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 a high-energy ball mill was studied by means of IR spectroscopy. It was demonstrated that the monomer molecules of mono-, polycarboxylic and aromatic acids get bound to aerosil through the molecules of adsorbed water: aerosil – adsorbed water – acid. Water molecules form rather strong hydrogen bonds with the basic surface centres of aerosil and with the hydroxyl of carboxylic groups of monomer acid molecules. Both basic and acidic centres of the support take part in the mechanochemical interaction of hydroxy acids, including aromatic, and amino acids, with aerosil.

INTRODUCTION
Silicon dioxide SiO₂ appears to be a promising material for the formation of composite structures of organic and inorganic nature. However, not very many works are performed in this area, though it was established as long ago as in 1959 that paramagnetic centres are formed on the surface of quartz after its mechanical activation (MA) in the inert atmosphere, and these centres are able to participate in chemical reactions [1]. It is the formation of these active paramagnetic centres having the acidic and basic nature that allows mechanochemical reactions, for example in the system Me(OH)ₙ + SiO₂ [2-6]. These reactions proceed rapidly in the mixtures with hydrated silicon dioxide [7]. The number of works studying mechanochemical reactions between an organic substance and silicon dioxide is much smaller. Thus, the authors of [8] showed that phenyl alanine mechanically activated together with various inorganic powders including SiO₂ coats the surface of fine particles of these powders with a thin layer thus preventing their aggregation and agglomeration. The acidity and basicity of the surface of inorganic powders after MA was studied. In particular, for SiO₂ the presence of surface acid centres and a small number of basic ones was established. The data of IR spectroscopy allows the authors to assume that the COO⁻ groups of phenyl alanine interact mechanochemically with the acid centres, while NH₃⁺ groups interact with basic centres on the surface of inorganic powders thus forming mechanocomposites. The results obtained are undoubtedly interesting from the viewpoint of modification of the surface of inorganic powders and obtaining new materials based on them.

It was established by means of diffuse reflectance infrared Fourier transform spectroscopy (DRIRFT) in the region of stretching (ν) vibrations of OH groups and NMR (proton) [9] that the joint mMA of indomethacin (IM) with SiO₂ involves mechanochemical dehydration as a consequence of the chemical (acid-base) reaction between the silanol groups of SiO₂ and carboxylic groups of IM, with the formation of mechanocomposite IM / SiO₂. According to the data obtained by means of EPR, the joint MA is accompanied charge transfer and leads to the formation of a bridging bond Si-O-C on the composite surface according to the scheme –COOH + –SiOH → Si-O-C + H₂O, and to the interaction of methoxy and carbonyl groups of IM with in-
duced free bonds on the surface of SiO$_2$. In the opinion of authors, this charge transfer is in agreement with the rule of electronegativity balancing and is confirmed by the data of X-ray photoelectron spectroscopy. However, presenting the IR spectra of diffuse reflection in the region 4000-3000 cm$^{-1}$, providing evidence that silanol groups of SiO$_2$ and carboxyl groups of IM participate in dehydration, the authors do not show the spectra in the region 1800-1100 cm$^{-1}$, which would confirm the formation of Si-O-C bonds, on the one hand, and would demonstrate the changes in the parameters of vibration bands related to carboxylic and methoxy groups. We think that these data are necessary for more complete understanding of the processes that take place during the joint MA of silica with IM.

Nanocomposites of difficultly soluble medical substances piroxicam and indomethacin were obtained by means of mechanochemical activation with silicon dioxide [10]. The possibility to increase the dissolution rate almost by a factor of 3 was demonstrated for piroxicam and by a factor of 28 for indomethacin. To our regret, no data on the character of bonds between IM and SiO$_2$ in the resulting mechanocomposite are reported. However, if we take into account the data of authors [9] who state that a bridging bond Si-O-C is formed during the joint MA of silicon dioxide and IM, and the interaction between oxygen atoms of carbonyl and methoxy groups with free bonds induced on the surface of SiO$_2$ occurs, the question arises whether the pharmacological activity of IM in such a composite is conserved. The authors did not discuss this aspect.

Composites in which biopreparations were immobilized on the surface of silica nanoparticles were obtained. The energies of formation of various complexes between separate elements of these preparations and the active centres on the surface of the support were calculated. The character of the bonds between the active substance and silicon dioxide in the composite was not analyzed [11].

The composites of europium (III) complexes with various organic substances were obtained using the silica matrix [12], and the occurrence of chemical bonds between the active substance and the support (that is, silicon dioxide) was established. At the same time, it was established in [13] that neither benzoic acid nor benzoate ion get sorbed on the surface of annealed SiO$_2$ during the joint mechanical activation. This means that no chemical bonds are formed between the acid and the annealed support. This is explained by the fact that the functional groups Si-O and Si-O-Si of silicon dioxide are weaker bases (even on the surface of silica particles after mechanical action) than benzoate ion and thus they cannot be acceptors of the protons of benzoic acid.

