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COVALENT ATTACHMENT OF SOME PHENOL DERIVATIVES TO THE SILICA SURFACE BY USE OF SINGLE-STAGE AMINOMETHYLATION

V. A. Tertykh[*], *V. V. Yanishpolskii and O. Yu. Panova*

Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Prospekt Nauki 31
252022 Kyiv, Ukraine

Abstract

The reaction conditions and component ratios were established for the attachment of 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN) and 8-hydroxyquinoline (8-HQ) to the silica surface by means of a single-stage Mannich reaction. The modified sorbents that were synthesized were characterized by an adsorption method, and DRIFT and UV spectroscopies. The concentrations of PAR, PAN and 8-HQ grafted to the silica surface that were attained were $2.8 \cdot 10^{-5}$, $8.5 \cdot 10^{-5}$ and $2.7 \cdot 10^{-4}$ mol g^{-1}, respectively.

Keywords: covalent bonding, 8-hydroxyquinoline, 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo)-resorcinol, silica, surface modification

Introduction

Transfer of the major complexing analytical reagents based on phenol derivatives [1–3], and in particular 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN) and 8-hydroxyquinoline (8-HQ), to a heterogeneous state is of great practical importance for the development of perspective adsorbents for the solid-phase extraction of metal ions. However, the covalent attachment of phenol and its derivatives to the surface of silica matrices via the functional groups of the carrier, with preservation of the main complexing groups of the corresponding organic reagents, is usually connected with appreciable difficulties (a multistage process and the introduction of additional chromophore groups) [4–6]. The indicated analytical complexing reagents were recently anchored to the surface of previously aminated silica [5, 7–9] by means of the Mannich reaction, with aminomethylation of the reagent in a surface layer in the presence of aldehydes.

The purpose of this work is to report on the conditions of chemisorption of some phenol derivatives to the silica surface by means of the one-stage Mannich reaction, and on the physicochemical characterization of the modified silicas obtained.

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[*] Author for correspondence: E-mail: tertykh@public.ua.net

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Experimental

Solutions of Cu(II) were prepared from $CuSO_4{\cdot}5H_2O$ by dissolving the analytical grade reagent in bidistilled water. A 0.025% solution of PAR (Reanal, Hungary) was produced by dissolving a weighed portion of the reagent in a 0.05 M solution of sodium tetraborate (pH 9.28). Silica gel (Chemapol L100/600, Czech Republic) was chosen as adsorbent. The complexing reagents PAR, PAN and 8-HQ, 3-aminopropyltriethoxysilane and paraformaldehyde (all from Fluka) were used. Solution acidity was measured with a glass electrode. Optical densities of solutions were monitored on SF-46 and Specord UV-VIS spectrophotometers.

For attachment to the surface, a weighed portion of the reagent was dissolved in ethanol at 60°C, and an equimolar amount of the amino component and twice as much of the aldehyde were added. Further, a weighed portion of the initial silica gel, which had previously been heated at 60°C for 5 h, was placed in the mixture. The modified silica gel obtained was washed with alcohol, and dried at 120°C for 2 h.

A weighed portion of PAN (99.7 mg) was gradually dissolved in 1–6 ml alcohol during heating up to 60°C. 0.18 ml (0.8 mmol) 3-aminopropyltriethoxysilane and 48 mg (1.6 mmol) dry paraformaldehyde were then added to 6 ml PAN solution (0.4 mmol). Further, 2 g of the initial silica gel was added and the mixture was heated at 70°C for 5 h with periodic stirring. The precipitate was separated by decanting, and washed with alcohol (10 ml, 15 times) while the washing liquid was light-green. The modified silica obtained was dried at 80°C for 1 h and at 100°C for 1.5 h. The product was then washed with 200 ml ethanol and finally dried at 100°C for 1.5 h.

A weighed portion of 8-HQ (730 mg, 5 mmol) was dissolved in 5–10 ml alcohol under slight heating. The volume was then brought to 15 ml, and 0.3 g (10 mmol) paraformaldehyde, 1 ml (5 mmol) 3-aminopropyltriethoxysilane and 10 g pure silica were added. The mixture was heated at 60°C for 5 h with periodic stirring. The modified silica was dried at 100°C for 2 h, washed with alcohol (20 ml, 7 times) and again dried at 120°C for 1.5 h.

A weighed portion of PAR (10 mg, 0.04 mmol) was dissolved in 3 ml ethanol at 60°C. 0.1 ml (0.04 mmol) 3-aminopropyltriethoxysilane, 0.5 ml of an ethanol solution of paraformaldehyde (0.08 mmol) and 1 g silica were then added, and the mixture was heated at 60°C for 6 h. The modified silica was dried at 100°C for 2 h, washed with ethanol and with water, and again dried at 120°C for 1.5 h.

The Cu(II) ion adsorption capacities of the resulting modified sorbents were determined. For this purpose, equal weighed portions of silica gel (30 mg) containing immobilized PAR, PAN or 8-HQ (SG-PAR, SG-PAN and SG-8-HQ, respectively) were placed into test-tubes, and equal volumes (5 ml) of $CuSO_4{\cdot}5H_2O$ solution were added (Cu(II) content $7.81{\cdot}10^{-5}$–$9.38{\cdot}10^{-3}$ mol dm^{-3}). The solutions were allowed to stand for 4 h, with periodic stirring. Sorbent capacity was determined via the change in Cu(II) concentration in the solution above the adsorbent. Cu(II) concentrations were determined by a colorimetric method with PAR as metal indicator.

