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Mechanochemical Interaction of Silicon Dioxide with Organic Acids

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Abstract

The interaction of amorphous silicon oxide (aerosil) with organic acids during mechanical activation in high-energy ball mill was studied by means of IR spectroscopy. It was demonstrated that monomer molecules of mono-, polyhydric and aromatic acids get bound with aerosil through the molecules of adsorbed water: aerosil–adsorbed water–acid. Water molecules form rather strong hydrogen bonds with the basic surface centres in aerosil and with hydroxyls of carboxylic groups in monomer molecules of acids. Both basic and acidic surface centres of the carrier take part in the mechanochemical interaction with aerosil.

Key words: mechanochemical activation, mechanochemical interaction, organic acids, silicon dioxide

INTRODUCTION

Silicon dioxide SiO_2 is a promising material to form composite structures of the organic and inorganic nature. At the same time, only few works in this direction are known, though it was established as early as in 1959 that paramagnetic centres able to enter chemical reactions are formed on quartz surface after mechanical activation (MA) in the inert atmosphere [1]. It is the formation of these active surface centres of acidic and basic character that allows mechanochemical reactions, for example in the systems $Me(OH)_n + SiO_2$ [2–6]. These reactions proceed rapidly in mixtures with hydrated silicon dioxide [7].

The number of works describing the investigation of mechanochemical reactions between an organic substance and silicon dioxide is much smaller. For example, the authors of [8] showed that phenylalanine during the joint MA with various inorganic powders including SiO_2 covers the surface of fine particles of the powder with a thin layer thus preventing their aggregation and agglomeration. The acidity and basicity of the used inorganic powders after MA were studied. In particular, for SiO_2, the presence of acidic centres and a small number of basic ones on the surface was established. Basing on the IR spectroscopic data, the authors of [8] assumed that COO^- groups of phenylalanine interact mechanochemically with acidic centres while NH_3^+ groups interact with the basic centres on the surface of inorganic powders forming mechanocomposites. These results are of interest from the viewpoint of modification of the surface of inorganic powders and obtaining new materials on their basis.

It was established by means of IR diffuse reflectance spectroscopy in the region of the stretching vibrations (ν) of OH groups and NMR (for protons) that the joint MA of indomethacin (IM) and SiO_2 involves mechanochemical dehydration as a consequence of the chemical (acid-base) reaction between silanol groups of SiO_2 and carboxylic groups of IM, with the formation of the IM/SiO_2 mechanocomposite. According to the EPR data, the joint MA is accompanied by charge transfer and leads to the formation of the bridging Si–O–Si bond on the composite surface according to the scheme

$-COOH + -SiOH \rightarrow Si-O-C + H_2O$
and the interaction of methoxy and carbonyl groups of IM with induced free bonds on SiO_2 surface. In the opinion of the authors of [9], this charge transfer corresponds to the rule of electronegativity balance and is confirmed by means of X-ray photoelectron spectroscopy. However, the authors of [9] show only the IR diffuse reflectance spectra within the region 4000–3000 cm^{-1} providing evidence of the participation of silanol groups of SiO_2 and carboxyl groups of IM in dehydration reaction. The authors of [9] do not report any IR spectra in the region of 1800–1100 cm^{-1} that would point to the formation of Si–O–C bonds and, on the other hand, would serve as a confirmation of the accompanying changes in the parameters of vibration bands related to the bonds of carboxyl and methoxy groups. At the same time, in our opinion, these data are necessary for more complete understanding of the processes that occur during the joint MA of silicon dioxide with IM.

On the basis of silicon dioxide [10], nanocomposites of difficultly soluble pharmaceutical substances – pyroxicam and IM – were prepared by means of mechanochemical activation. The possibility to increase the rate of dissolution by a factor of nearly 3 for pyroxicam and by a factor of 28 for IM was demonstrated. Unfortunately, the authors of [10] did not report any data on the character of IM bonds with SiO_2 in the resulting nanocomposite [10]. However, if we take into account the data reported in [9] concerning the fact that a Si–O–C bridging bond is formed between silicon dioxide and IM during their joint MA and the interaction of oxygen atoms of carbonyl and methoxy groups with free bonds induced on SiO_2 surface takes place, the question arises whether the pharmacological activity of IM in this nanocomposite is conserved. This question was no discussed by the authors of [10].

Composites in which biopreparations are immobilized on the surface of silica nanoparticles were obtained. Calculations of the energy of formation of various complexes by separate elements of these preparations and active centres on the support surface were carried out. The character of bonding between the active substance and silicon dioxide in the composite was not analysed [11].

The composites of the complexes of europium (III) with various organic substances involving the silica matrix were obtained [12], the existence of the chemical bond between the active substance and the support, *i. e.* silicon dioxide, was established.