Silicon dioxide is a promising support for the development of composite biopreparations [8-11], so it seems urgent to study the role of water and the character of bonds in the system SiO$_2$/active substance.

The present work was carried out to study chemical interaction between biologically active organic acids of different nature and aerosil (SiO$_2$) during their joint mechanical activation.

**EXPERIMENTAL**

Aerosil used in the work was nanometer-sized SiO$_2$ (< 10 nm). Organic acids were: monocarboxylic – stearic C$_{17}$H$_{35}$COOH, lauric C$_{11}$H$_{23}$COOH; dicarboxylic – succinic ($\text{CH}_2$)$_2$(COOH)$_2$; hydroxy acids – tricarboxylic citric acid ($\text{CH}_2$COOH)$_2$C(OH)COOH; aromatic acids – benzoic C$_6$H$_5$COOH and hydroxyl-containing salicylic acid C$_6$H$_4$(OH)COOH; monoamino acids – aminoacetic (glycine) NH$_2$CH$_2$COOH. All the mentioned organic acids are biologically active substances (BAS) and are use in pharmacy.
Mechanical activation (MA) was carried out in a ball mill of planetary type AGO-2 with water cooling (cylinder volume: 250 cm³, ball diameter: 5 mm, total mass of balls: 200 g, sample mass: ~ 4-6 g, the frequency of rotation of cylinders around a common axis: ~ 1000 r.p.m.).

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

RESULTS AND DISCUSSION

Mechanical activation of initial substances

It was established by us previously that MA of the organic acids used in the experiments, and their salts in a high-energy mill for more 10 min does not cause any substantial distortions of their structure [14-17].

Aerosil (SiO₂) is white powder with spherical or almost spherical particles, it possesses high absorption capacity depending on its dispersity (particle size) [18]. The IR spectrum of initial aerosil (Fig. 1 a) corresponds to the IR spectrum of amorphous SiO₂ [19]. The bands in the spectrum are clear with the maxima at 1100; 800 and 470 cm⁻¹, the first two bands belong to the stretching (ν³, ν₁) vibrations, the third to bending (ν₂) vibrations of SiO₄ tetrahedrons [19, 20]. The diffraction patterns of aerosil show an asymmetric halo in the small-angle region (Fig. 1b). The IR and XPA data provide evidence of the X-ray amorphous structure of aerosil. Weak bands: a broad one with the maximum at ~ 3430-3440 cm⁻¹ - ν OH (H₂O) and another with the maximum at 1640 cm⁻¹ - δ (H₂O) [21, 22] in the IR spectrum of aerosil (Fig. 1a) provide evidence of the presence of adsorbed water in aerosil. After MA for 5 min (Fig. 1a, curve 2), the band ν OH (H₂O) becomes asymmetric and broadens. At the same time, the maximum of the band ν₃ (O-Si-O, Si-O-Si vibrations) of SiO₄ tetrahedrons shifts to lower frequencies: 1100 cm⁻¹ → 1080 cm⁻¹. A shoulder of this band appears in the region 950-850 cm⁻¹. The band of bending vibrations ν₂ also shifts: 470 cm⁻¹ → 460 cm⁻¹.

![Figure 1](image-url)  
**Figure 1** IR spectrum (a) and diffraction patterns (b) of aerosil before (1) and after MA for 7 min (2).
The data obtained provide evidence that definite distortions of aerosil structure occur during its MA. These distortions allow assuming the formation of active centres on the surface of activated aerosil samples (τₐ > 1 min) as a consequence of the distortion of its structure [1]. According to the data reported in [8], the active centers on the surface of mechanically activated SiO₂ are acid in character, and only some of them are basic. It is likely that these basic centres can interact with adsorbed water molecules through hydrogen bonds. This is confirmed by the appearance of a shoulder near ν₃ SiO₄⁻ band in the region 950-850 cm⁻¹ in the spectra of activated samples. This absorption is to be attributed to pendular ρ H₂O [21-23] vibrations of water molecules bound with aerosil. The shape and position of the maxima of bands ν and δ OH (H₂O) change, too (Fig. 1 a, curve 2).

**Mechanochemical activation of the mixtures of aerosil with organic acids**

The analysis of IR spectra (Fig. 2-7) and diffraction patterns (Fig. 2-4) of the mixtures of aerosil with organic acids before and after MA and the comparison of these data with the IR spectra and XRD data for aerosil before and after activation (Fig. 1) suggest that silicon dioxide interacts mechanochemically with the acids.