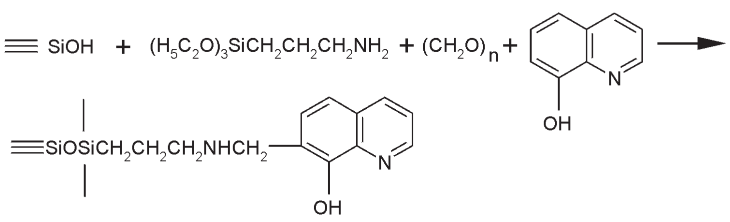
For quantitative determination of the concentrations of reagents attached to the surface, weighed portions of modified silica gel (5 mg) were fully dissolved in 5 ml

1 M KOH, and the UV spectra of the resulting solutions were recorded. The amount of reagent grafted to the silica surface was estimated from a calibration curve, with a solution of the appropriate pure reagent in 1 M KOH.

Results and discussion

It is known [1–6] that similar reagents can be immobilized on a silica surface via an azo coupling reaction. This is usually a multistage process, including a stage of amino-containing silica preparation, its diazotization and subsequent reagent bonding by means of an azo coupling reaction. We investigated the possibility of PAR, PAN and 8-HQ chemisorption on the surface of amino-containing silica by using the Mannich reaction. However, the attempt to immobilize PAR via the solid-phase aminomethylation reaction was negative. On completion of the process, the reagent was not retained on the matrix surface, as demonstrated by its gradual washing out. The marked difficulties with the Mannich reaction involving amino groups fixed on the surface of the modified matrix are probably connected with the essential change in acid-base properties of the grafted NH_2 groups in consequence of their interaction with the residual silanol groups on the silica surface.

We investigated an alternative approach to the preparation of sorbents with chemically bonded analytical reagents, whereby PAR, PAN and 8-HQ were immobilized according to the following single-stage scheme:



As this take place, the reagent aminomethylation proceeds simultaneously with the condensation of ethoxysilyl groups with silanol groups of the silica surface. It should be noted that the reagent amounts that can be taken for the synthesis by this method are limited by the solubilities. As the process is a single-stage one, the solution volume must be commensurable with the pore volume of the silica matrix.

For determination of the Cu(II) adsorption capacities of the resulting sorbents, adsorption from solutions containing various concentrations of metal ions was studied. The maximum capacities of the modified silicas in relation to Cu(II) ions and achieved concentrations of bonded reagents, determined by UV spectroscopy, are listed in Table 1. The degree of reagent anchorage attained on the surface of the silica matrix for PAR, PAN and 8-HQ was 70, 42 and 56%, respectively.

Table 1 Concentrations of reagents bonded to the silica surface that were attained in the immobilization of some phenol derivatives via the Mannich reaction

Modified silica	Concentration of reagent attached to surface/mol g^{-1}	
	UV spectroscopic data	Adsorption of Cu^{2+} ions
SG–PAR	–	$2.8\cdot10^{-5}$
SG–PAN	$8.50\cdot10^{-5}$	$8.5\cdot10^{-5}$
SG–8-HQ	$4.22\cdot10^{-4}$	$2.7\cdot10^{-4}$

The modified silica samples obtained were characterized by the diffuse reflectance infrared Fourier transform (DRIFT) method (Fig. 1). The absorption bands of the stretching vibrations of the C–H bonds in the surface chemical compounds were observed near 2800–3000 cm^{-1}. Bands in the region 1400–1600 cm^{-1} can be attributed to bending vibrations of the grafted organic molecules.

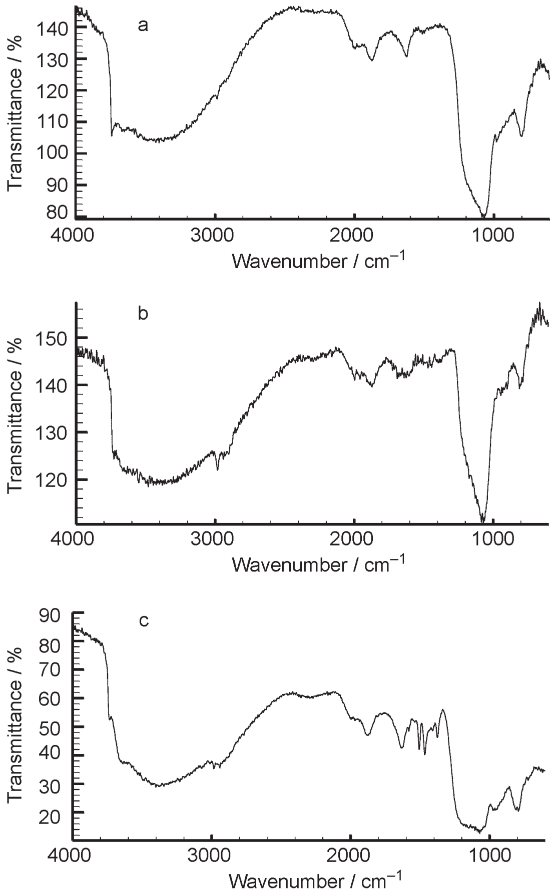


Fig. 1 DRIFT spectra of 1 – 4-(2-pyridylazo)resorcinol; 2 – 1-(2-pyridylazo)-2-naphthol and 3 – 8-hydroxyquinoline immobilized on silica gel surface

Conclusions

A single-stage method of immobilization of some important analytical reagents of phenolic type was developed, with simultaneous aminomethylation and condensation of the products of the Mannich reaction with the silanol groups of the silica surface. The possibility of the single-stage attachment of phenol derivatives to the silica surface via the Mannich reaction was illustrated on the examples of PAR, PAN and 8-HQ. Reaction conditions and component ratios were found for grafting of the analytical reagents. Physicochemical characterization of the synthesized modified silicas was carried out by spectral and adsorption methods. The materials obtained are of promise for use in planar chromatography and for the solid-phase extraction of metal ions.

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