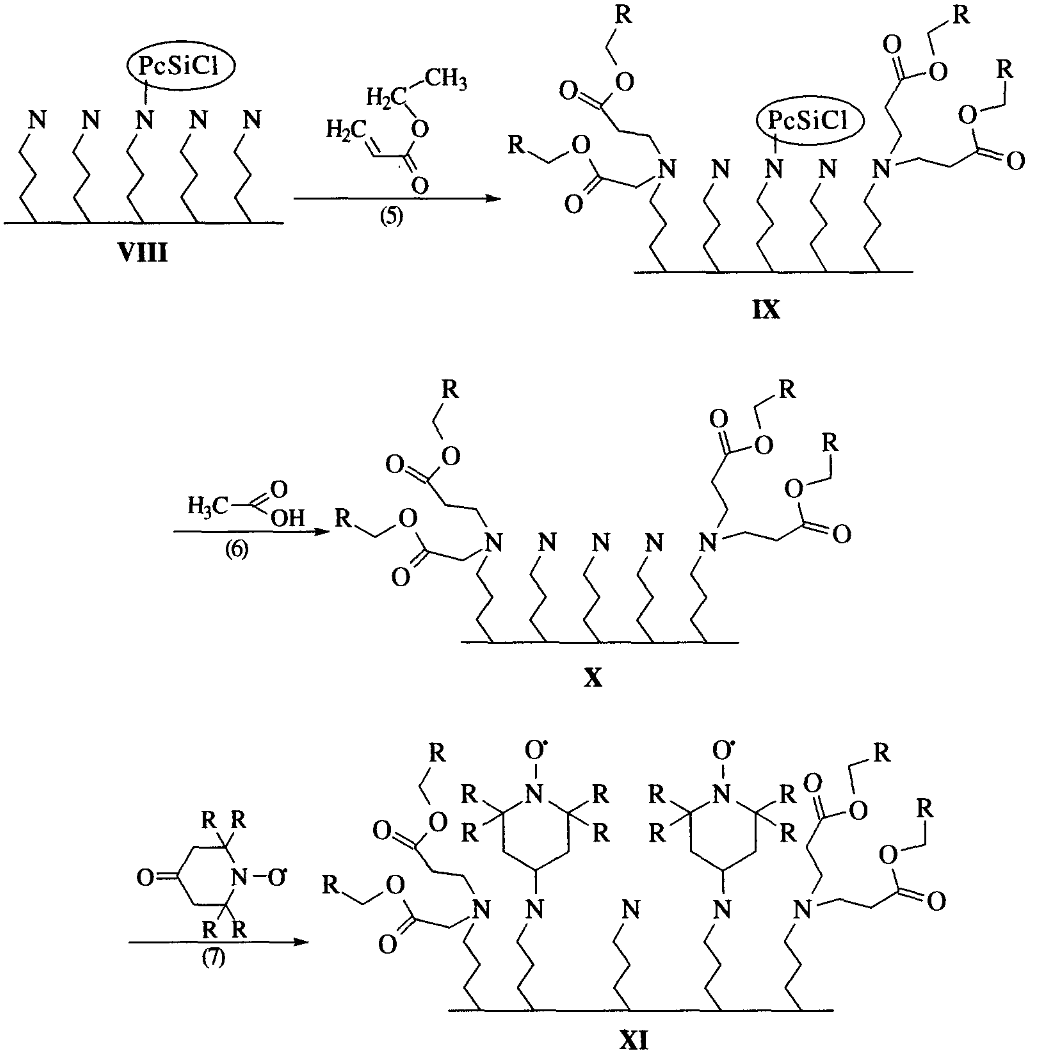
Fig. 10. Absorption spectra of (*1*) the toluene solution of $PcSiCl_2$, (*2*) glycerol suspensions of Silochrom, and (*3*) aminopropylated Silochrom containing chemisorbed $PcSiCl_2$.

out by the prolonged treatment of the sample with a solution of acetic acid in toluene (stage (6)), and sample **X** was obtained. Transfer of phthalocyanine into the solution at this stage was confirmed by spectrophotometry. The amount of $PcSiCl_2$ transferred into the solution proved to be equal to the amount of the substance contained in the sample before modification. This gives evidence that the complete desorption of $PcSiCl_2$ from the aminated surface occurred in fact.

To elucidate the surface structure of sample **X**, it was treated by the radical R_{II} according to reaction (7), which can be written in more detail as follows:



The radical R_{II} contains a ketone group that can react with accessible primary amino groups and does not react with ethyl acrylate groups.



Scheme 2.

Table 4. Comparative analysis of ESR spectra of supports **XI** and **XII**

Parameter of ESR spectrum	Sample **XI**	Sample **XII**
I_1/I_2	≈0.6	≈0.4
Average effective distance estimated from the I_1/I_2 parameter	≈3 nm	≈15 nm
Change in the signal with increasing power	no change	changed
Average surface concentration of paramagnetic centers, group/nm^2	$(4 \pm 0.2) \times 10^{-3}$	$(5 \pm 0.2) \times 10^{-3}$

Table 5. Adsorption of $PcSiCl_2$ on samples **X** and **XIII**

Sample	Adsorption × 10^7, mol/g	Equilibrium concentration of $PcSiCl_2$ in the solution × 10^5, mol/l
X	5.3	2.04
XIII	1.37	2.36

ESR spectra of samples **XI** and **XII** containing the grafted radical II in close surface concentrations and the statistical distribution of the radical in sample **XII** were recorded. As can be seen in Table 4, these samples are characterized by the substantially different distribution of a tracer on the surface, namely, a significant deviation from the uniform statistical distribution is observed for sample **XI**. As the distribution of the grafted radical R_{II} is determined by the distribution of the sections of aminopropylated silica, these data, in our opinion, confirm the island nature of the surface of sample **X**.

Adsorption of $PcSiCl_2$ from the toluene solution on sample **X** was studied. The capacity of the support to $PcSiCl_2$ was compared to that of the support without adsorbed $PcSiCl_2$ that was prepared by the treatment with ethyl acrylate (sample **XIII**) (Table 5). The concentration of esteric groups in sample **XIII** was equal to 3.96 group/nm^2. As compared to the standard sample **XIII**, sample **X** exhibited the enhanced capacity to $PcSiCl_2$ (by more than 3 times) at a lower (by 10%) equilibrium concentration of $PcSiCl_2$.

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