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Mechanochemical Interaction of Silicon Dioxide with Chelating Polyphenol Compounds and Preparation of the Soluble Forms of Silicon

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Abstract

Mechanochemical treatment of pyrocatechin and natural gallocatechins with amorphous silicon dioxide leads to an increase in the rate of silicon dioxide dissolution as a result of the formation of chelate complexes. On the basis of model systems, we propose a mechanism of the interaction of polyphenols with silicon dioxide including the interaction of hydroxyl groups on the surface of silica with polyphenols and the formation of surface complexes. Starting from the proposed mechanism, we developed a procedure for the directed hydroxylation of the surface. Its application causes an increase in the process efficiency.

Key words: silicon dioxide, pyrocatechin, mechanocomposite, increase in dissolution rate, surface complexes

INTRODUCTION

Silicon belongs to the group of elements that are necessary for the normal development of animal and human organisms. The daily mean dose of SiO_2 for humans is 25.0+19.4 mg. Silicon promotes the biosynthesis of collagen, bone calcification, participates in phosphor metabolism and in lipid exchange, is included into elastin of blood vessels rendering them elasticity and governing their permeability, improves assimilation of phosphates in plants, protects plants from fungal infections [1–5]. The highest biological efficiency is exhibited by the organic derivatives of orthosilicic acid: orthosilicic esters with proteins and polysaccharides, esters of oxycarboxylic and oxybenzoic acids, ethers of polyphenols [6].

Silicon forms chelate compounds with oxygen- and nitrogen-containing organic compounds in which silicon atom is coordinated by six polar atoms. Their formation requires the absence of spatial hindrance and the necessary orientation of coordinated atoms. Aromatic compounds containing hydroxyl groups in the ortho position meet these requirements. Pyrocatechin possesses the structure of this kind because its hydroxyl groups are located in the plane of the ring, and oxygen–oxygen distance is equal to the distance between oxygen atoms in the structure with octahedral coordination of silicon atoms.

Usual methods used to obtain the chelate complexes of silicon with polyphenols are those based on the interaction of reagents in aqueous solutions of bases under long-term heating [7–9]. Polyphenols in the liquid phase easily get oxidized and polymerized, so the search for synthesis methods devoid of side reactions is urgent. During the solid-phase mechanochemical synthesis, the reagents and products are in the stable solid form, which allows one to prevent

oxidation and losses of the major biologically active components [10].

Development of a simple method of obtaining silicon compounds soluble under normal conditions in the neutral media with the formation of monomeric forms of silicon dioxide opens the outlooks for the development of efficient preparations for plant cultivation, animal husbandry and prophylactic medicine.

The goal of the present work is experimental investigation of mechanochemical reactions of silicon dioxide with pyrocatechin modelling the natural polyphenol compounds that are present in plants, peat, and brown coal.

MATERIALS AND METHODS

Reactives

Silica gel for chromatography, the fraction 325–200 μm, with specific surface 290 m^2/g, pyrocatechin with the 99 % purity (Alfa Aesar), ammonium molybdate of chemically pure grade ("kh. ch.", GOST 3765–78), sulphuric acid ("kh. ch.", GOST 4204, Reakhim), ascorbic acid ("ch. d. a.", GOST 4815), oxalic acid ("kh. ch.", GOST 22180–76), ammonium acetate ("ch.", GOST 3117–78), ammonia ("kh. ch.", GOST 3760–79), sodium silicate (GOST 50418–92), KBr ("os. ch.", 22–3, GOST 4160–74), formalin ("kh. ch.", GOST 1625–89, Reakhim Co.), acetonitrile (grade 1, Kriokhrom Co., Russia), twice distilled water (GOST 6709–72) were used in the work.

Mechanical treatment of silica gel with polyphenol compounds

Mechanical treatment was carried out in a vibratory mill SPEX Mill 8000 (USA) and in a planetary centrifugal mill AGO-2 (ISSCM, SB RAS, Novosibirsk) with water-cooled cylinders. The conditions of mechanical treatment in AGO-2 were: reactor rotation frequency 630 min^{-1}, acceleration of milling bodies 20*g*. The residence time of the material under treatment in the affected zone was 40–120 s, the mass ratio of the reagents was 10 : 1.

