

HYDROSILYLATION REACTIONS IN SYNTHESIS OF SURFACE CHEMICAL COMPOUNDS

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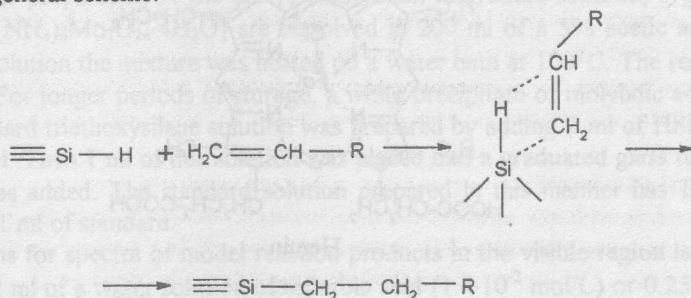
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Abstract

With the combined use of a catalytic hydrosilylation reaction and sol-gel formation, immobilization of a number of unsaturated organic compounds (quinine, quinidine, cinchonine, cinchonidine, alprenolol, N-allylrhodanine, and hemin) was carried out on a silica surface. The structure of the compounds formed and the nature of their bonding with the surface were studied by DRIFT and NMR spectroscopy. The concentrations of the olefins anchored to the surface layer of the silica matrix were estimated by a UV-spectroscopy method. A spectrophotometric method for the determination of $\equiv\text{SiH}$ group concentrations in solutions and on surfaces was developed. The method is based on the reduction of ammonium molybdate by silicon hydride groups and measuring the specific absorption at $\lambda=710$ nm of the blue solution of silicomolybdenum heteropolycomplex formed. The method allows for the determination microgram quantities of $\equiv\text{SiH}$ groups with a reasonable accuracy. Kinetic peculiarities of the hydrosilylation reaction between cinchonine and triethoxysilane in the presence of Speier's catalyst have been studied in toluene and isopropyl alcohol by use of a spectrophotometric method. It was shown that the hydrosilylation reaction of functional olefin is complicated by transformation of the catalytic system and secondary processes occurring in the solvent medium, in particular the hydrolysis of $\equiv\text{SiH}$ groups.

Introduction

As known, the synthesis of compounds with Si-C bonds often involves the hydrosilylation reaction consisting of the addition of unsaturated organic compounds to Si-H bonds under the influence of catalysts and elevated temperature [1]. In an early paper A.A. Chuiko et al [2] it was demonstrated that such a reaction on a silica surface is of particular interest for producing chemical modifications with Si-C bonds. The process proceeds according to the general scheme:



where R is a suitable organic radical with various functional groups and can be regarded as a hydrosilylation reaction in which the modified silica matrix containing $\equiv\text{SiH}$ groups acts as a heterogeneous hydrosilylating agent. This kind of reaction where one of the interacting species is fixed on a solid surface was classified as a solid-phase hydrosilylation processes [3]. Though an early attempt to carry out solid-phase hydrosilylation processes were made in 1952 by G.H. Wagner and A.N. Pines [4], the systematic and detailed development of such reactions and their use for chemical modification of silica surfaces became possible in the last few years as a result of efforts which were mounted a group of investigators from San Jose State University, USA [5-48] and the research team from the Institute of Surface Chemistry of the National Academy of Sciences of Ukraine [3, 48-70].

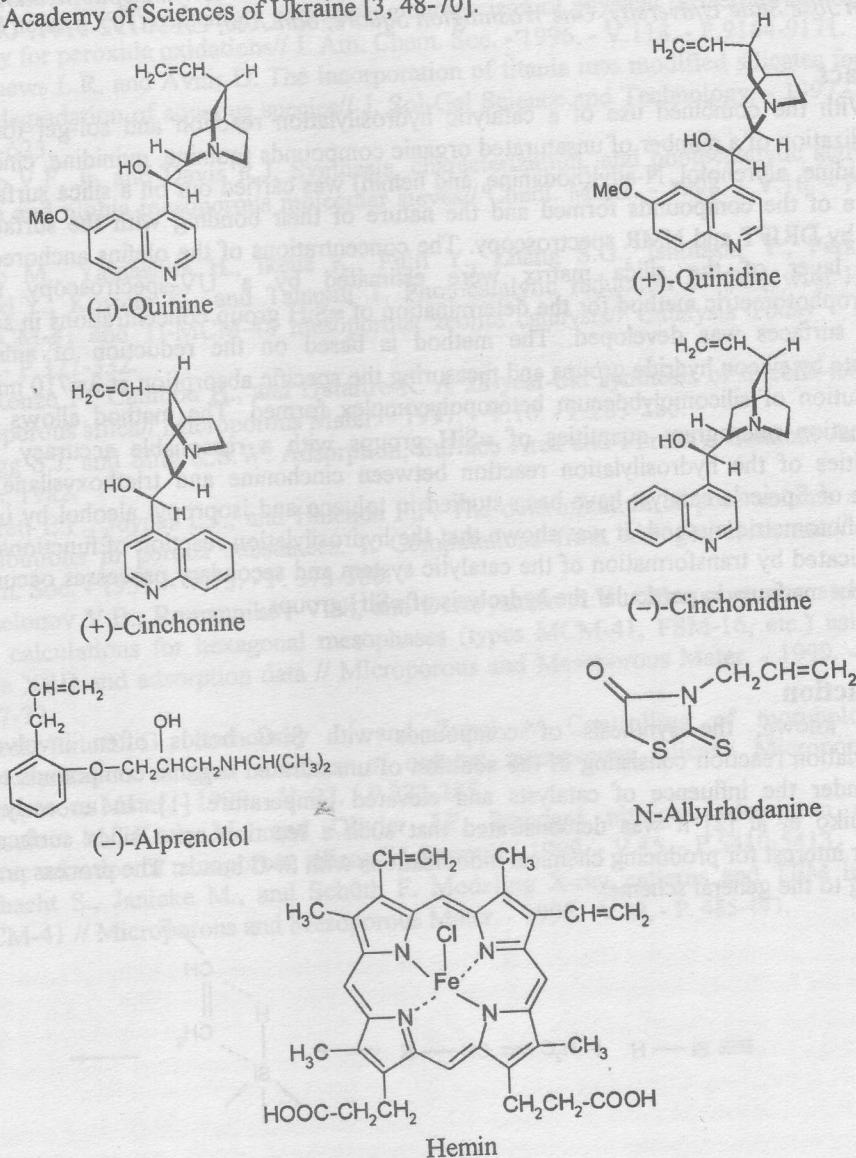


Fig. 1. Structural formulas of functional olefins used for immobilization on the silica surface.

Bonding of optically active compounds on a silica surface is of general interest because such an approach expands the opportunities for the synthesis of chiral stationary phases used for the separation of enantiomers in biological systems and clinical samples. In some cases the hydrosilylation reaction was utilized for such syntheses, for example in the case of quinine [71], menthol [72], calixarene [73] and R(+)-1-(α -naphthyl)ethylamine [28]. The formation of radicals in molecules with double bonds such as a number cinchonic alkaloids (quinine, quinidine, cinchonine, cinchonidine), and in alprenolol, hemin, and N-allylrhodanine (Fig. 1) permits one to use the catalytic hydrosilylation reaction for their immobilization on a silica surface [70]. In this paper the results of systematic research are discussed, including the effect of the component ratios and reaction conditions, kinetics of catalytic hydrosilylation of functional olefins, and the side reactions taking place under the test conditions.

