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pH-SENSITIVE MATERIALS BASED ON SILICA WITH CHEMICALLY IMMOBILIZED METHYL RED: SYNTHESIS AND PROTOLYTIC PROPERTIES

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The purpose of this work is to study the possibility of creating hydrolytically and chemically stable pH-sensitive materials using silica as a carrier and an acid-base indicator that changes color when the pH of medium is varied. Synthesis of pH-sensitive materials was carried out by covalent binding of methyl red dye with aminopropylsilica in the presence of 1,1'-carbonyldiimidazole as a coupling agent. The porous structure, the chemical composition of the surface, and the protolytic properties of the synthesized silica materials were characterized by low-temperature adsorption-desorption of nitrogen, quantitative chemical analysis, thermogravimetry, diffuse reflectance electron spectroscopy, pH-metry. It was proved that chemical immobilization of methyl red on the silica surface does not have a significant effect on the porous structure of initial silica: the isotherms of nitrogen adsorption-desorption and pore size distribution curves confirm retention of wide pore size distribution after chemical modification of silica. The content of the acid-base indicator chemically immobilized on the silica surface was determined by quantitative chemical analysis of synthesized materials, as well as by thermogravimetry and diffuse reflectance electron spectroscopy in the ultraviolet and visible regions. It was demonstrated that diffuse reflectance electron spectroscopy can be a reliable method of quantitatively determining an indicator dye chemically grafted to the silica surface. It was proved that chemically grafted dye retains the ability to protonation of tertiary amino group and formation of resonance azonium ion, which is responsible for changing the color of methyl red. It was found that the protonation of methyl red chemically fixed on the silica surface occurs at higher pH values than for individual indicator dye. Therefore, the color change of grafted dye takes place in less acidic solutions. The proposed synthetic approach can be used to produce regenerable and eco-friendly pH-sensitive materials.

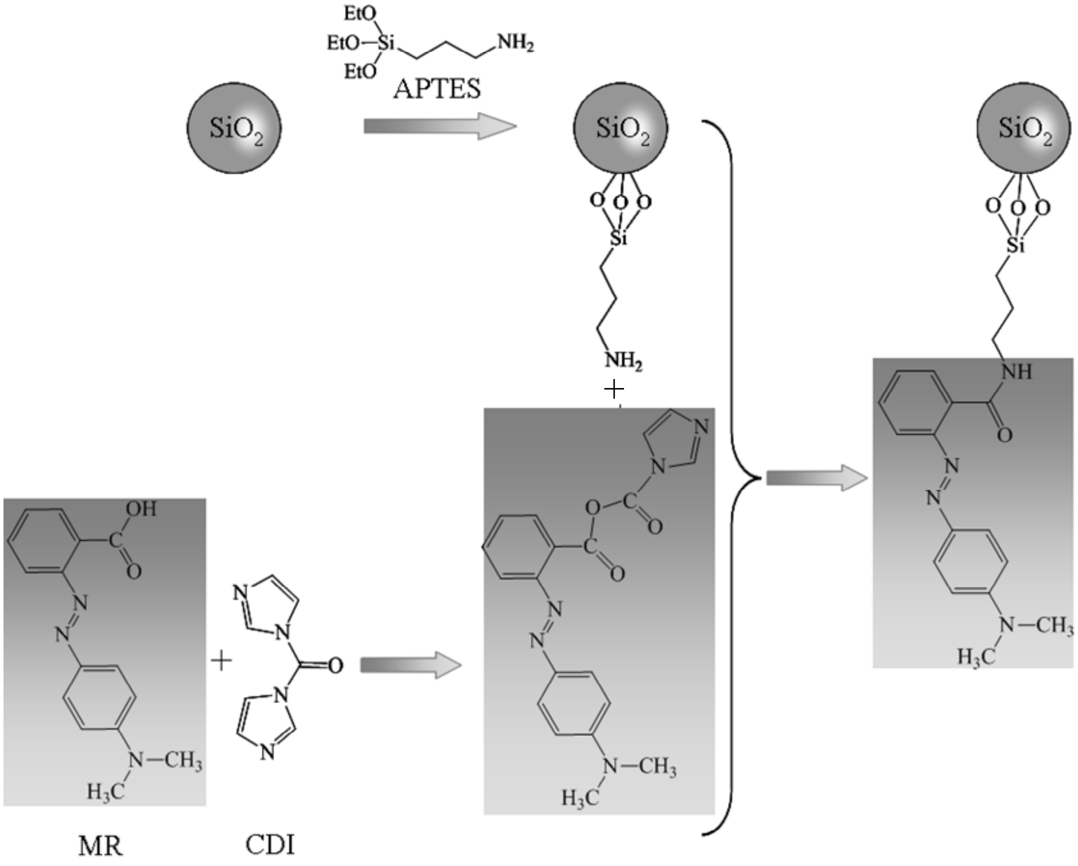
Keywords: *methyl red, silica, chemical immobilization, pH-sensitive material*

INTRODUCTION

pH indicators are usually weak organic acids or bases that change color in response to a variation of the hydrogen ion concentration. A properly selected acid-base indicator can be used for visual assessment of approximate solution pH. In view of high costs as well as toxic and carcinogenic effects of some pH indicators, the possibility of their immobilization on solid supports is attractive approach of pH sensor materials synthesis. Silica supports due to high chemical stability and mechanical strength have promising potential in creation of non-toxic, regenerable, reusable, eco-friendly sensor materials.

Acid-base indicators can be introduced into the silica materials by means of the direct doping in sol-gel synthesis [1–14], impregnation [15, 16] or covalent bonding by post-synthetic modification [17, 18]. In the case of doping strategy, pH indicator is added to the reaction mixture in the process of sol-gel synthesis and entrapped in the matrix during the polycondensation process. Molecules of pH-sensitive substance are surrounded by a silica framework, which prevents their noticeable elution at contact with solutions and protects them from external environment, providing higher chemical stability. At the same time, silica matrix obtained by sol-gel synthesis supports the transport of small molecules and enables successive response of pH indicator to analyte presence. Numerous studies confirm the ability of successful regulation of entrapped indicator release and its response to pH change by variation of structural parameters as well as chemical composition of silica framework prepared by sol-gel method [3, 4, 6–10]. Doping is the most widely used strategy to prepare pH sensor silica materials due to its obvious advantages such as mild reaction conditions, easy control of the content of entrapped pH indicator, possibility of direct alteration of chemical and structural properties of silica support. Despite of the simplicity of preparation, impregnated pH sensor materials are rarely used [15, 16] as they usually have short term stability. Washout of indicator molecules immobilized on silica carrier via physical absorption causes loose of sensor activity and gives erroneous results. Post-synthetic grafting requires the presence of reactive groups on both the pH indicator and silica material that makes it more tedious than the other two strategies. However, chemical immobilization is attractive alternative to impregnation or encapsulation within silica framework as assures firm retention of sensor moieties in the surface layer. Covalent bonds formation between receptor element and silica framework excludes washout of dye and provides direct contact of grafted pH indicator with analyte in the external environment [17, 18].