Investigation of the dissolution of silicon dioxide

Dissolution of the samples was performed in the 0.01 M buffer solution prepared from ammonium acetate, under permanent mixing with a magnetic mixer (600 rpm), with the hydromodulus equal to 1000, and temperature 25 °C. The pH of solution was determined on an Anion 4100 ionometer-conductometer. Samples were taken every 10–30 min. The samples were centrifuged for 5 min (7000 rpm). The supernatant was used for spectrophotometric analysis.

Determination of the concentration of soluble monomer forms of silicon using the spectrophotometric method

Analysis of the concentration of the monomer silicon forms was carried out by means of spectrophotometry [11] on an UNICO-2800 spectrophotometer (USA). The procedure was optimized taking into account the specific features of the reagents used in the work and mechanically activated samples. To eliminate the side effect of free phenols that form yellow complexes with ammonium molybdate, we chose formalin. We determined the optimal time between reagent adding procedures and chose the two-wavelength mode of photometric determination at the wavelengths of 810 and 1000 nm, which minimizes the background superpositions. During each photometric determination, simultaneously with the examination of solutions we carried out calibration with the standard solution. Silicon content was calculated with respect to this calibration.

Specific surface of the samples was determined by means of the thermal desorption of argon using a Katakon Sorbimetr M instrument (Russia).

The IR spectra were recorded with a Lumex-Siberia Infralyum-801 spectrophotometer (Russia) within the range 400–4000 cm^{-1} in tablets with KBr (4 mg of the sample with 540 mg of KBr).

TGA and DSC were carried out with a STA 449C Jupiter instrument for synchronous thermoanalysis (Netzsch, Germany). Sample tem-

perature was increased during experiments from 27 to 300 °C in argon flow with the heating rate of 2 °C/min.

RESULTS AND DISCUSSION

The starting point of the investigation was the examination of the dynamics of silicon dioxide dissolution in the presence of pyrocatechin in the alkaline medium. The time of sample dissolution approximately corresponds to the residence time of substances in the gastrointestinal tract (4–5 h). The results are presented in Fig. 1, *a*.

One can see that the introduction of pyrocatechin allows one to increase the dissolution rate with respect to the initial sample, most likely due to the formation of complex compounds. However, high pH values necessary for this are inapplicable in biological media. The medium for the dissolution of samples should be weakly alkaline or weakly acidic (pH ≤ 8). Because of this, in the main experiments we carried out the dissolution of samples in the buffer solution with pH 7, which is the optimal value compatible with different kinds of biological tissues. A decrease in the dissolution rate of silicon dioxide in fact by a factor of 2 in comparison with the previous case (at pH 9.5) was demonstrated. The dissolution rate of the physical mixture of pyrocatechin with silica gel only slightly differs from the dissolution rate of the initial silica gel (see Fig. 1, *b*). So, in this case the rate of silicon dioxide dissolution does not increase substantially, and the formation of the complex compounds is silicon does not occur.

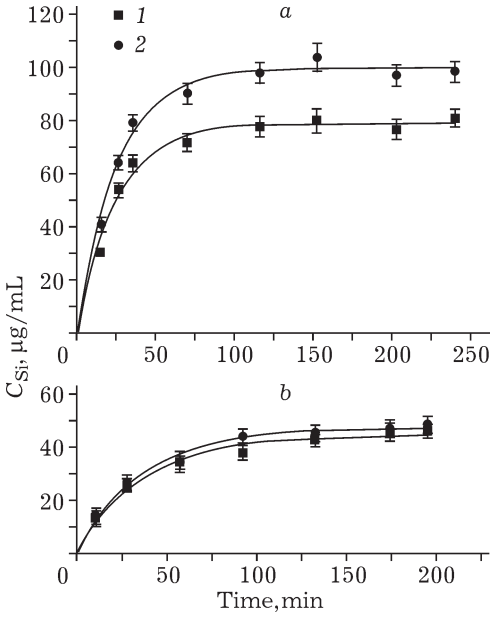

Fig. 1. Dissolution dynamics of initial silica gel (*1*) and silica gel in the solution of pyrocatechin (*2*). pH values: 9.5 (*a*), 7.0 (*b*).

We carried out the joint mechanical activation of silica gel and pyrocatechin. Optimal duration and intensity of action were chosen so that no degradation of samples occurred according to the data of chromatographic analysis.

We studied and optimized the processes that lead to the formation of the solid mechanocomposite of silica gel with pyrocatechin. This composite is a heterogeneous system composed of two phases. Its properties are defined by the developed interface. The physicochemical features of the mechanocomposite are determined by the excess energy arising as a result of the interphase surface interaction and activation of the initial phases. Improved conditions for mass exchange between the particles of the reagents comprise the one of the major properties of mechanocomposites. So, mechanochemical activation with partial transformation of phases occurs at the contact boundary.