Experimental

Quinine, quinidine, cinchonine, cinchonidine, alprenolol, N-allylrhodanine, hemin, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (all from Aldrich); triethoxysilane (chemically pure, Kremnepolimer), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (analytically pure, Reakhim), ascorbic acid (Kyiv vitamin factory); 2-propanol, toluene, glacial acetic acid, HCl, KOH, CaO (all chemically pure, Reakhim) and 4A molecular sieves were used. Silochrom with a specific surface area of about $100 \text{ m}^2 \text{ g}^{-1}$ was used as the silica support. Toluene and 2-propanol were subjected to additional drying by standard methods before use. Water was doubly distilled in a glass apparatus.

IR spectra were measured with a Fourier-transform IR spectrophotometer by the diffuse reflectance method in the range $4000\text{--}600 \text{ cm}^{-1}$. A GX-270 instrument equipped with a probe for cross polarization/magic angle spinning (CP/MAS) was employed to obtain solid-state ^{13}C -nuclear magnetic resonance spectra. The spectra of the functional olefins, the solutions investigated, and the concentrations of the bonded organic compounds after the dissolution of the weighed portion (10 mg) of modified silica in 5 ml (or in 4 ml) of 1 M potassium hydroxide solution were determined by UV spectroscopy (Specord UV-VIS).

Silicas with attached $\equiv\text{SiH}$ groups (samples I and II) were obtained by reaction of Silochrom with a solution of triethoxysilane in ethanol followed by drying at 70°C . Sample III was prepared by adding Silochrom to an ethanol/0.1 M HCl solution, holding the mixture for 1-2 h at 70°C in a regulated temperature bath, while adding triethoxysilane, and allowing the reaction to process for 2-3 h at the same temperature. Finally the product was washed in isopropanol or ethanol and then dried at 70°C .

The determination of $\equiv\text{SiH}$ group concentration in solution and on modified surfaces was conducted by a colorimetric method developed by the authors which is based on the spectral investigations of the reaction products with ammonium molybdate or yellow silicomolybdic heteropolyacid. For preparation of the 2.5 % ammonium molybdate solution, 5 g ammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ are dissolved in 200 ml of a 5% acetic acid solution. For complete dissolution the mixture was heated on a water bath at 100°C . The reagent can be used for a week. For longer periods of storage, a white precipitate of molybdic acid is usually formed. The standard triethoxysilane solution was prepared by adding 2 ml of $\text{HSi}(\text{OC}_2\text{H}_5)_3$ to 9.8 ml isopropanol. Then 1 ml of this solution was placed into a graduated glass tube and 9 ml of isopropanol was added. The standard solution prepared in this manner has $1.08 \cdot 10^{-5} \text{ mol}$ triethoxysilane in 1 ml of standard.

The solutions for spectra of model reaction products in the visible region is prepared as follows: either 0.2 ml of a water solution of ascorbic acid ($1.4 \cdot 10^{-2} \text{ mol/L}$) or 0.25 ml standard triethoxysilane solution in isopropanol ($1.08 \cdot 10^{-2} \text{ mol/L}$) or 10 mg of modified silica with

$1.4 \cdot 10^{-4}$ mol/g of bonded $\equiv\text{SiH}$ groups are added to 4 ml ammonium molybdate solution. Then 0.8, 0.75 or 1 ml isopropanol alcohol are respectively added. The mixture is stirred, then it is heated on a boiling water bath for 5 minutes. It is next cooled (in the case of silica it is also filtered) and finally the optical densities of the resulting solutions are measured. In the case of the reaction with yellow silicomolybdic heteropolyacid the procedure for the analysis is the same, except that 4 ml of yellow silicomolybdic heteropolyacid is added. Silicomolybdic heteropolyacid was prepared as follows: 0.012 ml of triethoxysilane was added to 79.988 ml of a 2.5 % ammonium molybdate solution (the resulting solution consists of $2.8 \cdot 10^{-6}$ mol of triethoxysilane in 4 ml).

Procedure for the determination of $\equiv\text{SiH}$ group content of compounds in solution. 4 ml of ammonium molybdate solution is introduced into each of two graduated tubes. Then in one tube from 0.01 to 0.5 ml of the test solution is placed (depending on the estimated concentration of $\equiv\text{SiH}$ groups) and the volume is brought up to 5 ml with 2-propanol. The tube with is then closed, stirred and placed in a regulated temperature bath at 80°C for 5-10 minutes. Then a stream of running water cools the tube. If the solution becomes cloudy after cooling, it is filtered. Then the solution is measured spectrophotometrically and the concentration of $\equiv\text{SiH}$ groups is determined from the calibration curve or it is calculated by use of a calibration curve equation. The concentration of $\equiv\text{SiH}$ groups in the analyzed solution was determined by use of the formula $C_{\text{SiH}} (\text{mol/L}) = C_{\text{calib}} \cdot 5$, where C_{calib} is the concentration of $\equiv\text{SiH}$ groups in the final mixture.

Procedure for the determination of $\equiv\text{SiH}$ group content of compounds bonded to the surface of silica. From 1 to 200 mg of a modified silica is introduced into a graduated tube (depending on the estimated concentration of $\equiv\text{SiH}$ groups), then 4 ml of ammonium molybdate solution and 1 ml isopropanol are added. The tube is closed, stirred and placed in a regulated temperature bath at 80°C for 5-10 minutes. Then the mixture is cooled by a stream of running water, filtered and the optical density of the blue solution is measured at 710 nm. A blank solution is prepared without adding silica. The concentration of $\equiv\text{SiH}$ groups in the final mixture is determined by a calibration curve or is calculated using the equation of calibration curve. The concentration of $\equiv\text{SiH}$ groups in analyzed weighed portion of silica is determined by use of the formula $C_{\text{SiH}} (\text{mol/L}) = C_{\text{calib}} \cdot 5 \cdot 10^{-3}/m$, where C_{calib} is the concentration of $\equiv\text{SiH}$ groups in the final mixture, m is a weight of silica in grams.

Procedure for kinetic measurements. For the preparation of all solutions identical concentrations of triethoxysilane ($3 \cdot 10^{-4}$ mol) and cinchonine ($3 \cdot 10^{-4}$ mol) were used. Depending on the experiment, the Pt-catalyst is added in an amount which in 1000 times ($3 \cdot 10^{-7}$ mol) or in 100 times ($3 \cdot 10^{-6}$ mol) is less than $\text{HSi}(\text{OC}_2\text{H}_5)_3$ concentration, β -cyclodextrin is taken in an amount $2.2 \cdot 10^{-6}$ mol. The 0.04 ml of the concentrated acetic acid is added for dissolution of cinchonine. Volume of solution is brought by solvent up to 10 ml. The triethoxysilane is added after 30 minutes after intermixing of olefin, Pt-catalyst and solvent. The solutions are placed in a thermostat at 80°C and after a fixed interval of time the tests of reaction mixtures are selected and are analyzed as it was described above.