At the same time, it was shown in [13] that neither benzoic acid nor benzoate ion get sorbed on the surface of annealed SiO_2 during their joint mechanical activation. This means that no chemical bonds are formed between the acid and annealed support. This is explained by the fact that Si–O and Si–O–Si functional groups of silicon dioxide are weaker bases (even on the surface of silica particles after mechanical action) than benzoate ion, and thus they cannot act as acceptors of the protons of benzoic acid.

Silicon dioxide is a promising support for the development of composite biopreparations [8–11], so investigation of the role of water and the character of bonding in the system SiO_2–active substance is urgent.

The goal of the present work was to study chemical interaction of various biologically active organic acids with aerosil (SiO_2) during their joint mechanical activation.

EXPERIMENTAL

In our work, we used aerosil, nanometer-sized SiO_2 (<10 nm) and organic acids: monocarboxylic (stearic $C_{17}H_{35}COOH$, lauric $C_{11}H_{23}COOH$), dicarboxylic (succinic $(CH_2)_2(COOH)_2$)), hydroxy acids tricarboxylic citric $(CH_2COOH)_2C(OH)COOH$)), aromatic (benzoic C_6H_5COOH and hydroxy acid – salicylic $C_6H_4(OH)COOH$), monoamino acids (aminoacetic (glycine) NH_2CH_2COOH). All the listed organic acids are biologically active compounds (BAC) and are used in pharmacy.

Mechanical activation was carried out in a ball mill of planetary type AGO-2 with water cooling (the volume of cylinder was 250 cm^3, the diameter of balls made of ball bearing steel was 5 mm, ball load was 200 g, the weighed portion of sample was 4–6 g, the frequency of cylinder rotation around the common axis was ~1000 min^{-1}.

The IR absorption spectra (IRS) were recorded with a Specord-75 IR and IFS-66 spectrometers. The samples were prepared for recording using the standard procedure. The X-ray phase analysis (XPA) was carried out with a DRON-3M and URD-63 diffractometers (CuK_α radiation).

RESULTS AND DISCUSSION

Mechanical activation of initial substances

We established previously that MA of the listed organic acids and their salts in a high energy strain mill for $\tau_a \leq 10$ min does not cause nay substantial changes of their structure [14–17].

Aerosil (SiO_2) is white powder with spherical or nearly spherical particles; it possesses high absorption ability which is determined by its dispersity [18]. The IR absorption spectrum of initial aerosil (Fig. 1, *a*) corresponds to the IRS of amorphous SiO_2 [19]. Te bands in the spectrum are clear, with the maximal at 1100, 800 and 470 cm^{-1}; the first two bands correspond to stretching (ν_3, ν_1) vibrations, and the third one relates to the bending (ν_2) vibrations of SiO_4^- tetrahedrons [19, 20]. The diffraction patterns of aerosil exhibit asymmetric halo in the region of small angles (see Fig. 1, *b*). The data of IRS and XPA provide evidence of the X-ray amorphous structure of aerosil. A broad weak band with the maximum at 3430–3440 cm^{-1} corresponds to ν OH (H_2O) vibrations, a weak band with the maximum at 1640 cm^{-1} relates to $\delta\, H_2O$ vibrations [21, 22]. These bands in the IRS of aerosil (see Fig. 1, *a*) provide evidence of the presence of adsorbed water in aerosil. After MA for 5 min (see Fig. 1, *a*, curve *2*), the ν OH (H_2O) band becomes asymmetric and broadens. At the same time, the maximum of ν_3 band (O–Si–O, Si–O–Si) of the vibrations of SiO_4^- tetrahedrons shifts to lower frequencies: 1100 → 1080 cm^{-1}. A shoulder of this band appears in the region of 950–850 cm^{-1}. The band of bending ν_2 vibrations also shifts: 470 → 460 cm^{-1}.

The data obtained provide evidence that definite perturbations of aerosil structure occur during its MA; this allows us to assume that active centres are formed on the surface of activated aerosil samples ($\tau_a > 1$ min) as a consequence of perturbations of its structure [1]. According to the data of the authors of [8], active centres on the surface of mechanically activated SiO_2 have acid character, and only a small part of them are basic in character. It is these basic centres that are likely to interact with adsorbed water molecules through hydrogen bonds. This is confirmed by the appearance of a shoulder of the ν_3 SiO_4^- band in the spectra of activated samples within the region 950–850 cm^{-1}, which should be attributed to the pendular vibrations of water molecules r H_2O [21–23] bound with aerosil. At the same time, the shape and positions of the maxima of ν and δ OH (H_2O) bands change (see Fig. 1, *a*, curve *2*).

