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IMMOBILIZATION OF OPTICALLY ACTIVE OLEFINS ON THE SILICA SURFACE BY COMBINED HYDROSILYLATION AND SOL–GEL TECHNOLOGY

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Abstract

By means of hydrosilylation reactions between functional olefins and triethoxysilane in the presence of Speier's catalyst and sol–gel transformations of the reaction products, a number of optically active and complexing alkenes (quinine, quinidine, cinchonine, cinchonidine, alprenolol, N-allylrhodanine and hemin) were immobilized on the surface of silica. The structures of the compounds formed and the nature of their bonding with the surface were studied by DRIFT and NMR spectroscopies. The concentrations of olefins anchored to the surface layer of the silica matrix were estimated by UV spectroscopy.

Keywords: catalytic hydrosilylation, functional olefins, immobilization, silica surface

Introduction

The immobilization of optically active compounds on a silica surface is of considerable interest; such an approach greatly expands the opportunities of synthesis of chiral stationary phases for the separation of optical isomers in biological systems and clinical samples [1–3]. After their immobilization, it is important to ensure not only a high degree of active compound grafting on the silica surface, but also the preservation of the main properties as potential chiral selectors.

In recent years, the prospect of the use of solid-phase hydrosilylation reactions for the preparation of hydrolytically stable surface chemical compounds with silicon–carbon bonds in the modifying layer of silica have been demonstrated [4–5]. The presence of radicals with double bonds in the molecules of a number of cinchonic alkaloids (quinine, quinidine, cinchonine and cinchonidine), and in the structures of alprenolol, hemin and N-allylrhodanine permits their immobilization on the silica surface via catalytic hydrosilylation reactions, which usually proceed under rather mild conditions. System-

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atic research in this direction has not been carried out, though quinine [7], *R*(+)-1-(α-naphthyl)ethylamine [3] and menthol [6] have been anchored on a silica surface by means of catalytic hydrosilylation reactions.

Experimental

Quinine, quinidine, cinchonine, cinchonidine, alprenolol, N-allylrhodanine, hemin (Aldrich) and triethoxysilane (Kremnepolimer) were used without preliminary purification. A 0.1 M solution of hexachloroplatinic acid (Aldrich) in 2-propanol (chemically pure, Reakhim) was used as the catalyst for the hydrosilylation reaction (Speier's catalyst). Isopropanol was previously subjected to additional drying over molecular sieve 4A. As a silica matrix, Silochrom with a specific surface area of about 100 $m^2 g^{-1}$ was applied.

IR spectra were measured with a Fourier-transform IR spectrophotometer by the diffuse reflectance method in the range 4000–600 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. After the dissolution of weighed portions (10 mg) of modified silica in 5 ml 0.1 M potassium hydroxide solution, the concentrations of grafted organic compounds were determined by UV spectroscopy (Specord UV-VIS).

Results and discussion

Many hydrosilylation reaction catalysts [8–10], e.g. various compounds and complexes of the platinum and transition metals (Pt, Rh, Pd, Ir, Ni, Cr and Ti), are known. The most effective, accessible and 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 chosen active compounds by solid-phase hydrosilylation reactions involving the participation of ≡SiH groups previously fixed on the silica surface. The data obtained revealed that the solid-phase hydrosilylation reactions involving surface ≡SiH groups and functional olefins proceed with low yields in relation to the surface sites. The difficulties can be explained on the basis of the mechanism put forward by Lewis and Lewis [11, 12] for the hydrosilylation reaction. In contrast with the reaction mechanism initially proposed by Chalk and Harrod, it is presumed that the hydrosilylation reaction catalysed by Pt-containing catalysts (basically by low-valence Pt-containing complexes), results in the formation of Pt-colloid, and attack on the hydrosilane precedes attack on the olefin. The important influence of oxygen as co-catalyst is taken into account; Pt-colloid is not formed in the absence of oxygen. Thus, with this mechanism in mind, one of the main stages of the catalytic hydrosilylation reaction is Pt-colloid formation. On the basis of the above reasoning, the difficulties involved in the solid-phase catalytic hydrosilylation reaction, as contrasted with similar processes in solution, can be connected with difficulties in the migration of the Pt-colloid formed along the silica surface.

The experimental data obtained allow the assumption that difficulties of immobilization of functional olefins by means of solid-phase catalytic hydrosilylation reactions may be solved if the hydrosilylation of the hydrosilane and olefin is performed in solution, with subsequent anchorage of the reaction product in the surface layer. Similar syntheses have been reported [7, 13]. For immobilization of the active compounds on the silica surface, we have combined into one process the hydrosilylation reaction and the common technological sol–gel transformations so as to ensure the processes reflected by the following general scheme:

a) $$(C_2H_5O)_3SiH+CH_2{=}CH\text{–}R \xrightarrow{H_2PtCl_6} (C_2H_5O)_3SiCH_2CH_2R$$

$$\equiv Si\text{–}OH+(C_2H_5O)_3SiCH_2CH_2R \xrightarrow{H_2O;\ 0.1\ M\ HCl} \equiv Si\text{–}O\text{–}\overset{|}{\underset{|}{Si}}\text{–}CH_2\text{–}CH_2\text{–}R$$

b) $$(C_2H_5O)_3SiCH_2CH_2R \xrightarrow{H_2O;\ 0.1\ M\ HCl} RCH_2CH_2SiO_{1.5}$$

The main experimental procedures used according to this scheme are described below on the example of cinchonine anchorage. 5 mmol (for 10 g silica) cinchonine, 20 isopropanol, 0.7 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 placed in a thermostat at 80°C for 30 min. The reaction mixture was periodically stirred. Thereafter, 5 mmol triethoxysilane was added to the reactor, and the mixture was held at 80°C for 6 h. It should be stressed that the amount of Speier's catalyst in the reaction mixture is 1000 times less on a molar basis than the amount of the hydride-containing component triethoxysilane. Then, 15 ml isopropanol and 10 g Silochrom were added to the reactor and the mixture was kept in the thermostat 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 grafted layer were synthesized in a similar manner. Appropriate amounts of reagents taken for the syntheses and the concentrations of grafted functional groups achieved are listed in Table 1.