Results and discussion

Numerous catalysts for use in hydrosilylation reactions [74-76], such as various compounds and complexes of platinum and transition metals (Pt, Rh, Pd, Ir, Os, Ni, Co, Cr, Ti, Fe), are known. The most effective and the most frequently used in practice are all Pt-containing catalysts (in particular, the Speier, Karstedt and Lamoreaux catalysts). It should be emphasized that the activity of Pt catalysts is increased in the presence of a number of

compounds (oxygen, aldehydes, unsaturated ketones, cyclodextrins, acetylenic ethers and alcohols) which can be regarded as co-catalysts of the hydrosilylation reaction.

In the first stage of this work, an attempt was made to immobilize the chosen active compounds by bonding to $\equiv\text{SiH}$ groups which were previously fixed on the silica surface. For this purpose, silica with $7.125 \cdot 10^{-4}$ mol/g $\equiv\text{SiH}$ groups was used (sample II which was obtained by the above-described method). The coverage of $\equiv\text{SiH}$ groups on silica was determined by the spectrophotometric method. Solid-phase catalytic hydrosilylation of cinchonic alkaloids was conducted as follows: 100 mg ($3.4 \cdot 10^{-4}$ mol) cinchonine, (or 110 mg ($3.4 \cdot 10^{-4}$ mol) quinine, 100 mg ($3.4 \cdot 10^{-4}$ mol) cinchonidine, 110 mg ($3.4 \cdot 10^{-4}$ mol) quinidine), 9.66 ml freshly-distilled toluene, and 0.04 ml freshly-distilled acetic acid were added into a glass reactor. The solution was heated on a water bath at 80°C in order to completely dissolve the alkaloid. Then 0.3 ml of Speier's catalyst (0.01 M solution $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in 2-propanol) was added to the reactor, which was controlled at 80°C for 1 h. Thereafter, 1 g Silochrom was added into the reaction solution. The contents were well stirred and were held at 80°C for 10 h. Solid-phase hydrosilylation reactions for other alkaloids were conducted in a similar manner. The modified silicas were dried at 80°C for 2-3 h and at 100°C for 2 h. Then the dried modified silicas were repeatedly washed by a 0.5 % solution of an acetic acid in 2-propanol, each time measuring the amount of alkaloids by spectra in the UV region. The washing of the silicas was conducted as long as the characteristic peaks of alkaloids appeared in the spectra of the rinsing liquid (usually, it was necessary for 100 to 150 ml of a solution of acetic acid in 2-propanol for washing of 1 g of modified silica). The products were dried at 80°C for 2 h and at 100°C for 2 h. The concentrations of bonded organic compounds were determined by UV spectroscopy and a calibration curve which was constructed from standard solutions of the alkaloids in 2-propanol. To do this, a weighed portion (10 mg) of modified silica was transferred into solution by dissolving in 4 ml of 1 M potassium hydroxide. As the spectra of alkaloids in solutions of 2-propanol and alkali are identical, a calibration curve for the concentration of bonded functional alkenes on 1 g of the silica was defined. The results obtained are shown in the Table 1.

Table 1

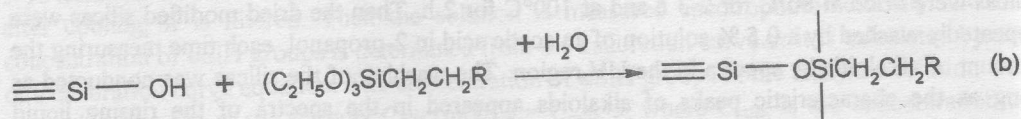
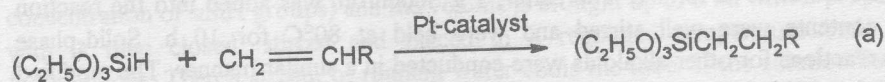
The immobilization of chiral selectors on a silica surface with bonded $\equiv\text{SiH}$ groups.

Bound olefin	Total amount of olefin used (mmol)	Amount of immobilized olefin on the silica surface (mmol/g)
cinchonine	0.34	0.0210
quinine	0.34	0.0344
cinchonidine	0.34	0.0324
quinidine	0.34	0.0229

Thus, on the basis of the data obtained it is observed that the solid-phase hydrosilylation reaction involving surface $\equiv\text{SiH}$ groups and functional olefins proceeds with low yields (up to 10 %) in relation to the surface sites. The problems encountered can be explained by invoking the mechanism proposed by Lewis [77, 78] for the hydrosilylation reaction. It is presumed that the hydrosilylation reaction is catalyzed by Pt-colloid (where Pt is in the zero valence state)

and the attack of the hydrosilane precedes the attack of the olefin. The important influence of oxygen as co-catalyst is taken into account; because a Pt-colloid is only formed in the presence of oxygen. From the proposed mechanism, one of the difficulties for carrying out of the solid-phase catalytic hydrosilylation reaction, as contrasted with similar processes in solution, can be related to the restricted migration of the Pt-colloid formed along the silica surface.

Hence, it is possible to assume that difficulties of immobilization of functional olefins by means of solid-phase catalytic hydrosilylation reaction may be solved if the hydrosilylation of the hydrosilane and olefin is performed in solution with subsequent formation of the reaction product on the surface layer. Similar syntheses have been reported [71, 73]. For immobilization of the active compounds on the silica surface we have combined into one process the hydrosilylation reaction (a) and the common sol-gel transformations (b) that results in a process described by the following general schemes:



The main experimental procedures used according to these reactions are described below using the example of cinchonine bonding. 2-propanol extra dried over 4A molecular sieves was used. 5 mmol (for 10 g silica) cinchonine, 20 ml isopropanol, 0.7 ml acetic acid and 0.05 ml Speier's catalyst (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol) were added to a glass reactor. The reactor was controlled at 80°C for 30 min. The reaction mixture was periodically stirred. Thereafter, 5 mmol triethoxysilane was added into the reactor, and the mixture was held at 80°C for 6 h. It should be noted that the amount of Speier's catalyst in the reaction mixture is 100 times less on a molar basis than the amount of the hydride-containing component triethoxysilane. Then, 15 ml of isopropanol and 10 g Silochrom were added into the reactor and the mixture was kept at the same temperature for 1 h. Thereafter, 1 ml (0.055 mol) water was added and reaction mixture was placed in a desiccator for 3 h at 100°C. The dried modified silica was repeatedly washed with isopropanol and the product was again dried for 6 h at 100°C.

Modified silicas, containing other functional olefins (quinine, quinidine, cinchonidine, alprenolol, N-allylrhodanine, and hemin) in the bonded layer, were synthesized in a similar manner. The appropriate amounts of reagent used for the syntheses and the final amounts of bonded organic moieties obtained are listed in the Table 2.

The synthesized samples, containing immobilized active compounds, were characterized by IR spectroscopy utilizing diffuse reflectance (DRIFT) and high-resolution solid state ^{13}C NMR. The concentrations of bonded active compounds were determined by means of UV spectroscopy, because the absorption spectra of the pure functional olefins and the absorption spectra of the same substances immobilized on a silica surface and then transferred into solution by treatment by alkali are the same. This allows one to use of the given spectral region for quantitative characterization of the immobilized substances. IR spectra of modified silicas with anchored cinchonine and N-allylrhodanine are shown in Fig. 2.