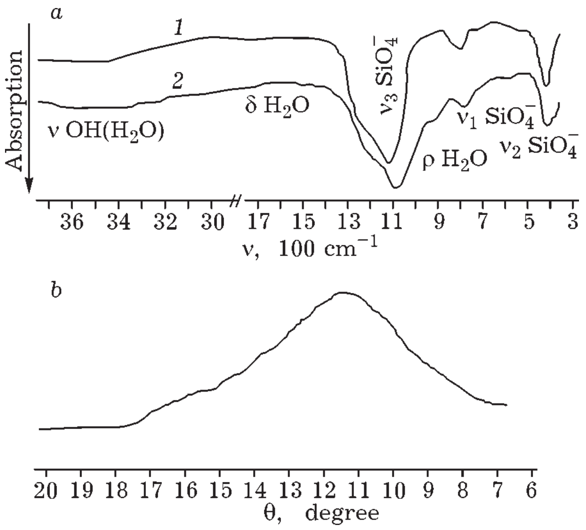


Fig. 1. IRS (*a*) and diffraction pattern (*b*) of aerosil before (*1*) and after MA for 5 min (*2*).

Mechanical activation of aerosil and organic acid mixtures

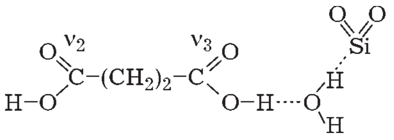
It follows from the analysis of IRS (Figs. 2–7) and diffraction patterns (see Figs. 2, 3) of the mixtures of aerosil with organic acids before and after MA and their comparison with the IRS and XPA data for aerosil before and after MA (see Fig. 1) that silicon dioxide interacts mechanochemically with the acids.

Aerosil and succinic acid mixtures

Indeed, we observe two bands in the IRS of the mixture of aerosil, for example, with dicarboxylic succinic acid (mass ratio of aerosil to the acid was equal to 20 : 1) activated for 3 min, instead of the band of stretching vibrations of carbonyl groups ν_1 C=O of the dimers of initial acid with the maximum at 1685 cm^{-1}: the first band has its maximum at 1725 cm^{-1} and the second is broad, with the maxima at ~1600 and 1550 cm^{-1} (see Fig. 2, *a*, curves *1*, *3* and *4*).

At the same time, the band with the maximum at 1420 cm^{-1} [ν C–O– + δ OH (COOH)] [24, 25] broadens noticeably, its maximum becomes less clear and shifts to ~1445 cm^{-1}. The ν OH band in the region of 3400–2500 cm^{-1} which is characteristic of dimer molecules of the acid [24, 25] disappears. The IRS of the mixture after MA exhibits a broad diffuse band at ~3750–2800 cm^{-1} in the region of the stretching vibrations of OH groups.

The changes of characteristic bands of aerosil in this situation are similar to those in the IRS of aerosil activated fro $\tau_a > 1$ min (see Figs. 1, *a* and 2, *a*, curves *2*). Also a band appears in the region 950–850 cm^{-1}. The data obtained allow us to assume that the MA of the mixture is accompanied by the rupture of bond in the associates of the acid, and its monomeric molecules interact through hydrogen bonds with water molecules that are, in turn, bound with the active centres on aerosil surface through hydrogen bonds. The proposed scheme of aerosil interaction with the acid is:



(1)

According to this scheme, the band with the maximum at 1725 cm^{-1} (see Fig. 2, *a*, curve *2*) should be attributed to ν_2 C=O vibrations of monomer acid molecules, a broad band with weakly pronounced maxima at 1600 and 1550 cm^{-1} – to (δ H_2O + ν_3 C+O) vibrations, and the band with the maximum at 1685 cm^{-1} – to ν_1 C=O vibrations of the initial dimer acid molecules. The band connected with ν C–O– vibrations, as expected [24], shifts to the direction opposite to the shift of ν C=O band, that is, 1420 → 1445 cm^{-1} (see Fig. 2, *a*, curve *2*). A broad diffuse band in the region 3750–2800 cm^{-1} corresponds to the stretching vibrations of OH groups, ν OH of monomeric acid molecules and water molecules bound through hydrogen bonds (see Fig. 2, *a*, curve *2*, and Scheme 1). This conclusion is also confirmed by the XPA data: reflections that belong to initial succinic acid are absent from the patterns of the mixture activated for 3 min (see Fig. 2, *b*, curve *2*).

Taking into account the value of the shift of ν C=O vibration band, we may assume that hydrogen bonds formed between water molecules and monomeric acid molecules are rather strong.