The synthesized samples containing immobilized active compounds were characterized by methods of IR spectroscopy involving diffuse reflectance (DRIFT) and high-resolution solid state ^{13}C NMR. The concentrations of grafted 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 silica and then transferred into solution by treatment by alkali are the same. This allows 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 given in Fig. 1. It is seen from the IR spectra of the modified

Table 1 Component ratios in the syntheses of modified silicas, and the concentrations of functional groups grafted to the matrix surface that were attained

Bound olefin	Olefin/ mmol	Solvent for olefin	Triethoxysilane/ mmol	Isopropanol/ ml	Silica/ g	Water/ ml	Grafted groups/ mmol g^{-1}
Cinchonine	5	20 ml *i*-C_3H_7OH+ 0.7 ml CH_3COOH	5	15	10	1	0.08
Quinine	5	10 ml *i*-C_3H_7OH+ 0.5 ml CH_3COOH	5	25	10	1	0.13
Cinchonidine	5	10 ml *i*-C_3H_7OH+ 0.7 ml CH_3COOH	5	25	10	1	0.13
Quinidine	2	10 ml *i*-C_3H_7OH+ 0.35 ml CH_3COOH	2.5	8	5	0.5	0.04
N-Allylrhodanine	5	10 ml *i*-C_3H_7OH+ 0.5 ml CH_3COOH	5	25	10	1	0.015
Alprenolol	2	10 ml *i*-C_3H_7OH+ 0.5 ml CH_3COOH	2.5	8	5	0.5	0.007
Hemin	1	4.5 ml $HCON(CH_3)_2$+ 10 ml *i*-C_3H_7OH+ 0.1 ml CH_3COOH	2.5	8	5	0.5	0.01

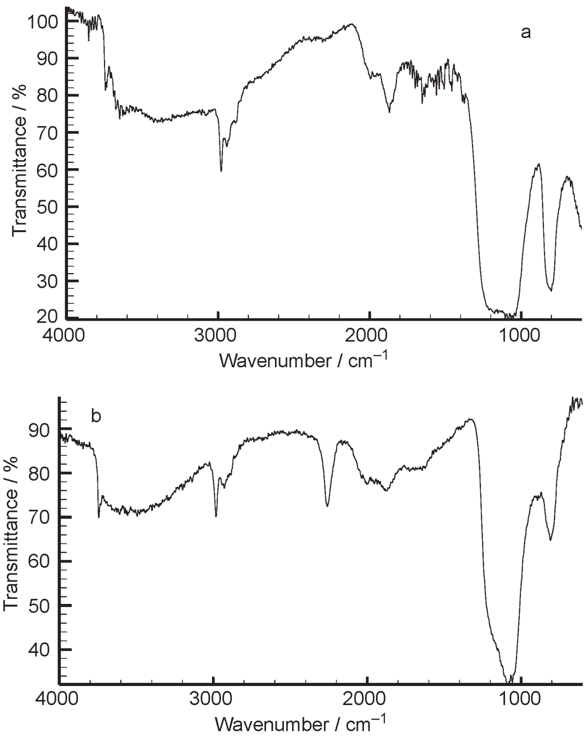

Fig. 1 DRIFT spectra of silica modified with a – cinchonine and b – allylrhodanine

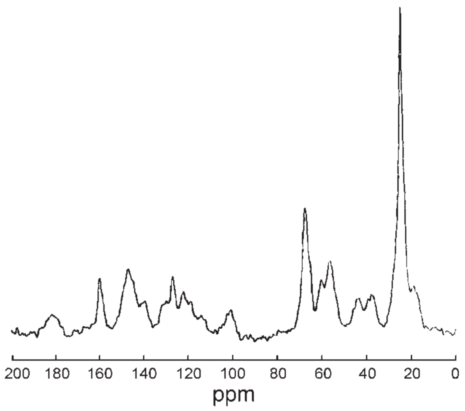

Fig. 2 ^{13}C NMR CP-MAS spectrum of silica containing immobilized quinine

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 ≡SiH groups). The sole exception is the spectrum of the silica sample containing immobilized N-allylrhodanine. The smaller degree of ≡SiH group substitution in the latter case is most probably determined by inhibition of the catalyst as a result of platinum chelation with N-allylrhodnanine.

The ^{13}C NMR spectrum for the modified silica containing grafted quinine (Fig. 2) 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.

Conclusions

The combined use of a catalytic hydrosilylation reaction and a sol–gel approach allows the anchorage on silica of many functional olefins, including optically active and complexing compounds. For some complexing reagents (e.g. N-allylrhodanine), a lower degree of ≡SiH group substitution is observed as a result of inhibition of the platinum catalyst.

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