In the present study, we report synthesis of pH-sensitive material consisting of acid-base indicator chemically immobilized on silica surface (Scheme 1).



Scheme 1. Chemical immobilization of methyl red on silica surface

At first, aminopropylsilica was synthesized by the reaction between silanol groups of silica surface and ethoxy groups of (3-aminopropyl)triethoxysilane (APTES). Then, grafting of acid-base indicator, methyl red (MR), on aminopropylsilica was realized under mild conditions by use of coupling agent 1,1′-carbonyldiimidazole (CDI). The quantity of MR moieties grafted to the silica support was estimated by quantitative chemical analysis as well as by thermogravimetry and diffuse reflectance ultraviolet-visible (DRUV) spectroscopy. The results obtained were compared to evaluate the usefulness of diffuse reflectance technique to quantitative determination of dye molecules chemically immobilized on silica surface. Acid-base equilibria of surface functional groups were studied by potentiometric titration method, and the ionization constants values were estimated to confirm the ability of synthesized material to pH response.

EXPERIMENTAL

Porous amorphous silica with particles size of 0.315–0.5 mm was used as starting material. Before chemical modification silica was heated in air at 400 °C for 2 h to remove adsorbed water and organic impurities. Concentration of free silanol groups on the surface of pretreated silica was 0.49 mmol/g.

(3-Aminopropyl)triethoxysilane (Merck, purity ≥ 99 %), 1,1'-carbonyldiimidazole (Merck, purity ≥ 98 %), methyl red, disubstituted sodium phosphate, monosubstituted potassium phosphate, and phosphoric acid (all from Reakhim, analytical grade), potassium bromide (AppliChem, pharma grade), benzene (Macrochem, analytical grade), sulfuric acid (Reakhim, chemical grade), sodium hydroxide (Macrochem, chemical grade) were used as received without additional purification. Toluene, N,N′-dimethylformamide (DMF), and acetone (all from Reakhim, pure analytical) were dried for 72 h by use of 4 Å molecular sieves.

Impregnation of MR into silica support. Two series of silica materials containing different amounts of MR were prepared by wetness impregnation. For this, the weighted amounts of aminopropylsilica (0.5 and 0.4 g) were placed in glass bottles and wetted with certain volume (2 ml) of MR solutions in benzene with concentration varying in the range of 0.043–0.171 and 1.49–4.47 mmol/l, respectively. The obtained suspensions were thoroughly stirred using shaking water bath at room temperature until complete evaporation of solvent and dried at 100 °C for 2 h. The resulting products were kept in a desiccator before use (Tables 1, 2).

Chemical immobilization of MR on silica support. Chemical immobilization of MR on silica surface was realized by two-step procedure: synthesis of 3-aminopropyl-functionalyzed silica and modification of its surface with MR in the presence of coupling agent.

Introduction of 3-aminopropyl groups into the surface layer of silica was achieved by the chemical reaction between isolated silanol groups of silica and ethoxy groups of APTES as described in [19]. Briefly, weighted amount of silica (10 g) preheated at 400 °C for 2 h was placed into a three-necked reactor supplied with a stirrer and a reflux condenser, and suspended in a small amount of toluene (50 ml) at room temperature for 40 min, then APTES (7.05 ml) was added. The reaction mixture was stirred at 110 °C for 6 h. After that the solid phase was transferred on a porous glass filter, washed with toluene until the absence of silane (absence of a violet color with the addition of ninhydrin), then acetone, distilled water (for hydrolysis of the ethoxy groups). The resulting NH_2-SiO_2 silica was dried in air at 150 °C during 6 h.

Immobilization of MR on 3-aminopropyl-functionalyzed silica surface was realized using the activation properties of 1,1'-carbonyldiimidazole. For this, the certain amount of anhydrous MR (0.01616–0.00808 g) was placed in a reactor supplied with an agitator and dissolved in dried DMF (1 ml). Then equimolar amount of CDI (0.01021–0.0051 g) dissolved in DMF (1 ml) was added dropwise in the reactor while stirring. Activation of MR by condensation of its carboxyl group with CDI was carried out at 20 °C for 2 h. After that the solution containing CDI-activated MR was slowly dropped to the suspension of aminopropylsilica in DMF (1 g/2 ml of solvent) which was stirred at 20 °C for 20 h. Thereafter silica material with grafted MR was transferred on a porous glass filter and washed sequentially with DMF and acetone. The air-dried product was washed with benzene, kept at room temperature until complete evaporation of solvent, and dried at 100 °C for 2 h. Then, it was cooled to room temperature and stored in a desiccator before use (Tables 1, 2).

Transmittance UV-Vis studies of MR in solutions. Ultraviolet-visible studies of 0.033 and 0.017 mmol/l solutions of MR in phosphate buffers and benzene, respectively, were carried out over the 200–650 nm spectral range with a Specord M-40. Quartz cells with 1 cm pathlength were used.

DRUV studies of MR chemically immobilized and impregnated into silica support. Silica materials with various content of chemically immobilized and deposited MR were used without dilution or mixed with KBr in the ratio 1:20, ground in a mortar and employed for recording of DRUV spectra over the 350–600 nm spectral range with a Specord M-40 in the optical density mode. To avoid the uncertainties arising from the wide particle size distribution the measurements of the reflectance were repeated several times for each sample using the parent silica or its mixture with KBr in the ratio 1:20 as background. Content of MR chemically immobilized on aminopropylsilica was estimated from calibration curve plotted for a series of aminopropylsilicas with impregnated indicator dye across a range of its contents from 7.45 to 22.35 μmol/g.

Thermogravimetry of MR-containing silica materials. Thermogravimetric analysis of synthesized silica materials was carried out on a Perkin Elmer 7 series thermal analyzer. A batch of powdered silica was used for each test. The experiment was performed from ambient temperature to 900 °C at the heating rate of 10 °C/min in open ceramic crucibles in static air atmosphere.