Table 2

Component ratios in the syntheses of modified silicas and the final amounts of functional groups bonded to the matrix surface.

Bound olefin	Olefin (mmol)	Solvent for olefin	Tri-ethoxy-silane (mmol)	2-pro-panol (ml)	Silica (g)	Water (ml)	Bonded groups (mmol/g)
Cinchonine	5	20 ml <i>i</i> -C ₃ H ₇ OH + 0.7 ml CH ₃ COOH	5	15	10	1	0.08
Quinine	5	10 ml <i>i</i> -C ₃ H ₇ OH + 0.5 ml CH ₃ COOH	5	25	10	1	0.13
Cinchonidine	5	10 ml <i>i</i> -C ₃ H ₇ OH + 0.7 ml CH ₃ COOH	5	25	10	1	0.13
Quinidine	2	10 ml <i>i</i> -C ₃ H ₇ OH + 0.35 ml CH ₃ COOH	2.5	8	5	0.5	0.04
N-Allylrhodanine	5	10 ml <i>i</i> -C ₃ H ₇ OH + 0.5 ml CH ₃ COOH	5	25	10	1	0.015
Alprenolol	2	10 ml <i>i</i> -C ₃ H ₇ OH + 0.7 ml CH ₃ COOH	2.5	8	5	0.5	0.007
Hemin	1	4.5 ml HCON(CH ₃) ₂ + 10 ml <i>i</i> -C ₃ H ₇ OH + 0.1 ml CH ₃ COOH	2.5	8	5	0.5	0.01

It is seen from the IR spectra of the modified silicas that the absorption of Si-H bonds is completely absent (disappearance of the band at 2250 cm⁻¹ relating to the stretching vibrations

of the $\equiv\text{SiH}$ groups). The sole exception is the spectrum of the silica sample containing immobilized N-allylrhodanine. The lower degree of $\equiv\text{SiH}$ group substitution in the latter case is most probably determined by inhibition of the catalyst as a result of platinum chelation with N-allylrhodanine.

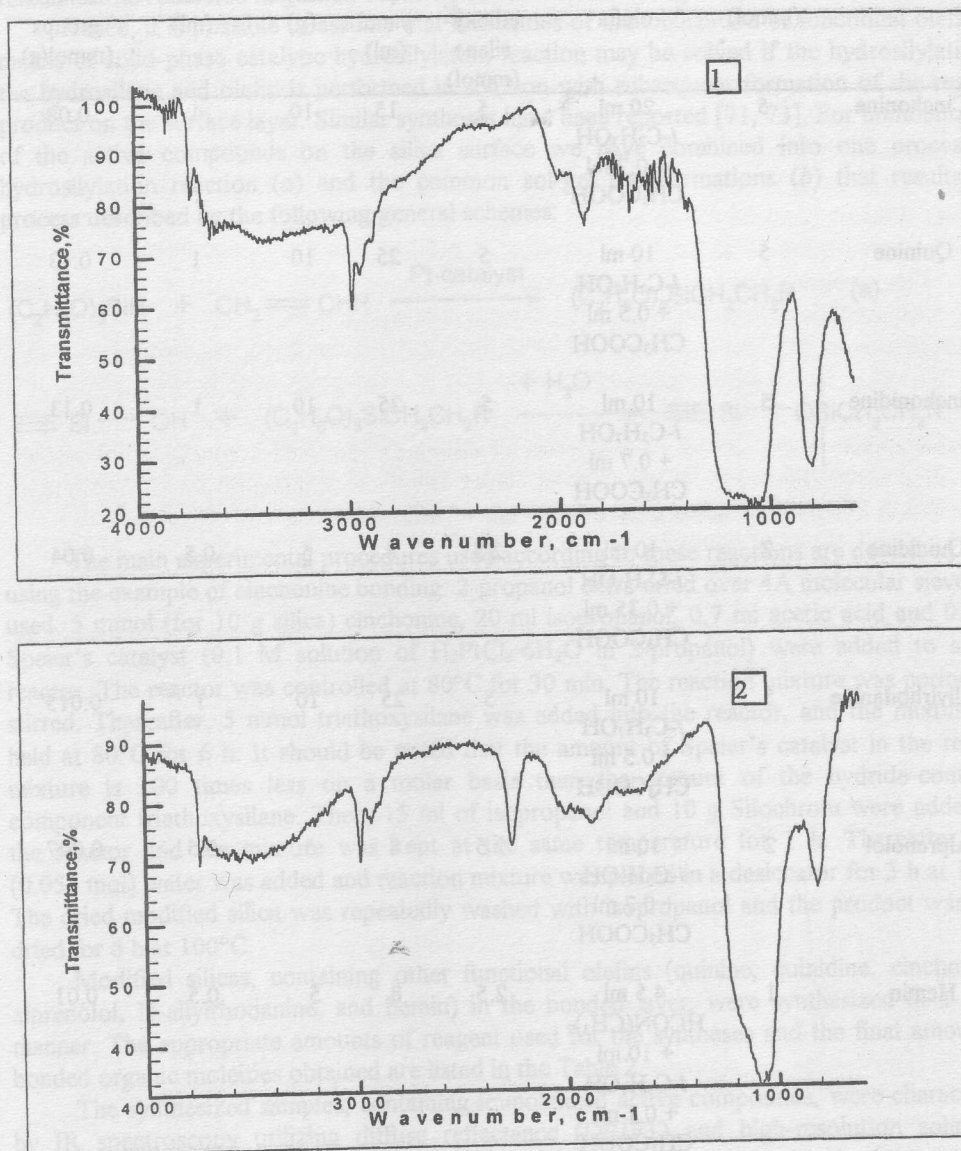


Fig. 2. DRIFT spectra of cinchonine (1) and N-allylrhodanine (2) bonded to a silica surface.

The ^{13}C NMR spectrum for the modified silica containing bonded quinine (Fig. 3) shows the characteristic peaks for the carbon atoms bearing different substituents in the quinine

molecule, and a peak at 20 ppm corresponding to the carbon atom directly bonded to the silicon atom and to the adjacent carbon atom.