After the addition of water to mechanocomposite, the interaction between components starts. The reaction rate at the interface is much higher than that for the dissolved components. As a result, the mechanical activation of silica gel in the presence of pyrocatechin allows one to increase the rate of its dissolution in the neutral medium by a factor of 3–5 in comparison with the samples of the same silica gel subjected to mechanical activation under the same conditions but without additives (Fig. 2, *a*).

Activated silica gel dissolves in the solution of pyrocatechin with somewhat higher rate than that for water (see Fig. 2, *a*). However, the rate of dissolution is much lower than the rate of dissolution of the mechanocomposite of silica gel with pyrocatechin, especially at the initial stages of dissolution. This circumstance points to the possibility of the interaction of silicon dioxide and pyrocatechin as early as at the stage of the joint mechanical activation.

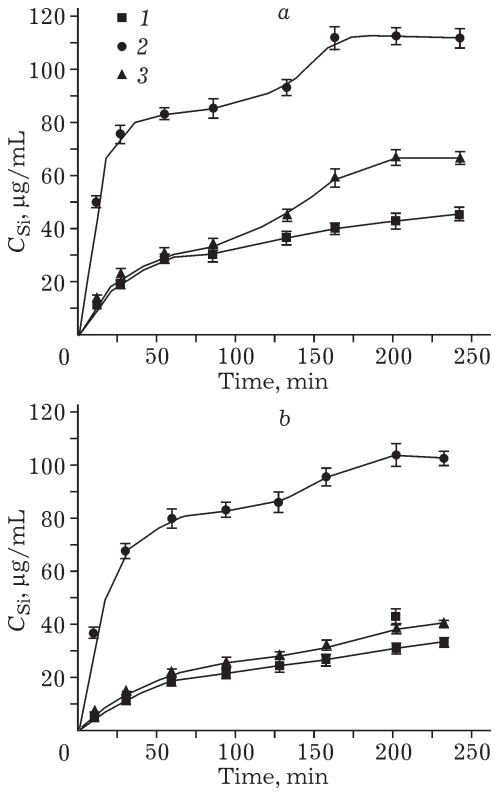

Fig. 2. Dynamics of the dissolution of activated silica gel (*1*), silica gel with pyrocatechin activated together (*2*), activated silica gel in the solution of pyrocatechin (*3*): *a* – freshly prepared systems; *b* – systems after storage in the solid state for 14 days.

It is known that mechanically activated samples are capable of relaxation: depending on the conditions of treatment and the type of treated material, annealing of the defects in the activated sample is observed during storage; as a consequence, its reactivity decreases. The effect under discussion can be enhanced under the action of external factors: temperature difference, changes of humidity *etc*. Relaxation processes are often localized on the surface and levels the effect of the developed interface.

To study the stability of the resulting preparations during storage, we carried out dissolution under identical conditions after 14 day and after a month since mechanical treatment. The dissolution curve for the mechanocomposite remained in fact unchanged, while the rate of dissolution of activated silica gel in water and in the solution of pyrocatechin decreased by approximately 30–40 % (see Fig. 2, *b*).

Thus, it was established that no substantial changes of the properties of resulting mechanocomposites occur during their storage, while the preparations based on mechanically treated silica without additives are unstable due to relaxation processes.

Investigation of the kinetics and mechanism of the interaction in silica gel–pyrocatechin system was carried out for the purpose of increasing the process efficiency.

Several regions can be distinguished on the dissolution curve of the mechanocomposite (see Fig. 2, *a*). Within the first 30–40 min, dissolution rate is maximal; the curve has a steep slope. During the next 60–80 min, dissolution rate decreases sharply, and we observe a break of the curve; dissolution curve is parallel to the time axis. On the third region, dissolution rate again increases. This dissolution can be represented as a superposition of the dissolution of active and inactive forms. It is likely that the active form is rapidly dissolving at the first region, after which the kinetics of product formation is determined by its accumulation.

This active form may be amorphous silicon dioxide with surface hydroxyl groups through which the interaction with pyrocatechin proceeds.