Quantitative chemical analysis of MR-containing silica materials. To evaluate content of MR grafted on aminopropylsilica surface, acid-base hydrolysis of synthesized organosilicas was carried out. Briefly, the batch of MR-containing silica (0.05 g) was placed in a reactor with a reflux condenser, suspended in a small amount of H_2SO_4 (10 ml, 1 mol/l) and refluxed at 100 °C for 2 h. After that the suspension was cooled to room temperature and neutralized to pH~7 with NaOH solution. Resulting suspension was mixed with NaOH solution (7 ml, 5 mol/l), refluxed at 100 °C for 2 h, cooled to room temperature, neutralized to pH 7.0 and diluted up to 100 ml with water. pH of solution was precisely controlled with an Ionometer I-120.1. Content of MR in analyzed solution was calculated using the calibration curve fitted in the range of concentrations 1.63–16.3 mmol/l.

Porous structure of MR-containing silica materials. Parameters of porous structure of parent silica and synthesized organosilicas with chemically immobilized MR were obtained from the low-temperature adsorption-desorption of nitrogen at −196 °C using a Kelvin-1042 Sorptometer. At first, silica material was outgassed in a vacuum at 140 °C for 20 h and then analyzed in the region of relative pressures from 0.06 to 0.99 in increment of 0.015. Specific surface area (S_{BET}) was evaluated by the Brunauer-Emmet-Teller method, pore diameter (D) was calculated by the nonlocal density functional theory (NLDFT), and pore volume (V_p) was determined at $p/p_o = 0.95$.

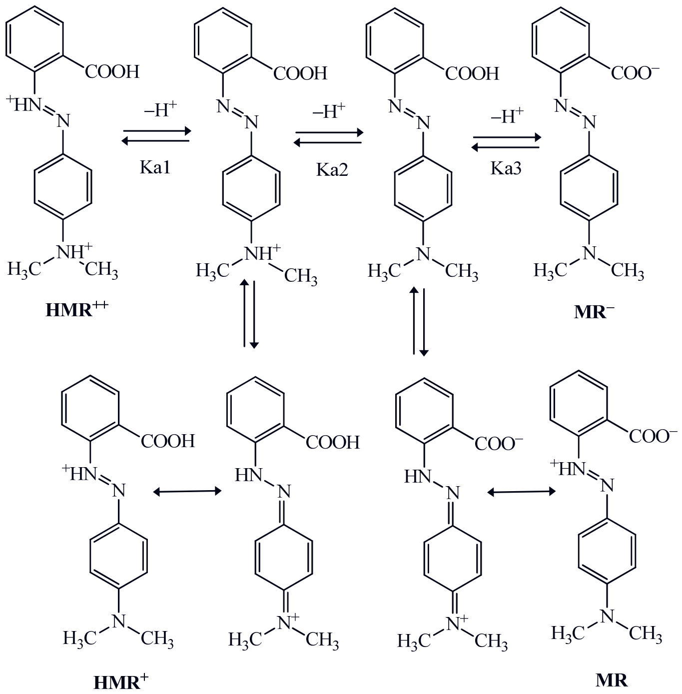
Protolytic properties of MR chemically immobilized on silica support. The potentiometric titration technique was applied to determine the influence of chemical immobilization on MR protolytic properties. For this, the batches of MR-containing silica (0.5 g) were suspended in 1 M NaCl (25 ml) to stabilize the system at a given ionic strength. The potentiometric titration of aqueous silica suspensions was started from pH near 6.5 and performed by stepwise addition of equal volumes (20 μl) of titrant (0.2 M, 0.4 M or 1 M HCl) with continuous stirring at 20 °C. The equilibrium pH values of suspensions were measured by an Ionometer I-120.1 that was calibrated for optimal precision using standard buffer solutions of pH 1.68 and pH 6.86. The equilibrium attainment for each addition of the titrant was estimated by control of the stability of measured pH value. The apparent constants of ionization were calculated from the potentiometric titration data of MR-containing silica materials using the Henderson-Hasselbach equation $pK = pH + lg[(1-\alpha)/\alpha]$ for $\alpha \to 0$ [20]. The potentiometric titration of each sample was repeated at least in triplicate to confirm the results and enhance the accuracy of experiment.

RESULTS AND DISCUSSION

MR is a well-known indicator dye that has complex acid-base equilibria in the pH range 2–8 [21]. It changes the color from red (below pH 3.1) to yellow (over pH 6.2), between these values of pH MR is colored in orange (Scheme 2).

The value of its pK_{a2} is 2.38±0.05 at 25 °C [21], whereas pK_{a3}, which corresponds to the equilibrium between neutral and ionized forms of MR, varies from 4.85±0.01 to 5.05±0.05 in the temperature range 25–30 °C [21–23]. Covalent bonding of MR on aminopropylsilica surface that proceeds through formation of highly reactive intermediate of MR with CDI and its subsequent conjugation with primary amino groups of silica surface via amide bonds leads to the lost of carboxylic functionality (Scheme 1). Therefore, chemical immobilization of MR on silica support may affect substantially the protolytic properties of acid-base indicator. It was mentioned [10] that MR loses the ability to change color depending on the pH variation at encapsulation within a silica matrix. As MR has two color transitions caused by transition of carboxylic group in the unionized form and protonation of terminal amino group (Scheme 2), involving of carboxylic group into the chemical reaction with 3-aminopropyl functionalities of silica surface should not lead to fully deprive of the pH sensor properties of chemically immobilized azobenzene dye. It can be supposed that grafted MR will retain the ability for protonation of tertiary amino group and formation of resonance azonium ion which are responsible for the color change at pH variation. However, the acid-base equilibrium of this process could be shifted in comparison with the initial dye. To confirm this assumption, protolytic properties of silica with chemically immobilized dye moieties were studied.

The transmittance UV-Vis spectra of MR in solutions (Fig. 1) were compared with diffuse reflectance ones of dye chemically immobilized and impregnated into silica support (Figs. 2, 3).