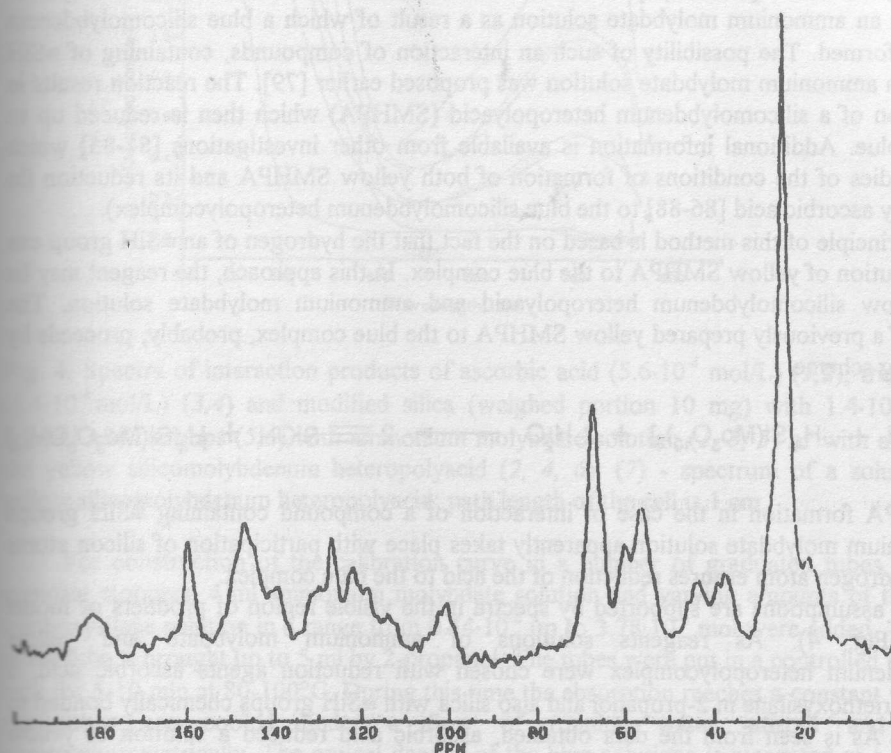


Fig. 3. ^{13}C NMR CP-MAS spectrum of silica with immobilized quinine.

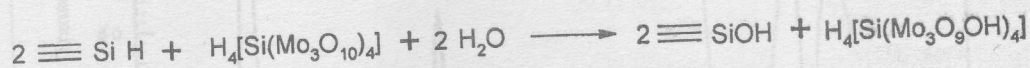
This spectral information clearly demonstrates that immobilization of functional olefins can be achieved by the combined use of hydrosilylation reactions and sol-gel technology and that the concentration of functional groups bonded to the surface matrix in this case is higher than the amount of bonded by solid-phase catalytic hydrosilylation.

Studies of the kinetics of the catalytic hydrosilylation reaction of functional olefins and possible secondary processes were conducted to determine the reasons hindering a greater degree of completion of the reaction, in order to find conditions which will improve the yield. It is particularly important to study such processes in order to have available a sensitive, reproducible and reliable method for the quantitative determination of $\equiv\text{SiH}$ groups both in individual compounds and in bonded groups on the surface of solids. It has long been known that volumetric methods [8, 79, 80], based on hydrolysis of $\equiv\text{SiH}$ groups in an alkaline medium is most frequently used for these purposes. In such a process gaseous hydrogen is evolved. The gas is collected above mercury in a graduated tube (as in Cerevitinov's apparatus [79]) or the amount of liberated hydrogen is determined by gas chromatography [8]. Often, however, the determination of $\equiv\text{SiH}$ groups by this method is difficult for a large number of samples because it is labor intensive and due to the difficulty of estimating the partial pressure of solvents, in particular when determining a small amount of $\equiv\text{SiH}$ groups.

For this reason, the application of colorimetric methods, based on the use of the reduction properties of silicon hydride species, appear more practical. The reasonably fast and

convenient spectrophotometric method for the determination of rather small amounts of $\equiv\text{SiH}$ groups in compounds which are in solution or fixed on a surface of solids (in particular, silica) was investigated in the present paper. The method is based on a reaction of silicon hydride groups with an ammonium molybdate solution as a result of which a blue silicomolybdenum complex is formed. The possibility of such an interaction of compounds, containing of $\equiv\text{SiH}$ groups, with ammonium molybdate solution was proposed earlier [79]. The reaction results in the formation of a silicomolybdenum heteropolyacid (SMHPA) which then is reduced up to molybdate blue. Additional information is available from other investigations [81-85] which describe studies of the conditions of formation of both yellow SMHPA and its reduction (in particular, by ascorbic acid [86-88] to the blue silicomolybdenum heteropolycomplex).

The principle of this method is based on the fact that the hydrogen of an $\equiv\text{SiH}$ group can reduce a solution of yellow SMHPA to the blue complex. In this approach, the reagent may be both a yellow silicomolybdenum heteropolyacid and ammonium molybdate solution. The reduction of a previously prepared yellow SMHPA to the blue complex, probably, proceeds by the following scheme:



SMHPA formation in the case of interaction of a compound containing $\equiv\text{SiH}$ groups with ammonium molybdate solution apparently takes place with participation of silicon atoms while the hydrogen atom ensures reduction of the acid to the blue complex.

These assumptions are supported by spectra in the visible region of products of model reactions (Fig. 4). As reagents solutions of ammonium molybdate and yellow silicomolybdenum heteropolycomplex were chosen with reduction agents ascorbic acid, a solution of triethoxysilane in 2-propanol and also silica with $\equiv\text{SiH}$ groups chemically bonded to the surface. As is seen from the data obtained, ascorbic acid reduced a solution of yellow SMHPA (Fig. 4, curve 2). As expected, in the absence of a silicon source ascorbic acid does not reduce the ammonium molybdate solution (Fig. 4, curve 1). In contrast, the triethoxysilane solution, being not only a reduction agent, but also silicon source, reacts with both solutions (curves 3, 4). The maxima of the absorption bands of the reaction products (Fig. 4, curves 2-4) which are in the range of 700-720 nm belong to the same compound - blue silicomolybdenum heteropolycomplex. Absorption in this region is also observed in the case of modified silica as a reducing agent with $\equiv\text{SiH}$ groups chemically bonded on its surface. The case of triethoxysilane, the formation of blue reaction product was detected not only in the case of interaction of the silica, containing silicon hydride species, with yellow SMHPA (Fig. 4, curve 6), but also in the case of contact of the modified silica surface with an ammonium molybdate solution (Fig. 4, curve 5). It was observed that absorption by silica of the reaction product does not happen, and the solid matrix remains practically colorless, but the solutions in the immediate vicinity of the silica surface are dyed blue. It is quite probable that the amount of soluble silica forms in near the surface layer is enough for SMHPA formation, and the reduction to the blue heteropolycomplex is carried out by surface silicon hydride species.

It was determined that the formation of the product of interaction between silicon hydride-containing compounds and ammonium molybdate solution is complete in 2.5 h at room temperature. The reaction is complete after 5-10 minutes of heating the solutions on a boiling water bath. Optical densities of the solutions studied at 710 nm are unchanged over 2-5 hours. The experimental data obtained validate the spectrophotometric method for determination of $\equiv\text{SiH}$ group concentration in compounds that are in a solution or bonded to a solid surface.