It should be noted that the IRS of the mixtures of aerosil with succinic acid with the mass ratio less than 20 : 1 after MA for $\tau_a \geq 5$ min conserves the bands belonging to dimer acid molecules. For example, for the mass ratio of 6 : 1, the ν_2 C=O band of acid monomer is asymmetrical and has a maximum not at 1725 but at 1720 cm^{-1}, and the shoulder at ~1700 cm^{-1} due to

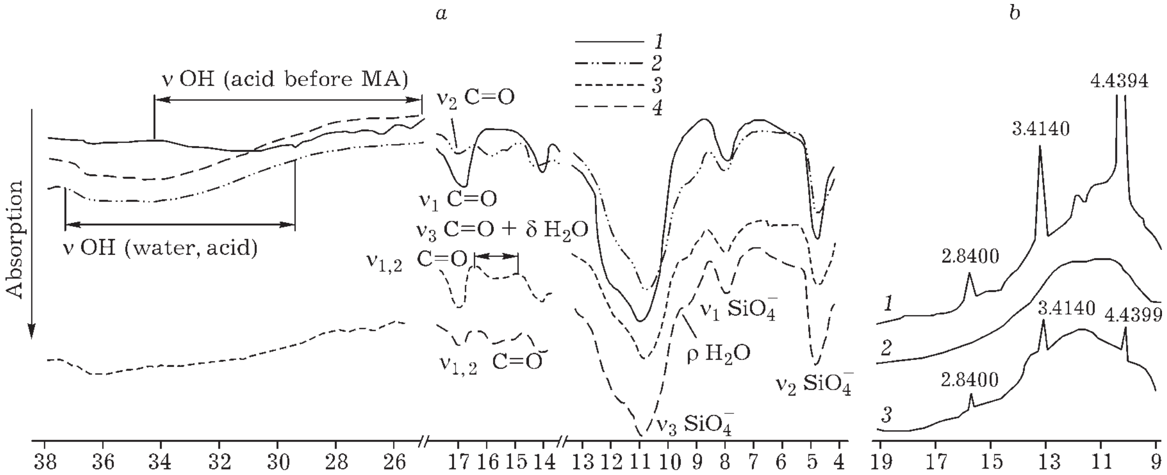


Fig. 2. IRS (*a*) and diffraction patterns (*b*) of the mixtures of aerosil with succinic acid before (*1*) and after MA for 3 min (*2*), 5 min (*3*), 5 min MA + 0.5 mL H_2O (*4*). Mass ratio aerosil/acid = 20 : 1 (*1*, *2*, *4*) and 6 : 1 (*3*, *4*).

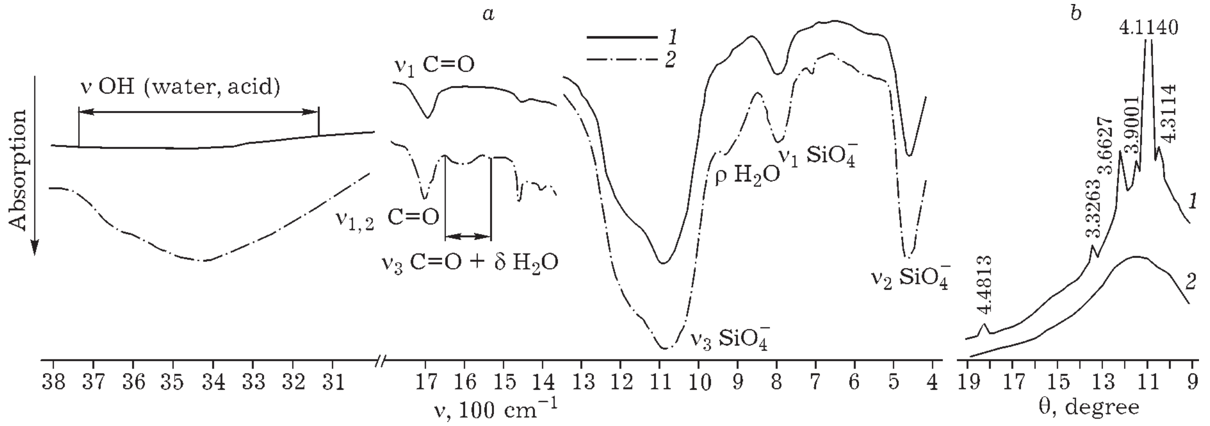


Fig. 3. IRS (*a*) and diffraction patterns (*b*) of the mixtures of aerosil with stearic acid before (*1*) and after MA for 9 min (*2*). Mass ratio aerosil/acid = 20 : 1.

the vibrations of C=O groups of dimer acid molecules ν_1 C=O (see Fig. 2, *a*, curve *3*). In the region of the stretching vibrations of OH groups (3000–2500 cm^{-1}) there are weak but clear maxima characteristic of ν OH of dimer molecules of succinic acid. The diffraction patterns of the same also conserve the reflections of initial succinic acid (see Fig. 2, *b*, curve *3*). We suppose that the presence of the bands of dimer acid molecules in the IRS and diffraction patterns provides evidence of the lack of basic active centres on aerosil surface to bind a larger amount of the acid. Addition of water to the mixture of aerosil with succinic acid at the mass ratio of 6 : 1 in the amount of 0.5 ml does not cause any changes of the situation: the bands of dimer acid molecules are conserved in the IRS of the product of MA. These results additionally confirm our assumption concerning the participation of only basic active centres of aerosil in the mechanochemical interaction with succinic acid. The necessary condition for the completeness of reaction is that the mass ratio of aerosil to succinic acid should exceed 6 : 1.