Scheme 2. Protolytic equilibria of methyl red [21]

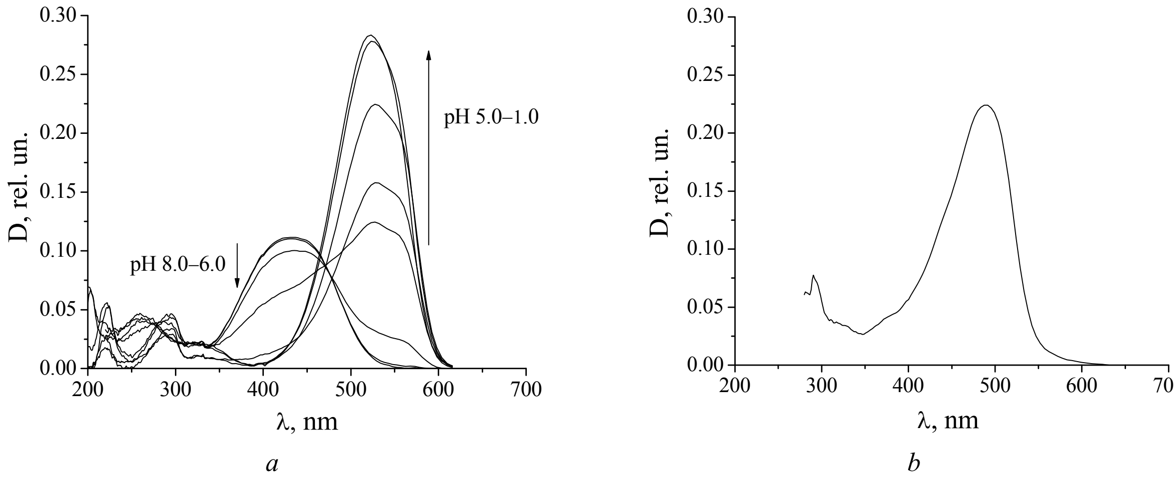
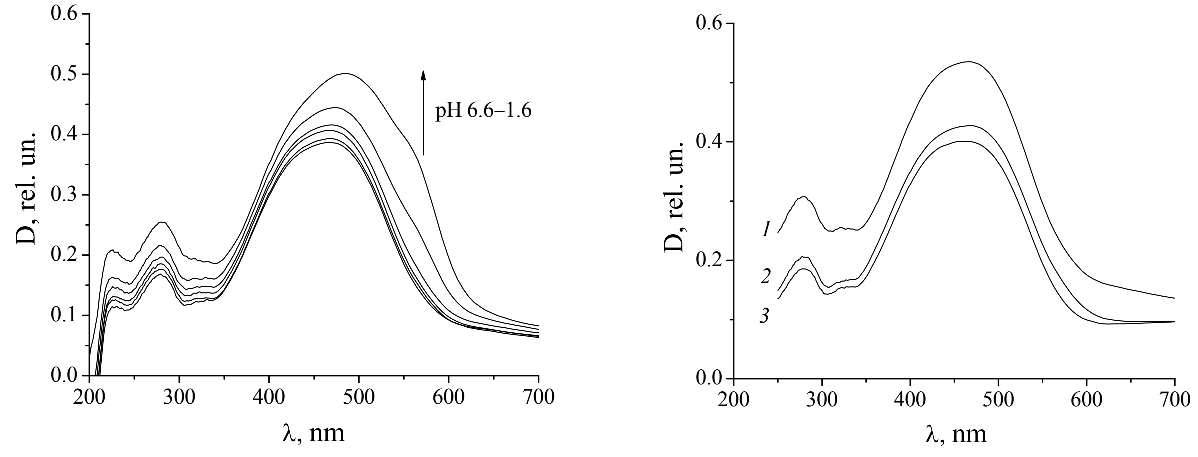


Fig. 1. Transmittance UV-Vis spectra of MR: *a* – in phosphate buffer solutions (C_{MR}=0.0334 mmol/l); *b* – in benzene (C_{MR} = 0.0171 mmol/l)

As can be seen from Fig. 1 *a*, absorption bands at 200, 260, and 428 nm are observed in the transmittance UV-Vis spectrum of MR in a phosphate buffer solution at pH 8.0. They are attributed to the benzene rings with carboxylic and amino substituents as well as azo group of azobenzene dye that can be regarded as chromophore. Lowering of pH value leads to the transformation of MR from its ionized form to the neutral one (Scheme 2). As a result, noticeable reducing of absorption bands intensity in the visible and ultraviolet spectral regions and the bathochromic shift of the low-wavelength absorption peak are observed (Fig. 1 *a*). Moreover, the shoulder around 520–560 nm imputed to formation of the azonium tautomeric forms of azobenzene dye responsible for the color change starts to appear at pH ~6.0. It is known that azo group can exhibit both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations. Protonation under acidic conditions leads to the transition of one of the lone pare of azo nitrogens to a bonding state and, as a result, more tight holding of electrons and lowering of molecular orbital levels. So, the bathochromic shift of the absorption peak at 428 nm to 520 nm confirms formation of MR form of indicator dye. Positions of high-wavelength absorption maxima of MR and HMR$^+$ forms of indicator dye are close to each other, therefore in acid medium they are merged together into the strong band around 520 nm. In addition, the bathochromic shift of absorption band at 260 nm to 291 nm caused by $n \rightarrow \pi^*$ transition of the amino group where lone pair is delocalized and contributes to the resonance structures of the azonium tautomers is observed (Fig. 1 *a*). As the whole, acidification of aqueous solution leads to the subsequent color change of MR from yellow to orange and red.

UV-Vis spectra of acid-base indicators are often sensitive to polarity of environment as solvent alters the electronic energy levels of chromophore [24]. In the spectrum of MR solution in benzene (Fig. 1 *b*) the distinct absorption band with maximum near 489 nm belonging to the $n \rightarrow \pi^*$ transition of the –N=N– group is registered. Hydrophobic benzene environment causes noticeable bathochromic shift of this absorption band in comparison with its position in phosphate buffer solution with pH = 6.0–7.0.

Silica surface effect on the electronic structure of azobenzene dye is clearly seen by comparing the DRUV spectra of MR grafted on aminopropylsilica with transmittance ones registered in phosphate buffer solutions of dye (Figs. 1, 2).