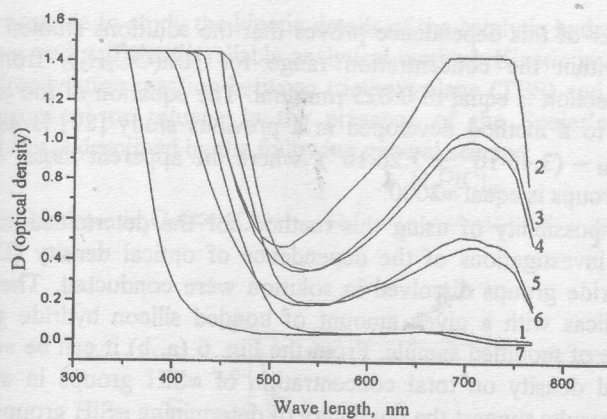


Fig. 4. Spectra of interaction products of ascorbic acid ($5.6 \cdot 10^{-4}$ mol/L) (1,2), triethoxysilane ($5.4 \cdot 10^{-4}$ mol/L) (3,4) and modified silica (weighed portion 10 mg) with $1.4 \cdot 10^{-4}$ mol/g of bonded $\equiv\text{SiH}$ groups (5,6) with ammonium molybdate solution (1, 3, 5) or with a solution of the yellow silicomolybdenum heteropolyacid (2, 4, 6); (7) - spectrum of a solution of the yellow silicomolybdenum heteropolyacid; path length of the cell is 1 cm.

For construction of the calibration curve in a number of graduated tubes, fitted with compact stoppers, 4 ml ammonium molybdate solution and varying amounts of the standard triethoxysilane solution in a range from $0.54 \cdot 10^{-6}$ up to $3.78 \cdot 10^{-6}$ mol were added. The volume in the tube is brought up to 5 ml by 2-propanol. The tubes were put in a controlled temperature bath for 5-10 min at $80-100^\circ\text{C}$. During this time the absorption reaches a constant value. Then the tubes are cooled under a flow of running water, stirred and measured spectrophotometrically. The optical density of the blue solutions is measured at a wavelength of 710 nm in cell with a thickness of 1 cm. A comparison solution is used as a control test consisting of 1 ml 2-propanol added to 4 ml of ammonium molybdate solution. The measured values of optical density (D) and the appropriate desired concentration of triethoxysilane in the standard solutions ($C_{\text{Si-H}}$) are used to construct a calibration curve (Fig. 5).

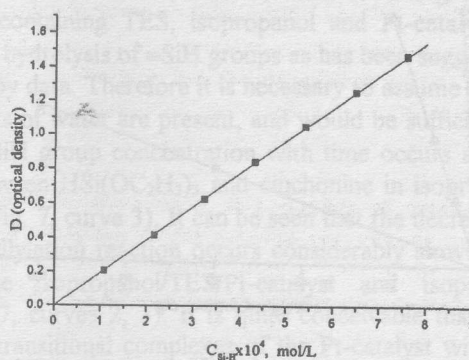


Fig. 5. Dependence of an optical density (D) of ammonium molybdate solution at $\lambda=710$ nm in cell with a thickness of 1 cm vs. the concentration of added triethoxysilane ($C_{\text{Si-H}}$).

The rectilinear character of this dependence proves that the solutions studied obey the Lambert-Buger-Beer law within the concentration range for $\text{HSi}(\text{OC}_2\text{H}_5)_3$ from 0.1 to 0.8 mmol/L. The limit of detection is equal to 0.025 $\mu\text{mol/ml}$. The equation of the calibration curve, calculated according to a method developed in a previous study [89] is as follows: $D = (1946.188 \pm 15.014) \cdot C_{\text{Si-H}} - (3.45 \cdot 10^{-3} \pm 7.26 \cdot 10^{-3})$, where the apparent molar extinction coefficient (E) of the $\equiv\text{SiH}$ groups is equal ≈ 2000 .

In order to study the possibility of using this method for the determination of $\equiv\text{SiH}$ groups on a silica surface, investigations of the dependence of optical density (D) on the concentration of silicon hydride groups dissolved in solution were conducted. These results were obtained by use of silicas with a given amount of bonded silicon hydride groups or varying amounts of one type of modified sample. From the Fig. 6 (a, b) it can be seen that a linear dependence of optical density on total concentration of $\equiv\text{SiH}$ groups in solution is observed in both cases. The results suggest the possibility of determining $\equiv\text{SiH}$ groups not only in compounds which are in a solution, but also those that are part of compounds bonded to a silica surface.

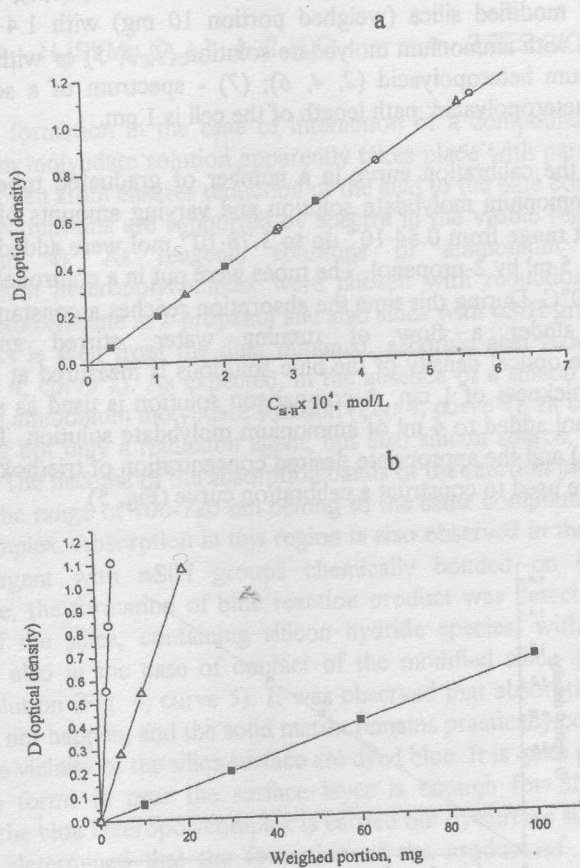


Fig. 6 (a, b). Results of determination of $\equiv\text{SiH}$ groups in various samples of modified silica [■ - sample I with the contents of fixed $\equiv\text{SiH}$ groups $1.75 \cdot 10^{-5}$ mol/g (weighed portions - 10, 30, 60, and 100 mg), ○ - sample II with the contents of fixed $\equiv\text{SiH}$ groups $7.125 \cdot 10^{-4}$ mol/g (weighed portions - 2, 3, and 4 mg), △ - sample III with the contents of fixed $\equiv\text{SiH}$ groups $1.4 \cdot 10^{-4}$ mol/g (weighed portions - 5, 10, and 20 mg)].