**Aerosil + succinic acid**

![Figure 2](image-url)  
**Figure 2** IR spectrum (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 + 0,5 ml H₂O (4); mass ratio aerosil : acid = 20 : 1 (1, 2, 4) and 6 : 1 (3, 4)
Indeed, the IR spectrum of a mixture of aerosil with dicarboxylic succinic acid (Fig. 2a, curves 1, 2) activated for 3 min, with the mass ratio (mr) of aerosil to the acid mr = 20 : 1 instead of the band of stretching vibrations of carbonyl groups ν1, C=O of the dimers of initial acid, with the maximum at 1685 cm⁻¹, exhibits two bands, one of them has its maximum at 1725 cm⁻¹ and a broad one has maxima at ~ 1600 and 1550 cm⁻¹.

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 not so clear and shifts to ~ 1445 cm⁻¹. The band ν OH in the region 3400-2500 cm⁻¹ is characteristic of dimer acid molecules [24, 25]. The IR spectrum of the mixture after MA has a broad diffuse band in the region of stretching vibrations of OH groups at ~ 3750-2800 cm⁻¹.

The changes in the characteristic bands of aerosil are similar to those in the IR spectra of aerosil activated for more 1 min (Fig. 1 a and 2 a, curves 2). Also, a band in the region 950-850 cm⁻¹ appears. The data obtained allow us to assume that the MA of the mixtures is accompanied by bond rupture in the associates of the acid, and its monomer molecules interact through hydrogen bonds with water molecules, in turn, the latter are bound through hydrogen bonds with active centres on aerosil surface. The assumed scheme of aerosil interaction with the acid:

\[
\begin{align*}
\text{O} & \quad \nu_2 \quad \text{C} = \text{O} \quad \text{C} \quad \text{O} \\
\text{H} & \quad \text{O} \quad \text{H} \\
\text{H} & \quad \text{O} \quad \text{H}
\end{align*}
\]

Scheme I. Interaction of aerosil with succinic acid

According to this scheme, the band with the maximum at 1725 cm⁻¹ (Fig. 2a, curve 2) should be related to vibrations ν2, C=O of monomer acid molecules, while a broad band with weakly pronounced maxima at 1600 and 1550 cm⁻¹ to vibrations (δH₂O + ν3, C=O), ν1, C=O – to the vibrations of initial dimer acid molecules. The band connected with vibrations ν C-O–, as expected [24], shifts to the direction which is opposite to the shift of the ν C=O band, that is, 1420 cm⁻¹ → 1445 cm⁻¹ (Fig. 2a, curve 2). A broad diffuse band in the region of 3750-2800 cm⁻¹ belongs to the stretching vibrations of OH groups, ν OH of monomer acid molecule and water molecules bound with hydrogen bonds (Fig. 2a, curve 2; scheme 1). This conclusion is confirmed by the XPA data. Reflections belonging to initial succinic acid are absent from the X-ray diffraction patterns of the mixture activated for 3 min (Fig. 2b, curve 2).

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

It should be noted that the bands belonging to dimer acid molecules are conserved in the IR spectra of the mixtures of aerosil with succinic acid, having mr. < 20 : 1 after MA for more 5 min. For example, for mr. = 6 : 1 the band ν2, C=O of acid monomer is symmetrical and has a maximum not at 1725 cm⁻¹ but at 1720 cm⁻¹, and the shoulder at ~ 1700 cm⁻¹ due to the vibrations of C=O groups of dimer acid molecules, ν1, C=O (Fig. 2a, 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 reflections of initial succinic acid are also conserved in the diffraction patterns of the sample (Fig. 2b, curve 3). We suppose that the presence of the bands of acid dimers in the IR spectra and in diffraction patterns provides evidence of the lack of the basic active centres on aerosil surface to bind larger amount of acid. Addition of water to the mixture of aerosil and succinic acid with mr = 6 : 1 in the amount of 0,5 ml does not changes the situation: the bands of
dimer acids are still present in the IR spectra of the product of MA. These results provide additional confirmation of our assumption concerning the participation of only basic surface centres of aerosil in the mechanochemical interaction with succinic acid. A necessary condition for the completion of reaction is the mass ratio of aerosil to succinic acid > 6 : 1.

**Aerosil + monocarboxylic acids**

![Figure 3](image)

**Figure 3** The IR spectra (a) and diffraction patterns (b) of the mixtures of aerosil with stearic acid before (1) and after MA for 9 min (2).

Aerosil to acid mass ratio \(mr = 20 : 1\)

The interaction during the joint MA of aerosil with saturated monocarboxylic acids, stearic (HSt) and lauric (HL), proceeds similarly. For example, for stearic acid (Fig. 3 a, curves 1, 2) the interaction is clearly observed only for aerosil to acid mass ratio \(mr \leq 20 : 1\). Hydrogen bonds of monomer molecules of carboxylic acid with adsorbed water molecules (according to Scheme 1) are likely to be weaker than in the case with succinic acid.