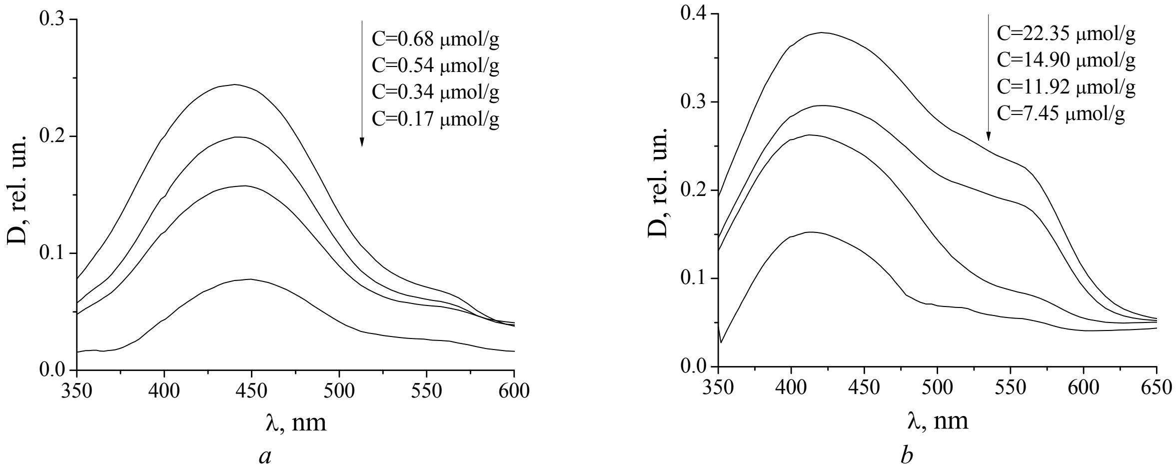
a *b*

Fig. 2. DRUV spectra of MR-SiO$_2$ silicas diluted in a 1:20 ratio with KBr powder: *a* – 3-MR-SiO$_2$ rinsed with phosphate buffer solutions with different acidity; *b* – 1-MR-SiO$_2$ (*1*), 2-MR-SiO$_2$ (*2*), 3-MR-SiO$_2$ (*3*) rinsed with benzene (*b*)

The DRUV spectra of MR chemically immobilized on silica surface exhibit three distinct peaks in the visible and ultraviolet spectral regions. However, their positions are slightly different from their positions in the spectra of MR in solutions with the same values of pH (Figs. 1, 2 *a*). Obviously, grafting of MR on silica surface through amide bond formation causes the electron density redistribution and alteration of molecular orbital levels in chemically immobilized dye. In particular, amide bond forms resonance structure that pulls the electron density away from the azobenzene ring. Its electron withdrawing resonance effect is stronger than that occurring in carboxylic group of MR. Therefore, bathochromic shift of the reflection band belonging to the $n \to \pi^*$ transition of the surface azonium group is less pronounced than that in the case of individual azobenzene dye at solution acidification. At the same time, negative resonance effect of amide group decreases the contribution of amino group with electron pair delocalized in azobenzene rings. As a result, position of absorption band registered at 291 nm in the transmittance UV-Vis spectra of MR is shifted to 279 nm for 3-MR-SiO_2. In addition, increase in optical density of all absorption bands and bathochromic shift of chromophore band are observed upon pH rise (Fig. 2 *a*). The appearance of the shoulder around 550 nm in the spectra of 3-MR-SiO_2 silica takes place only in highly acidic medium after rinsing with buffer solutions with pH 2.7 and pH 1.6 (Fig. 2 *a*). This fact confirms the change of indicator dye protolytic properties as a result of its chemical immobilization on the silica surface: protonation of surface functionalities proceeds at lower pH as compared with individual MR. So, the color change from orange to red takes place in more acidic solutions.

Rinsing of synthesized pH-sensitive materials with benzene and their subsequent drying at 100 °C for 2 h does not influence the profile of DRUV spectra (Fig. 2). Moreover, reflection maximum belonging to the $n \to \pi^*$ transition of the –N=N– group in benzene pretreated organosilicas coincides with that of 3-MR-SiO_2 silica rinsed with buffer solutions (pH 4.8–6.6) and is registered at 468 cm^{-1}.

The DRUV studies of silica materials with deposited dye molecules results in the spectra comparable with those of MR in phosphate buffer solutions and MR chemically immobilized on NH_2-SiO_2 (Figs. 1–3). The profiles of the spectra are similar although there are some alterations in the position of their maxima (Figs. 1–3). As can be seen from Fig. 3 *a*, the reflection band at 445 nm is registered in the DRUV spectra of MR deposited on silica surface in content range 0.17–0.68 μmol/g. Its position is bathochromically shifted in comparison with the absorption band of MR in phosphate buffer solution with pH = 6–7. It can be supposed that non-ionized silanols interact with basic nitrogen of indicator dye, as well as surface 3-aminopropyl groups – with carboxylate functionalities of deposited MR moieties through hydrogen bonds formation and affect the red shift of chromophore band. Increase of deposited MR content up to 22.35 μmol/g causes appearance of intense reflection band near by 415 nm and the shoulder around 560 nm (Fig. 3 *b*). Their positions are close to the corresponding reflections in the transmittance spectra of azobenzene dye at pH 6–7.



a *b*

Fig. 3. DRUV spectra of MR deposited on NH_2-SiO_2 from benzene solution: ground samples (*a*), ground samples diluted in a 1:20 ratio with KBr powder (*b*)

In the present work, attempts were made to elucidate influence of MR chemical immobilization on structural parameters of silica carrier, to quantify the content of covalently bonded azobenzene moieties in MR-SiO$_2$ silicas using DRUV spectral analysis, and to compare with the results of chemical and thermogravimetric analysis.

The isotherms of nitrogen adsorption-desorption on initial and chemically modified silicas belong to type V according to the IUPAC classification (Fig. 4). Isotherms of this type describe adsorption on the surface of mesoporous sorbents with weak affinity for adsorbate. Intensive rise of isotherm curves is observed at relative pressures above 0.8. The appearance of the hysteresis loop on the isotherms of parent and chemically modified silica materials indicates the condensation of nitrogen in mesopores. Pore size distribution curves obtained from the desorption branches of the isotherms prove the mesoporous structure of silica materials (Fig. 5). Introduction of 3-aminopropyl as well as MR-containing functional groups in silica surface does not influence noticeably the wide pore size distribution typical for initial silica (Fig. 5). Structural parameters of silica materials calculated from nitrogen adsorption-desorption isotherms are represented in Table 1.