Aerosil and monocarboxylic acids mixtures

The interaction during the joint MA of aerosil with saturated monocarboxylic acids – stearic (HSt) and lauric (HL) – proceeds in a similar way. For example, for stearic acid (see Fig. 3, *a*, curves *1*, *2*) this interaction is similarly clearly observed only at the mass ratio of aerosil/acid ≤ 20 : 1. Hydrogen bonds of monomer acid molecules with the molecules of adsorbed wa-

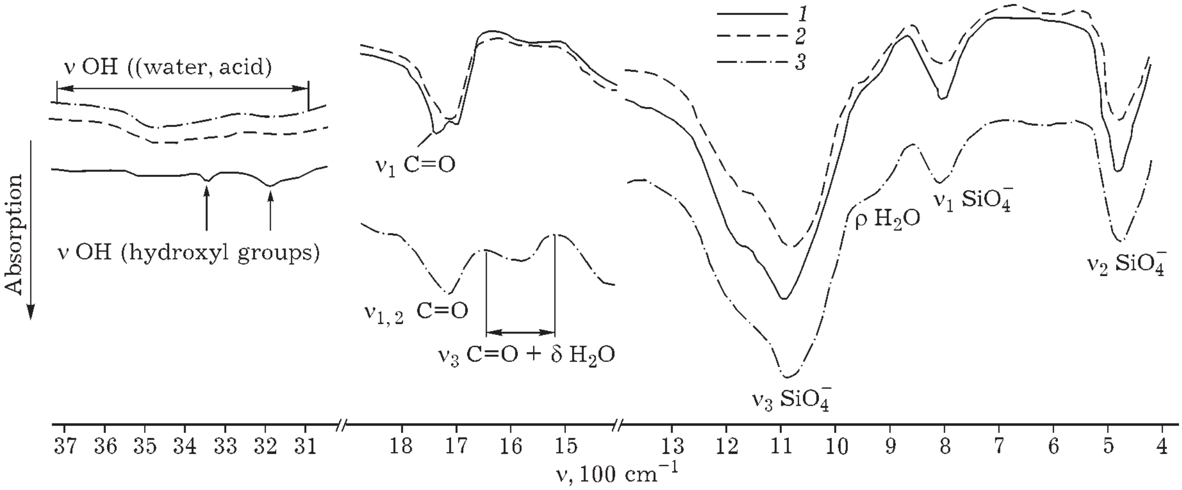


Fig. 4. IRS of the mixtures of aerosil with citric acid after MA for 0.5 (*1*), 3 (*2*) and 5 min (*3*). Mass ratio aerosil/acid = 3 : 1.

ter (see Scheme 1) are likely to be weaker than those in the case of succinic acid.

Indeed, in the IRS of the activated mixture HSt + SiO_2 a broad band (δ H_2O + ν_3 C=O) is shifted to higher frequencies to 1620–1590 cm^{-1}, while the ν_3 SiO_4^- band has a maximum at 1085 cm^{-1}. In the product of MA of aerosil with stearic acid, the maximum ν_3 SiO_4^- is observed 1070 cm^{-1}; the maxima of the sum band (δ H_2O + ν_3 C=O) appear at 1600 and 1550 cm^{-1}.

In the diffraction patterns of aerosil + HSt mixture (at the mass ratio of 20 : 1) activated for 7 min, the reflections of the acid are absent (see Fig. 3, *b*, curve *2*).

The participation of adsorbed water in the mechanochemical interaction of aerosil with mono- and polycarboxylic saturated acids (see Scheme 1) is suggested by the fact that the IRS of composites formed during MA remain unchanged after exposure at 155–160 °C for 3 h.

Aerosil and hydroxy acids mixtures

Mechanical activation of a mixture of aerosil with tricarboxylic hydroxy acid, fro example with citric acid, also leads to the formation of chemical bond between its components. Indeed, the IRS of the activated mixture of aerosil + citric acid, the changes of the bands of silicon dioxide and the acid are observed (see Fig. 4).