To study the role of surface hydroxyl groups in the reaction between silica gel and pyrocatechin, we carried out preliminary hydroxylation of silica gel surface. The sample in mixture with water (0.4 %) was treated in mechanical activator AGO-2 for 80 s. Mechanical treatment involves distortion of Si–O–Si bonds on the surface; as a result, the probability of hydrolysis accompanied by the formation of Si–OH groups increases. Then pyrocatechin was added, and treatment was carried out for 40 s to perform the reaction.

As a result, the rate of dissolution of the mechanocomposite based on hydroxylated silicon dioxide increases with respect to the dissolution rate of mechanocomposite obtained without preliminary hydroxylation. The dissolution curve has a monotonous character (Fig. 3). Thus, almost the whole surface of silicon dioxide becomes active for the interaction with pyrocatechin.

Annealing of initial silica gel at 300 °C for 3 h causes dehydroxylation of the surface with the formation of siloxane bonds that inactivate the surface. The dissolution of mechanocom-

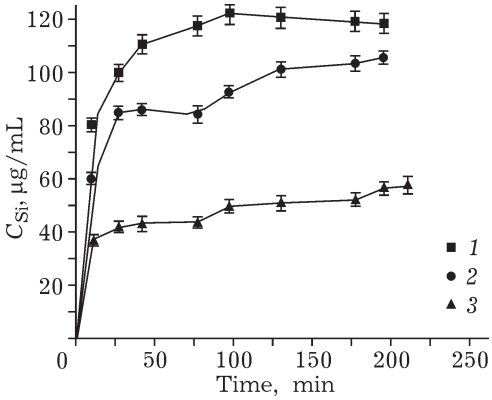

Fig. 3. Dynamics of silica gel dissolution after mechanical activation with the addition of water: *1* – silica gel, pyrocatechin and water activated together (10 : 1 : 0.4); *2* – silica gel and pyrocatechin (10 : 1) activated together; *3* – annealed silica gel and pyrocatechin (10 : 1) activated together.

posite based on pyrocatechin and annealed silicon dioxide is characterized by a decrease in dissolution rate and a substantial decrease in the level of the plateau to which the dissolution curve comes within 4 h.

Experiments with preliminarily hydroxylated and dehydroxylated samples show that hydroxyl groups on the surface determine the reactivity of amorphous silicon dioxide in its interaction with polyphenol compounds. It was discovered that hydroxylation affects the dissolution rate only in the case if the chelating agent is present in the system. This is evidenced by the coincidence of dissolution curves for initial, hydroxylated and annealed silica gel. This is connected with the fact that dissolution of silicon dioxide in the absence of chelating agent proceeds according to Iler's mechanism [3].

The interaction of pyrocatechin with the hydroxyl groups of silica gel results in the formation of surface complexes. The transport of pyrocatechin molecules to the surface of silica gel can proceed over the gas phase or liquid. According to TGA data, sublimation of pyrocatechin is observed at as low a temperature as 80–90 °C. This allows one to assume that pyrocatechin molecules pass over the gas phase to the freshly formed silica gel surface during mechanical treatment. Sufficient temperature in local regions can be achieved according to the hot-region mechanism.

Transportation of pyrocatechin can proceed also over the liquid phase during the dissolution of the mechanocomposite. In this case the mechanocomposite plays the part of a microreactor with the higher efficiency due to shortened diffusion routes of the reagents.

According to the IR spectroscopic data, for the mechanocomposite based on hydroxylated silica gel and pyrocatechin, we observe smearing of the peaks corresponding to the bending vibrations of Si–O–Si at the frequency of 1100 cm^{-1}. As a rule, this effect points to disordering of the structure and to the formation of new bonds, for example Si–O–C, as the bending vibrations of the latter are within the range region.

Thus, an increase in the yield of monomer forms of silicon dioxide in solution can occur either due to surface activation by hydroxylation and increase in the efficiency of the formation of surface complexes, or due to activation of silica gel and accumulation of excess energy in it as a consequence of the deformation of bonds.

SUMMARY

1. Mechanochemical reaction of silica gel with pyrocatechin causes a substantial increase in the rate of dissolution of silicon dioxide in the neutral medium.

2. On the basis of data obtained, we propose a mechanism of the interaction of pyrocatechin with silica gel. The mechanism includes the interaction of hydroxyl groups on the surface of silica gel with pyrocatechin and the formation of surface complexes.

3. Relying on the proposed mechanism, we chose the procedure for directed surface modification; the application of this procedure allows one to increase the process efficiency and dissolution rate.

4. No substantial changes occur in the obtained mechanocomposites during storage, while preparations based on mechanically treated silica are unstable.

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