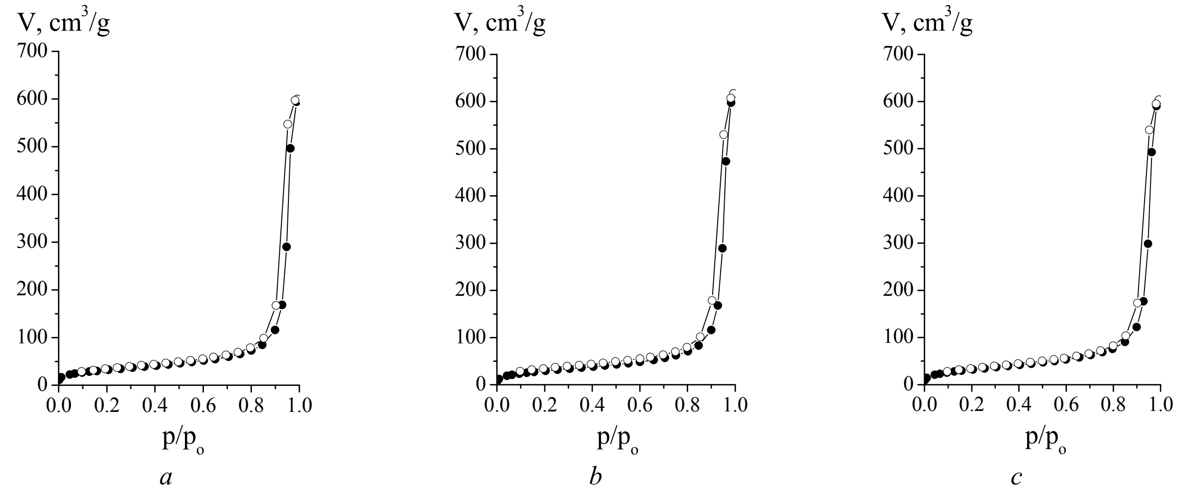


Fig. 4. Isotherms of low-temperature nitrogen adsorption-desorption for initial silica (*a*), NH$_2$-SiO$_2$ (*b*), and 3-MR-SiO$_2$ (*c*)

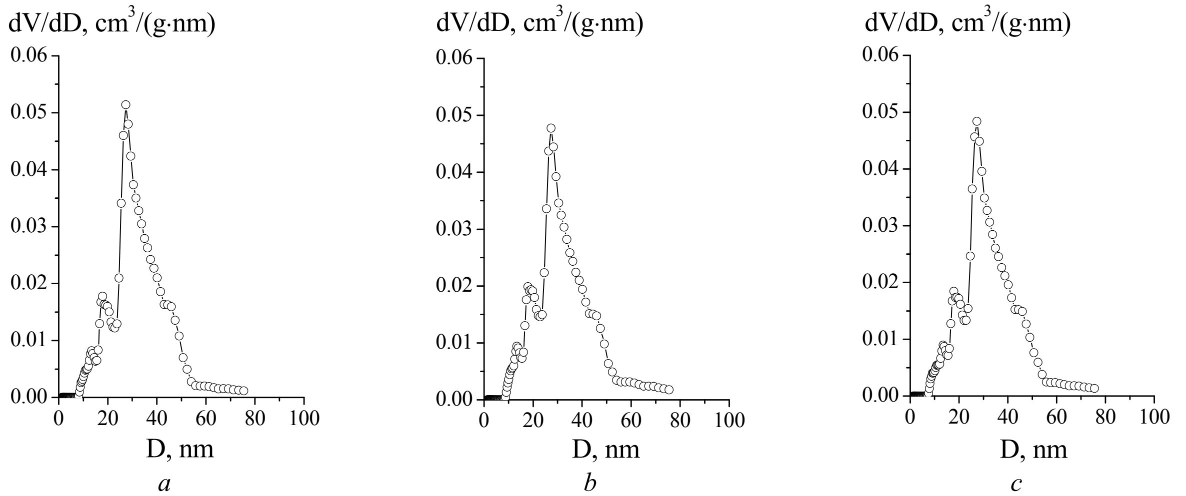


Fig. 5. Pore size distributions for initial silica (*a*), NH$_2$-SiO$_2$ (*b*), and 3-MR-SiO$_2$ (*c*)

Table 1. Parameters of porous structure for silica materials calculated from low-temperature adsorption-desorption of nitrogen

Silica	S_{BET}, m^2/g	V, cm^3/g	D, nm
Initial silica	141	0.93	27.4
Aminopropylsilica NH_2-SiO_2	116	0.96	27.4
MR-containing silica 3-MR-SiO_2	107	0.94	27.4

For the determination of the amount of chemically bonded methyl red by DRUV spectroscopy, calibration curves plotted for a series of standards across a range of dye contents impregnated into aminopropylsilica near its expected values in synthesized organosilicas were used (Figs. 3, 6). As particle size and morphology may affect the optical signal, all the reflectance spectra were registered for grounded parent silica materials or diluted with KBr ones against aminopropylsilica or its mixture with KBr, respectively, as background. Obtained results imply that calibration curves plotted as reflectance of MR impregnated into aminopropylsilica against its content show a linear character in both studied regions (Fig. 6). However, position of reflection maxima in the spectra of silica materials with lower content of MR impregnated into NH_2-SiO_2 is closer to the reflection maxima in the DRUV spectra of chemically immobilized azobenzene dye. Therefore, determination of the amount of chemically bonded MR by DRUV spectroscopy was realized using calibration curves plotted for a series of silicas with content of impregnated MR in the range 0.17–0.68 μmol/g. Obtained results are represented in Table 2.