The bands of the stretching vibrations of OH groups of carboxylic and hydroxy groups (3700–2900 cm^{-1}) disappear; bands with the maximum at 1725 cm^{-1} appear (ν_2 C=O), as well as at 1650–1550 cm^{-1} (δ H_2O + ν_3 C=O) and 950–850 cm^{-1} – ρ H_2O. In the IRS of non-activated mixture, the ν_1 C=O band of citric acid before MA has two maxima (1710 and 1750 cm^{-1}) belonging to the vibrations ν C=O of the associates of the acid and carboxylic groups that do not participate in the formation of associates, respectively. The diffraction patterns of the activated mixture do not contain reflections of citric acid. These data allow us to assume that not only OH groups of carboxyl but hydroxy groups of the acid participate in the mechanochemical interaction in the system aerosil + citric acid; these hydroxy groups interact with the acid centres on aerosil surface [8]. As a result, the bridging bond is formed between the support and the acid; water is also formed [8, 9]:

$$-\mathrm{C{-}OH} + \mathrm{Si{-}OH} \xrightarrow{\mathrm{MA}} \mathrm{C{-}O{-}Si} + H_2O$$

Citric acid can interact with aerosil at the mass ratio of dioxide/acid = 3 : 1, which is likely due to the possible participation of hydroxy groups of the acid in the interaction.

Aerosil and aromatic acids mixtures

Monocarboxylic acids. The changes of the parameters of SiO_4^- bands in the IRS of activated mixtures of aerosil with benzoic acid at the mass ratio of 20 : 1 (see Fig. 5) are similar tot eh changes in the IRS of the mixtures considered above (see Figs. 2–4). Also the band ρ H_2O appears (950–850 cm^{-1}); the band ν_1 C=O broadens noticeably and becomes asymmetric, the character of absorption in the regions 3750–2400 cm^{-1} changes (the vibrations ν OH, of

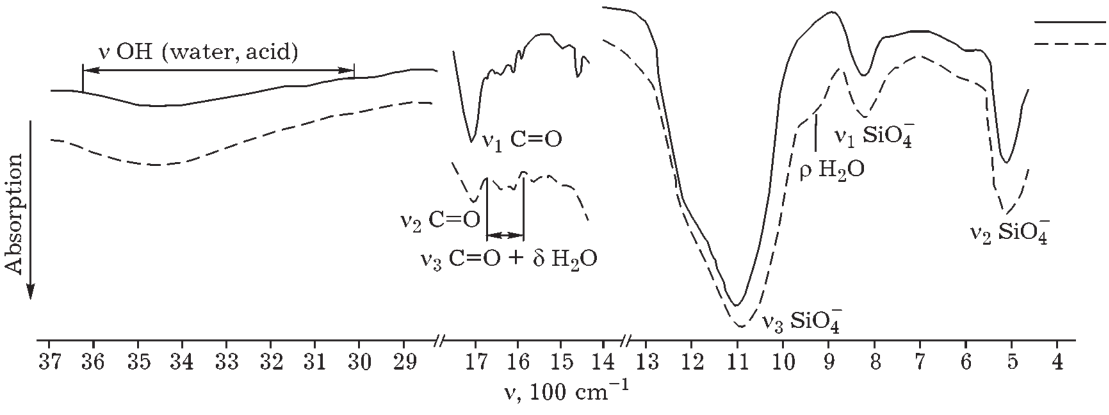


Fig. 5. IRS of the mixtures of aerosil with benzoic acid before (*1*) and after MA for 3 min (*2*). Mass ratio aerosil/acid = 20 : 1.