It is possible to study the kinetic details of the catalytic hydrosilylation reaction by using a convenient and sufficiently reliable analytical method. Kinetic investigations were conducted on the hydrosilylation reaction between triethoxysilane (TES) and cinchonine in a medium of either isopropanol or toluene in the presence of the Speier's catalyst. The process of hydrosilylation is described by the following general scheme:

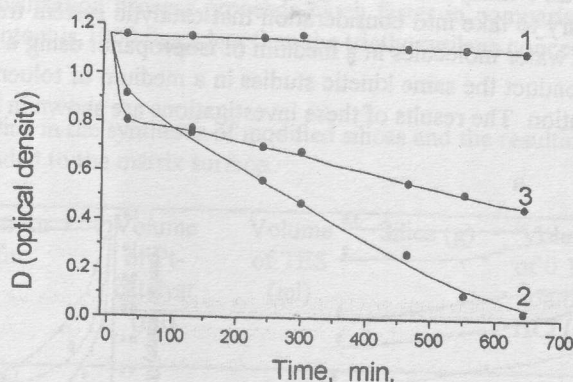
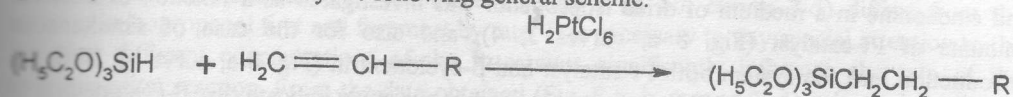


Fig. 7. Kinetic curves of the decrease of $\equiv\text{SiH}$ group concentration in chemically pure isopropanol: (1) - $\text{HSi}(\text{OC}_2\text{H}_5)_3$ solution ($3 \cdot 10^{-4}$ mol) in isopropanol; (2) - solution of $\text{HSi}(\text{OC}_2\text{H}_5)_3$ ($3 \cdot 10^{-4}$ mol) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-7}$ mol) in isopropanol; (3) - solution of $\text{HSi}(\text{OC}_2\text{H}_5)_3$ ($3 \cdot 10^{-4}$ mol), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-7}$ mol) and cinchonine ($3 \cdot 10^{-4}$ mol) in isopropanol.

The kinetic curves for the decrease of the concentration $\equiv\text{SiH}$ groups in an isopropanol medium (chemically pure) as a function of time are shown in Fig. 7. For TES in isopropanol solution no changes occur as evidenced by constant values of the optical density (D) as a function of time (Fig. 7, curve 1). In contrast, a fast decrease of $\equiv\text{SiH}$ group content takes place with time in the solution containing TES, isopropanol and Pt-catalyst (Fig. 7, curve 2). Pt-catalysts can catalyze the hydrolysis of $\equiv\text{SiH}$ groups as has been suggested [49] on evidence derived from IR-spectroscopy data. Therefore it is necessary to assume that in chemically pure isopropanol residual amounts of water are present, and would be sufficient to hydrolyze $\equiv\text{SiH}$ groups. The decrease of $\equiv\text{SiH}$ group concentration with time occurs also in the case of the hydrosilylation reaction between $\text{HSi}(\text{OC}_2\text{H}_5)_3$ and cinchonine in isopropanol solution in the presence Speier's catalyst (Fig. 7, curve 3). It can be seen that the decrease of the $\equiv\text{SiH}$ group concentration in this hydrosilylation reaction occurs considerably slower as compared to the loss $\equiv\text{SiH}$ groups in the isopropanol/TES/Pt-catalyst and isopropanol/cinchonine/Pt-catalyst/TES systems (Fig. 7, curves 2, 3). It is quite conceivable that in the course of the hydrosilylation process the transitional complexes of the Pt-catalyst with the olefin and TES are formed, resulting in a slower process of hydrolysis.

To prevent hydrolysis, the study of the kinetics of the decrease of the $\equiv\text{SiH}$ group concentration was done in a medium of carefully dried isopropanol (dried above CaO and 4A molecular sieves and then distilled). The results obtained are shown in Fig. 8a. For the system

TES/isopropanol (Fig. 8 a, curve 1) the results coincide with data obtained earlier (Fig. 7, curve 1). The hydrolysis process of $\equiv\text{SiH}$ groups in the system isopropanol/TES/Pt-catalyst can be practically eliminated by the use of dried isopropanol (Fig. 8 a, curve 2). The decrease of the $\equiv\text{SiH}$ group content with time in the case of the hydrosilylation reaction between TES and cinchonine in a medium of dried isopropanol was investigated as a function of different amounts of Pt-catalyst (Fig. 8 a, curves 3, 4), and also for the case of simultaneous introduction into the system both Pt-catalyst and β -cyclodextrin (Fig. 8 a, curve 5). Both the data of previous work [90] and the results obtained in our study indicate that β -cyclodextrin in combination with a Pt-catalyst accelerates hydrosilylation process.

It is necessary to take into consideration that catalytic system transformations can result in the presence of water molecules in a medium of isopropanol using a Pt-catalyst. Therefore it was decided to conduct the same kinetic studies in a medium of toluene which previously was purified by distillation. The results of these investigations are shown in Fig. 8b.

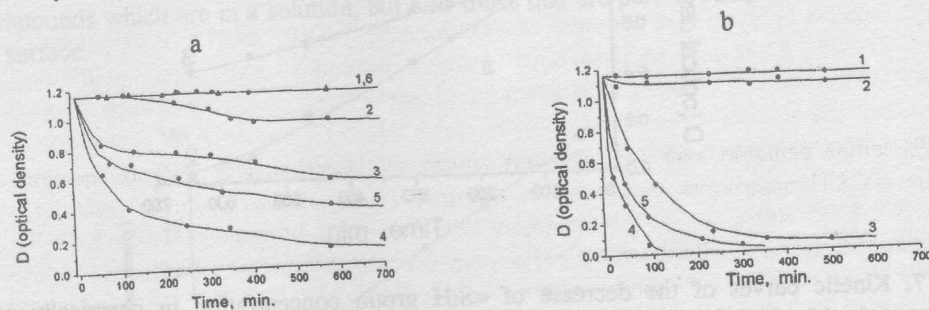


Fig. 8. Kinetic curves for the decrease in $\equiv\text{SiH}$ group concentration in the medium of dried isopropanol (a) and toluene (b): 1 - solution TES ($3 \cdot 10^{-4}$ mol); 2 - solution TES ($3 \cdot 10^{-4}$ mol) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-7}$ mol); 3 - solution TES ($3 \cdot 10^{-4}$ mol), cinchonine ($3 \cdot 10^{-4}$ mol) and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-7}$ mol); 4 - solution TES ($3 \cdot 10^{-4}$ mol), cinchonine ($3 \cdot 10^{-4}$ mol), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-6}$ mol); 5 - solution TES ($3 \cdot 10^{-4}$ mol), cinchonine ($3 \cdot 10^{-4}$ mol), $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ($3 \cdot 10^{-7}$ mol) and β -cyclodextrin ($2,2 \cdot 10^{-6}$ mol); 6 - solution TES ($3 \cdot 10^{-4}$ mol) and β -cyclodextrin ($2,2 \cdot 10^{-6}$ mol) in isopropanol.

From the above results it appears that the changes in the $\equiv\text{SiH}$ group concentration which were observed with time can not be described by any simple kinetic equation because in parallel with the hydrosilylation process various secondary processes and transformations of the catalytic system take place. The $\equiv\text{SiH}$ group hydrolysis is a major secondary process. In another report [91] it was pointed out that in the case of a hydrosilylation reaction in an isopropanol medium another side reaction (alkoxylation) occurs in which triethoxyisopropoxysilane is formed. Also it is necessary to take into account that in the case of a hydrosilylation reaction in the presence $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ additional transformations of the catalytic system occur which may be connected to the reduction of Pt (IV) to Pt (II) and then on to Pt (0) (deactivation of the Pt-catalyst happens based on evidence derived from other data [92]).