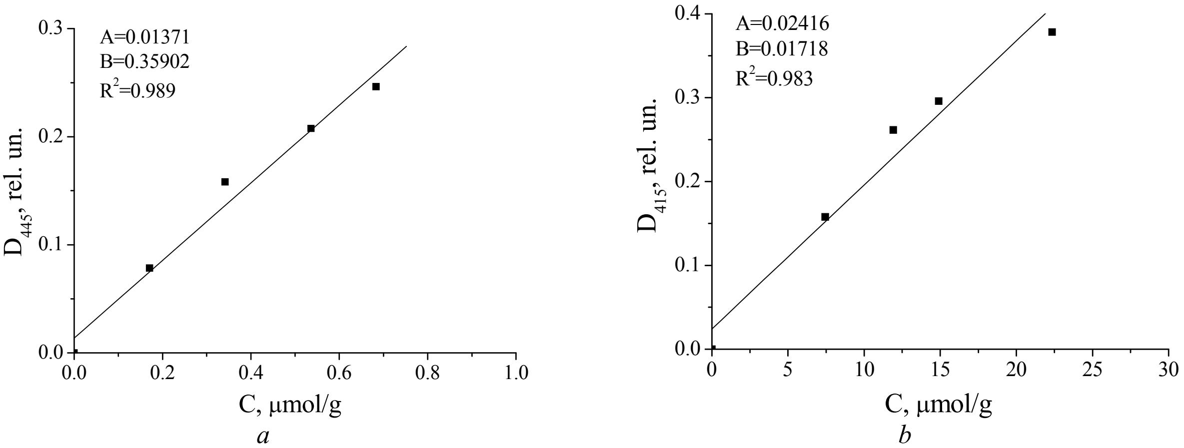
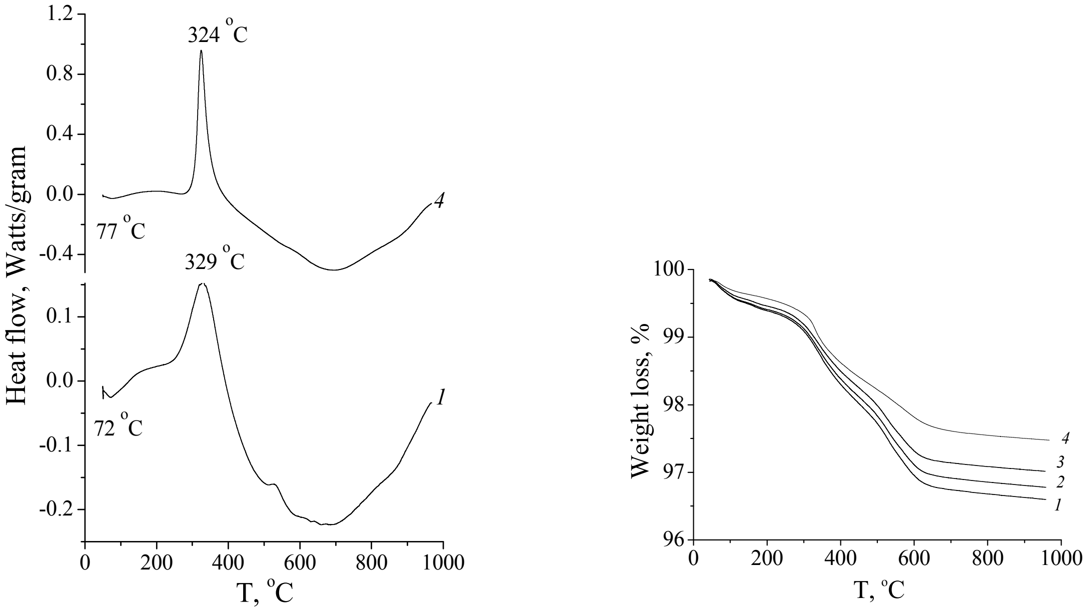


Fig. 6. Calibration curves obtained from DRUV spectra of MR impregnated into NH_2-SiO_2 from benzene solution: ground samples (*a*), ground samples diluted in a 1:20 ratio with KBr powder (*b*)

Cleavage of grafted MR from the carrier surface was achieved by acid-base hydrolysis of amide bonds in MR-SiO_2 in aqueous medium. This procedure leads to the formation of 3-aminopropyl groups on silica surface, whereas indicator passes into the solution and its quantity can be determined by transmittance UV-Vis spectroscopy using calibration curve. The results of quantitative chemical analysis of MR-SiO_2 silicas are represented in Table 2.

The thermal stability of synthesized silica materials was characterized by thermogravimetry. As can be seen from Fig. 7 *a*, endothermic effect is observed on the curves of differential thermal analysis (DTA) for NH_2-SiO_2 and 1-MR-SiO_2 at low temperatures. It is caused by removal of adsorbed water from the surface of organosilicas and proceeds with the mass loss on the curves of thermogravimetric analysis (TG) (Fig. 7 *b*). Thermal decomposition of organic surface layer of NH_2-SiO_2 begins at temperatures around 250 °C and is accompanied by distinct exothermic effect with $T_{max} = 324$ °C on the DTA curve. Two-step mass loss on the TG curve (Fig. 7 *b*, curve 4) in temperature range of 250–650 °C belongs to the gradual destruction of 3-aminopropyl groups. Introduction of indicator dye in the structure of aminopropylsilica leads to the substantial changes in the character of thermodestruction (Fig. 7 *a*, curve 1). Thermal decomposition of individual MR proceeds with exothermic effect with $T_{max} = 212$ °C [25]. Formation of strong amide bond between indicator dye and silica surface provides increase of its thermal stability and, as a result, shift of exothermic effect in higher-temperature region. On the DTA curve of 1-MR-SiO_2 we can see the complex exothermic effect with $T_{max} = 329$ °C originated from destruction of chemically immobilized 3-aminopropyl as well as MR-containing groups. Immobilization of MR on NH_2-SiO_2 causes pronounce increase in mass loss for all synthesized silicas (Fig. 7 *b*, curves 1–3). The content of grafted MR was determined from the difference in mass loss registered in temperature region 150–650 °C for NH_2-SiO_2 and MR-SiO_2 silicas (Table 2).



a *b*

Fig. 7. The curves of differential thermal analysis DTA (*a*) and thermogravimetric analysis TG (*b*) for 1-MR-SiO_2 (*1*), 2-MR-SiO_2 (*2*), 3-MR-SiO_2 (*3*), and NH_2-SiO_2 (*4*)

Table 2. Content of methyl red chemically immobilized on silica surface

Silica	Content of methyl red, mmol/g		
	DRUV spectroscopy	chemical analysis	thermogravimetry
1-MR-SiO_2	0.026	0.024	0.027
2-MR-SiO_2	0.020	0.020	0.022
3-MR-SiO_2	0.018	0.016	0.015

Comparison of the MR content estimated by chemical, DRUV, and thermogravimetric analyses (Table 2) proves good agreement of obtained results. So, it can be stated that DRUV spectroscopy is reliable technique for quantitative determination of indicator dye chemically grafted on silica surface.

Formation of amide linkage between silica surface and indicator dye at chemical immobilization of MR may affect its acid-base properties substantially. It can be expected that higher negative resonance effect of amide bond in comparison with carboxylic group will change the acidity of azo group responsible for the color change. To confirm this assumption and evaluate ionization constants of surface functional groups, potentiometric titration of synthesized pH-responsive material was realized using hydrochloric acid as the titrant. Aqueous pH-sensitive material suspensions were titrated from pH near 6.0 when silanol groups of silica surface are partially ionized, whereas residual 3-aminopropyl groups are not protonated. The experiment was stopped when the pH was around zero in order to avoid possible hydrolysis of amide bond. The dependence of the suspension pH on the added volume of titrant is represented in Fig. 8. It has been found that the obtained potentiometric titration curves demonstrate gradual pH decrease at addition of hydrochloric acid with concentration 0.2 and 0.4 mol/l. Increase in titrant concentration up to 1 mol/l leads to the appearance of barely noticeable inflection. To determine the equivalence point more precisely, a first derivative plot of the titration curve was obtained (Fig. 8).