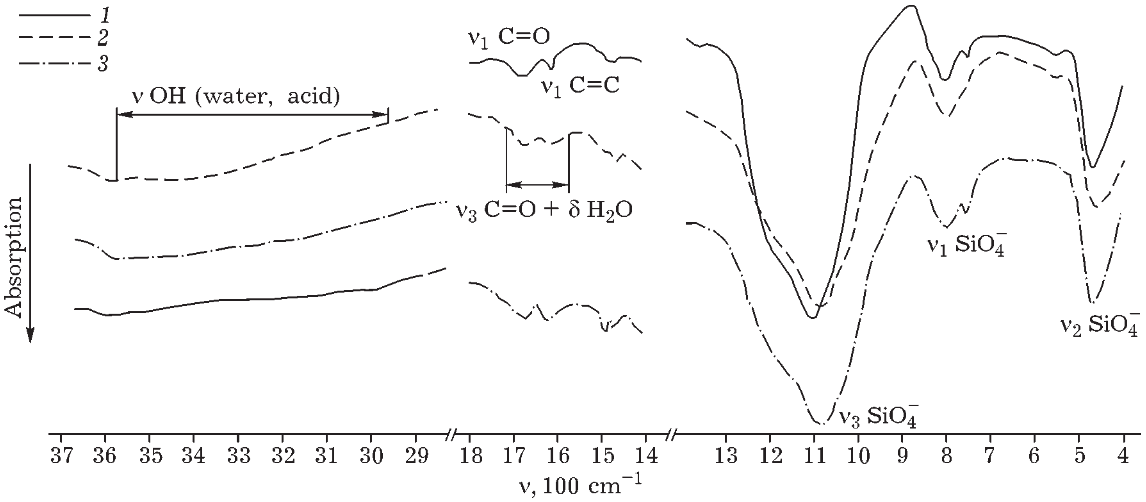


Fig. 6. IRS of the mixtures of aerosil with salicylic acid before (1) and after MA for 3 (*2*), 5 min (*3*). Mass ratio aerosil/acid = 14 : 1 (*1*, *2*) and 7.5 : 1 (*3*).

water and benzoic acid). However, these changes are less clear, perhaps due to the presence of five bands of the in-plane vibrations of the skeleton ν C=C in the region of 1650–1430 cm^{-1} [24, 25]; one of these bands is shifted to lower frequencies (1585 → 1560 cm^{-1}) because the position of the band depends on the type of substituents. These facts, including the shift of one of the ν C=C bands, can be the evidence of the presence of mechanochemical interaction of aerosil with benzoic acid during the joint MA. This is also indicated by the XPA data: acid reflections are absent from the diffraction patterns of the aerosil/benzoic acid composite.

According to the data of the authors of [13], such an interaction in the system SiO_2 + benzoic acid is impossible in the case of annealed SiO_2. We used non-annealed aerosil; therefore, it is water that serves as the binder in the mechanocomposite aerosol/benzoic acid.

Aromatic hydroxy acids. The mechanochemical interaction of aerosil with salicylic acid differs substantially from its interaction with benzoic acid because aromatic hydroxy acids can exhibit chemical properties of monocarboxylic acids and monoalcohols.

Indeed, it follows from the analysis of IRS (see Fig. 6) that after MA of a mixture of salicylic acid with aerosil (at the mass ratio of 14 : 1) for 1 min the intensity of the band at 1665 cm^{-1} (ν_1 C=O of carboxylic groups of the acid) decreases noticeably; the band broadens and its maximum becomes diffuse. In the region of 1650–1550 cm^{-1} instead of a narrow band ν C=C (1615 cm^{-1}) [24, 25] a broad band appears, with two maxima at ~1615 and 1595 cm^{-1} (the latter is more clear). Similarly to the mixture of aerosil with mono- and polycarboxylic acids, the shift of ~1615 and 1595 cm^{-1} bands is observed in the IRS of the mixture. However, unlike for the examples considered above, the ρ H_2O band as a shoulder of the ν_3 SiO_4^- band in the region of 850–950 cm^{-1} is minimum perceptible (see Fig. 6). So, taking into account the features of the chemical properties of aromatic hydroxy acids, we may assume that both the carboxyl groups and phenol hydroxyls of salicylic acid participate in the mechanochemical interaction with aerosil. Phenol (alcohol) hydroxyls of acids, similarly to hydroxy groups of hydroxy acids, interact with the acidic centres on SiO_2 surface to form water. Carboxylic groups of the acid interact with aerosil during MA similarly to the interaction of mono- and polycarboxylic acids (see Scheme 1), that is, through hydrogen bonds between the hydroxyls of carboxylic groups of monomer acid molecules and water molecules which are, in turn, bound through rather strong hydrogen bonds with the basic centres on the surface of aerosil. The position of the maximum of the band ν C=C (1615 cm^{-1}) in the IRS of aromatic compounds depends on the presence and the nature of substituents [24, 25]. Exactly for this reason, the maximum of the ν C=C band in the IRS of the product