It should also be noted that during the first 80-100 minutes of the hydrosilylation reaction in isopropanol medium (Fig. 8a, curves 3-5) a significant decrease of the $\equiv\text{SiH}$ group concentration (initial portion of the kinetic curve of $\equiv\text{SiH}$ group loss) occurs. The greatest rate

of the reaction corresponds to this portion of the curve. Thereafter the reaction rate is sharply decreased and is stabilized. In an earlier work [91] it was stated that the reason for an increased rate of reaction in the first stage is due to the process of reduction $\text{Pt(IV)} \rightarrow \text{Pt(II)} \rightarrow \text{Pt(0)}$ where an unstable intermediate complex of platinum [Pt(III) and Pt(I)] have increased reactivity. The hydrosilylation in a toluene medium (Fig. 8b, curves 3-5) differs from the reaction in isopropanol first and foremost by rate. It is necessary to pay special attention to the fact that different concentrations of the Pt-catalyst significantly influence the rate of the hydrosilylation reaction. From the data obtained (Fig. 8 a, b, curves 3, 4) it is obvious that in the case of the addition of Pt-catalyst in an amount in 100 times smaller than TES concentration, the hydrosilylation process proceeds much faster in comparison to the system where the Pt-catalyst content is 1000 times less than the triethoxysilane concentration.

Table 3

Optimum component ratios in the syntheses of modified silicas and the resulting concentrations of functional groups bonded to the matrix surface.

N	Weight of cinchonine (mg)	Solvent for olefin	Volume of Pt-catalyst (ml)	Volume of TES (ml)	Silica (g)	Volume of 0,1 M solution HCl (ml)	Amount of bonded groups (mmol/g)
1	100	9.74 ml toluene + 0.04 ml CH_3COOH	0	0.22	1	1	0.0012
2	100	9.71 ml toluene + 0.04 ml CH_3COOH	0.03	0.22	1	1	0.0128
3	100	9.44 ml toluene + 0.04 ml CH_3COOH	0.3	0.22	1	1	0.0676
4	100	6.74 ml toluene + 0.04 ml CH_3COOH	3	0.22	1	1	0.0340
5	100	9.71 ml <i>i</i> - $\text{C}_3\text{H}_7\text{OH}$ + 0.04 ml CH_3COOH	0.03	0.22	1	1	0.0200
6	100	9.44 ml <i>i</i> - $\text{C}_3\text{H}_7\text{OH}$ + 0.04 ml CH_3COOH	0.3	0.22	1	1	0.0404

With the combined use of the catalytic hydrosilylation and sol-gel technology studies in order to determine the conditions of the synthesis that provide maximum coverage of the functional olefin on the surface of silica were carried out. A number of syntheses utilizing catalytic hydrosilylation and sol-gel transformation were used to bond cinchonine to the surface of silica, and in so doing the concentration of Pt-catalyst and the nature of a solvent were varied. The syntheses were performed simultaneously and concentrations of the cinchonine (0.34 mmol) and TES (1.2 mmol) were kept constant (it should be noted that the TES concentration was four times greater than that of cinchonine). A 0.01 M solution of $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol (Speier's catalyst) was used. The toluene and acetic acid were previously distilled. 2-Propanol was dried above calcium oxide and 4A molecular sieves and then was distilled. The syntheses were executed as follows: the cinchonine was dissolved in toluene (or in 2-propanol) along with acetic acid, then the appropriate amount of Speier's catalyst was added and the solution was placed in a regulated temperature bath at 80°C for 2 h. Then the TES was added. The reaction solution was stirred well. The reaction solution was again placed in the controlled temperature bath at 80°C for 10 h. After that, 1 g Silochrom and 1 ml 0.1 M of solution HCl were added into the solution and the mixture was held at 80°C for 2 h with periodic stirring. The modified silicas were dried at 70-80°C for 2 h and at 100°C for 2 h. Then the dried modified silicas were repeatedly washed by a 0.5 % solution of acetic acid in 2-propanol. Washing was conducted until the characteristic peaks of cinchonine disappeared from the spectra of the rinsing liquid. The clean modified silicas were dried at 80°C for 2 h and at 100°C for 2 h. 10 mg of the modified silica was dissolved in 4 ml 1 M solution KOH for the determination of the amount of bonded cinchonine and the spectrum of the alkaline solution in the UV region was taken. The concentrations of bonded groups in mol/L were defined from the calibration curve for standard solutions of cinchonine in 2-propanol and the concentrations of bonded cinchonine groups in mmol/g were estimated by making the necessary calculations. The results obtained are shown in the Table 3.

From these studies it can be seen that the greatest amount of the cinchonine bonded to the silica surface occurred under the conditions of the synthesis listed in number 3 (Table 3). In this case toluene was used as a solvent, and the concentration of the Pt-catalyst is in 100 times less than the concentration of the cinchonine.

Table 4
Component ratios in the syntheses of modified silicas, and the final concentrations of functional groups bonded to the matrix surface.

Bound olefin	Amount of olefin [mmol (mg)]		Solvent for olefin	Amount of bonded groups (mmol/g)
Quinine	0.34	(110)	9.43 ml toluene + 0.05 ml CH_3COOH	0.093
Cinchonidine	0.34	(100)	9.43 ml toluene + 0.05 ml CH_3COOH	0.112
Quinidine	0.34	(110)	9.43 ml toluene + 0.05 ml CH_3COOH	0.096
N-Allylrhodanine	0.34	(59)	9.48 ml toluene	0.034
Alprenolol	0.34	(97)	9.44 ml toluene + 0.04 ml CH_3COOH	0.063
Hemin	0.17	(110)	0.14 ml $HCON(CH_3)_2$ + 9.34 ml toluene	0.028

Using these conditions for the greatest yield of bonded cinchonine (Table 3, synthesis 3; the solvent is toluene and the concentration of the catalyst in 100 times less than the concentration of the olefin), the immobilization of other functional olefins was undertaken. The amount of TES (1.2 mmol), the volume of Pt-catalyst (0.3 ml), the weight of the silica (1 g) and the volume of the 0.1 M HCl solution (1 ml) were identical for all syntheses. The results obtained are shown in Table 4. The sequence of operations for all syntheses was the same as described for cinchonine. In the case of hemin bonding the washing of the modified silica involved N,N-dimethylformamide and followed by 2-propanol.

Conclusions

The bonding of functional olefins to an $\equiv\text{SiH}$ group on a silica surface is accompanied by a number of difficulties which may be avoided partially if the process is conducted under the catalytic hydrosilylation/sol-gel technology protocol. By use of this approach the amount of bonded functional groups can be increased some times. A spectrophotometric method for the determination of $\equiv\text{SiH}$ groups in solution and on the surface of silica was described. This method was applied to kinetic studies of the hydrosilylation reaction. It is necessary to take into account the possible secondary processes that take place during a catalytic hydrosilylation reaction. In particular, it is necessary to take into account such parameters as the type and amount of catalyst, experimental conditions and the solvent. On the basis of the conducted studies the optimum conditions of synthesis (amount of the catalyst, reagent ratios, the most appropriate solvent) were determined. The method reported here can be used to produce modified silicas with high amounts of the bonded functional groups that it is especially important for many practical applications.

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