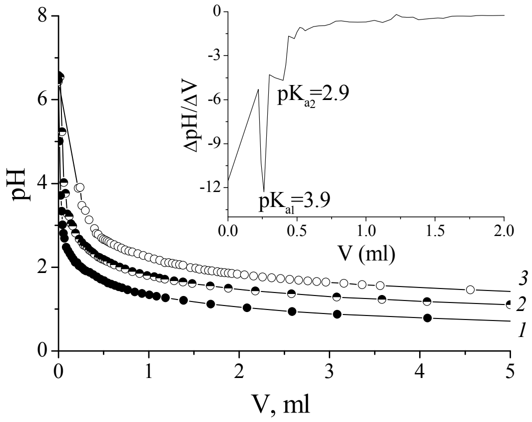


Fig. 8. Potentiometric titration curves of 3-MR-SiO_2 in 1 M NaCl with 0.2 M (*1*), 0.4 M (*2*) and 1 M HCl (*3*) at 20 °C. The inserted figure shows the first derivative of the potentiometric titration curve of 3-MR-SiO_2 in 1 M NaCl with 0.2 M HCl at 20 °C

It can be claimed that obtained values of pK_a belong to the residual 3-aminopropyl groups of silica surface (p$K_{a1} = 3.9$) and tertiary amino groups of chemically immobilized azobenzene dye (p$K_{a2} = 2.9$). So, grafted MR retains the ability for protonation and formation of resonance azonium ion responsible for the colour change at pH variation. However, the acid-base equilibrium of this process is shifted in comparison with the initial dye.

CONCLUSIONS

Modification of silica surface with acid-base indicator, methyl red, was realized by chemical assembly method. To estimate parameters of porous structure and chemical composition of synthesized materials, their detailed characterization was carried out using low-temperature nitrogen adsorption-desorption, quantitative chemical analysis of silica surface, thermogravimetry, diffuse reflectance ultraviolet-visible spectroscopy. The results obtained by transmittance and diffuse reflectance ultraviolet-visible spectroscopy proved that grafted MR retains the ability for protonation of tertiary amino group and formation of resonance azonium ion responsible for the colour change at pH variation. To evaluate the changes in protolytic properties of indicator dye caused by its chemical immobilization on silica carrier, aqueous potentiometric titration was performed. It has been found that the protonation of surface MR-containing functionalities proceeds at higher pH values in comparison with individual indicator dye. So, the color change from orange to red for methyl red linked to the silica surface takes place in less acidic solutions compared to individual indicator dye.

pH-чутливі матеріали на основі кремнезему з хімічно іммобілізованим метиловим червоним: синтез та протолітичні властивості

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Мета цієї роботи – вивчення можливості створення гідролітично і хімічно стійких pH-чутливих матеріалів з використанням кремнезему як носія та кислотно-основного індикатора, що змінює забарвлення при варіюванні pH середовища. Синтез pH-чутливих матеріалів було здійснено шляхом ковалентного зв'язування барвника метиловий червоний з амінопропілкремнеземом у присутності 1,1′-карбонілдиімідазолу як зшиваючого агента. Пориста структура, хімічний склад поверхні та протолітичні властивості синтезованих кремнеземних матеріалів охарактеризовано за допомогою низькотемпературної адсорбції-десорбції азоту, кількісного хімічного аналізу, термогравіметрії, електронної спектроскопії дифузного відбиття, pH-метрії. Встановлено, що хімічна іммобілізація метилового червоного на поверхні кремнезему не спричиняє суттєвого впливу на пористу структуру вихідного кремнезему. Вміст кислотно-основного індикатора, хімічно іммобілізованого на поверхні кремнезему, визначено шляхом кількісного хімічного аналізу синтезованих матеріалів, а також методами термогравіметрії та електронної спектроскопії дифузного відбиття в ультрафіолетовій та видимій області. Продемонстровано, що електронна спектроскопія дифузного відбиття може бути надійним методом кількісного визначення індикаторного барвника, хімічно прищепленого до поверхні кремнезему. Доведено, що іммобілізований барвник зберігає здатність до протонування третинної аміногрупи і утворення резонансного іона азонію, який відповідає за зміну кольору метилового червоного. Встановлено, що протонування метилового червоного, хімічно закріпленого на поверхні кремнезему, здійснюється при більш високих значеннях pH у порівнянні з індивідуальним індикаторним барвником. Тому зміна забарвлення прищепленого метилового червоного відбувається в менш кислих розчинах. Запропонований синтетичний підхід може бути використаний для одержання екологічно чистих pH-чутливих матеріалів багаторазового використання.

Ключові слова: *метиловий червоний, кремнезем, хімічна іммобілізація, pH-чутливий матеріал*

pH-чувствительные материалы на основе кремнезема с химически иммобилизованным метиловым красным: синтез и протолитические свойства

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Цель настоящей работы – изучение возможности создания гидролитически и химически устойчивых pH-чувствительных материалов с использованием кремнезема в качестве носителя и кислотно-основного индикатора, изменяющего окраску при варьировании pH среды. Синтез pH-чувствительных материалов был осуществлен путем ковалентного связывания красителя метиловый красный с аминопропилкремнеземом в присутствии 1,1′-карбонилдиимидазола в качестве сшивающего агента. Пористая структура, химический состав поверхности и протолитические свойства синтезированных кремнеземных материалов охарактеризованы с помощью низкотемпературной адсорбции-десорбции азота, количественного химического анализа, термогравиметрии, электронной спектроскопии диффузного отражения, pH-метрии. Установлено, что химическая иммобилизация метилового красного на поверхности кремнезема не оказывает существенного влияния на пористую структуру исходного кремнезема. Содержание кислотно-основного индикатора, химически иммобилизованного на поверхности кремнезема, установлено путем количественного химического анализа синтезированных материалов, а также методами термогравиметрии и электронной спектроскопии диффузного отражения в ультрафиолетовой и видимой области. Продемонстрировано, что электронная спектроскопия диффузного отражения может быть *надежным методом количественного определения индикаторного красителя, химически привитого к поверхности кремнезема. Доказано, что иммобилизованный краситель сохраняет способность к протонированию третичной аминогруппы и образованию резонансного иона азония, который отвечает за изменение цвета метилового красного. Установлено, что протонирование метилового красного, химически закрепленного на поверхности кремнезема, осуществляется при более высоких значениях pH по сравнению с индивидуальным индикаторным красителем. Поэтому изменение окраски привитого метилового красного происходит в менее кислых растворах. Предложенный синтетический подход может быть использован для получения экологически чистых pH-чувствительных материалов многократного использования.*

Ключевые слова: *метиловый красный, кремнезем, химическая иммобилизация, pH-чувствительный материал*

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