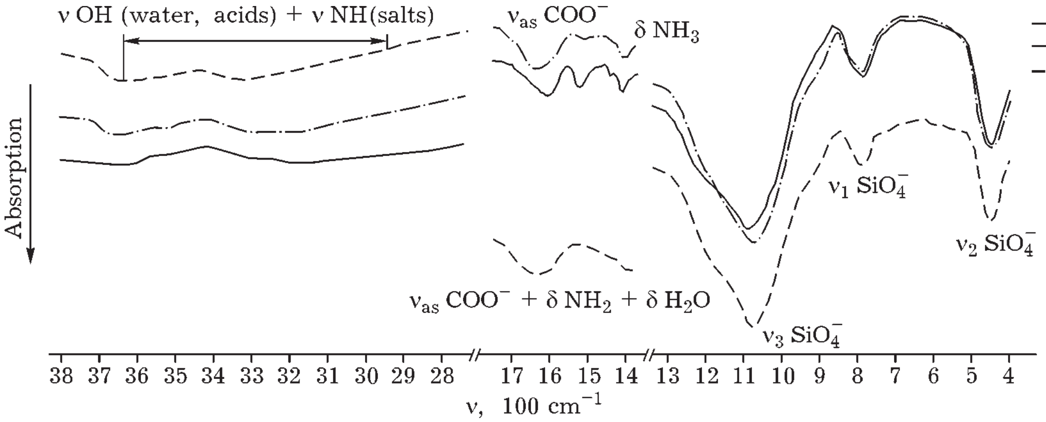


Fig. 7. IRS of the mixtures of aerosil with aminoacetic acid before (*1*) and after MA for 3 (*2*), and 5 min (*3*). Mass ratio aerosil/acid = 8 : 1.

of MA of the mixture of aerosil with salicylic acid shifts to lower frequencies 1615 → 1595 cm^{-1}. The reflections of the acid are absent from the diffraction patterns of the activated mixture of aerosil with the acid.

Aerosil and monoamino acids mixtures

Changes in the characteristic bands of aerosil in the IRS of activated mixtures of aerosil with, for example, glycine after MA are similar to the changes in the IRS spectra of activated systems considered above. For example, in the IRS of SiO_2 + glycine mixture at the mass ratio of 8 : 1 (see Fig. 7) after MA for 3 min, the bands characteristic of the stretching and bending vibrations of NH_3^+ groups disappear: in the regions 3400–2300, 2200–2050 and 1550–1450 cm^{-1}, respectively, as well as the ν_{as} band of COO^- (1700–1550 cm^{-1}) [24, 25]. Instead of the indicated bands, the following bands appear: a broad diffuse band with hardly noticeable maxima at 3650 and 3250 cm^{-1} in the region of 3700–2700 cm^{-1} and a broad band with the maximum at 1635 cm^{-1}. However, unlike for the IRS of activated mixtures of aerosil with aromatic acids, in this case the band of out-of-plane bending vibrations ρ H_2O of bound water is hardly noticeable (see Fig. 7, region 950–850 cm^{-1}).

Similar changes of the bands belonging to the vibrations of NH_3^+ and COO^- groups of amino acids were observed by the authors of [26] when studying MA of leucine with talc and phenylalanine with kaolin, talc, SiO_2 and α-, γ-Al_2O_3 [8]. They assumed that leucine and phenylalanine in activation products are present in the form $NH_2CHRCOO^-$, with both nitrogen and oxygen atoms bound to the support. Relying on the above, as well as on the fact that the ρ H_2O band of water molecules bound with dioxide is almost absent from the IRS of activated aerosil + glycine mixtures, we suppose that the interaction of aerosil with glycine occurs without the participation of water molecules. In the resulting composite material, the amino groups of the acid interact with the basic centres on the surface of the support, while carboxylic groups interact with its acid centres.

In the IRS of glycine + aerosil mixture after MA the band in the region of 3700–2700 cm^{-1} corresponds to the stretching vibrations of NH_2 groups and water molecules, possibly bound with glycine anion and aerosil [21, 24, 26]. The band with the maximum at 1635 cm^{-1} should be attributed to several vibrations: antisymmetric stretching vibrations of COO^- groups of glycine [24, 25], water molecules [21–23] and bending vibrations of NH_2 groups [24, 25]. Overlapping of these bands does not allow us to determine the positions of each of them. The reflections of aminoacetic acid are absent from the diffraction patterns of these samples.

CONCLUSIONS

1. By means of IRS and XPA, we studied the mechanochemical interaction of non-an-

nealed aerosil with biologically active organic acids and established the formation of the chemical bond between the components of composite materials aerosil/BAC.

2. It was shown that in the case of mono-, poly- and aromatic carboxylic acids the molecules of water adsorbed on aerosil serve as the binder between the support and the monomer acid molecules: aerosil–adsorbed water–acid. Water molecules form hydrogen bonds with the basic surface centres of aerosil and with the hydroxyls of carboxylic groups of monomer acid molecules. Hydrogen bonds of the acid with water are rather strong.

3. In the case of hydroxy acids, including aromatic ones, the process of their mechanochemical interaction with aerosil is participated by both the basic and acidic groups surface centres of aerosil: hydroxy groups (phenolic) interact with the acidic centres, while hydroxyls of carboxyl groups, similarly to the hydroxyls of COOH groups of acids, form hydrogen bonds with the molecules of adsorbed water bound through hydrogen bonds with the basic centres on aerosil surface.

4. It was established that amino groups of glycine get partially deprotonated during the interaction with the basic active centres of aerosil on its surface, while COO^- groups interact with its acidic centres.

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