Indeed, in the IR spectrum of the activated mixture HSt + SiO₂ a broad band (\(\delta (H_2O) + v_3 \text{C}=\text{O}\)) is shifted to higher frequencies to 1620-1590 cm⁻¹, while the band \(v_3 \text{(SiO₄)}\) has a maximum at 1085 cm⁻¹. In the product of MA of aerosil with stearic acid: \(v_3 \text{(SiO₄)} - 1070 \text{ cm}^{-1}\), and the maxima of the total band (\(\delta (H_2O) + v_3 \text{C}=\text{O}\)) - 1600 и 1550 cm⁻¹.
The reflections of the acid are absent from the diffraction patterns of the mixture of aerosil and HSt (mr = 20 : 1) activated for 7 min (Fig. 3 b, curve 2).

The participation of adsorbed water in the mechanochemical interaction of aerosil with mono- and polycarboxylic saturated acids (Scheme 1) is evidenced by the fact that the IR spectra of the composites obtained during MA remain unchanged after exposure at \( t = 155-160^\circ \text{C} \) for 3 hours.

\[ \text{Aerosil} + \text{hydroxy acids} \]

**Figure 4** IR spectra of the mixtures of aerosil with citric acid after MA for 30 s (1), 3 min (2), 5 min (3). Aerosil to acid mass ratio mr = 3 : 1

MA of a mixture of aerosil with tricarboxylic acid, for example citric acid, also leads to the formation of chemical bonds between the components. Indeed, the IR spectra of the activated mixture of aerosil with citric acid exhibit changes of the bands of silicon dioxide and acid (Fig. 4). The bands of the stretching vibrations of OH groups of carboxylic and hydroxy groups at 3700-2900 cm\(^{-1}\) disappear; the bands with maximum at 1725 cm\(^{-1}\) appear: \( \nu \text{C}=\text{O} \), and also in the regions 1650-1550 cm\(^{-1}\) and 950-850 cm\(^{-1}\). In the IR spectrum of non-activated mixture the band \( \nu \text{C}=\text{O} \) of citric acid before MA had two maxima: 1710 cm\(^{-1}\) and 1750 cm\(^{-1}\), belonging to the vibrations of \( \nu \text{C}=\text{O} \) of the associates of the acid, and \( \nu \text{C}=\text{O} \) of carboxylic groups that do not participate in the formation of associates. The reflections of citric acid are absent from the diffraction patterns of activated mixture (Fig. 4 b, curve 2). The data obtained allow us to assume that not only OH groups of carboxylic fragments but also the hydroxy groups of the acid, interacting with acid centres on the surface, participate in the mechanochemical interaction [8]. As a result, a bridging bond between the support and the acid is formed, and water as well [8, 9]:

\[ \text{MA} \]

\[ \text{C-OH} + \text{Si-OH} \rightarrow \text{C-O-Si} + \text{H}_2\text{O} \]

Citric acid can interact mechanochemically with aerosil in the case when the mass ratio of dioxide to the acid mr = 3 : 1, which is likely connected with the possibility for hydroxy groups of the acid to participate in this process.

In the IR spectra of activated mixtures of aerosil with benzoic acid, mr = 20 : 1 (Fig. 5), changes of the parameters of vibration bands of SiO\(_4\) – tetrahedrons of silicon dioxide are similar to the changes in the IR spectra of above-considered mixtures (Fig. 2-4).
Also, the band ρ H₂O appears at 950-850 cm⁻¹; band ν₁ C=O broadens noticeably and becomes asymmetric, the character of absorption changes in the regions: 3750-2400 cm⁻¹ - vibrations ν OH, water and benzoic acid; and 1700-1400 cm⁻¹. However, these changes are less clear, perhaps due to the presence of five bands of in-plane skeleton vibrations ν C=C in the region 1650-1430 cm⁻¹ [24, 25]; one of these bands shifts 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 bands ν C=O, may be the evidence of the presence of mechanochemical interaction of aerosil with benzoic acid during the joint MA. The XPA data provide evidence, too. The reflections of the acid are absent from the X-ray diffraction patterns of the composite aerosil / benzoic acid.

According to the data reported in [13], such an interaction in the system SiO₂ + benzoic acid is impossible in the case of calcined SiO₂. We used non-calcined aerosil, so, water is indeed a binding link in the mechanocomposite aerosil / benzoic acid.

**Aromatic hydroxy acids**

Mechanochemical interaction of aerosil with salicylic acid differs substantially from its interaction with benzoic acid, because due to the chemical nature aromatic hydroxy acids can behave both as monocarboxylic acids and is monoatomic alcohols.

Indeed, it follows from the analysis of the IR spectra (Fig. 6) that after MA of the mixture of salicylic acid with aerosil (mr = 14 : 1) for 1 min the intensity of the band at 1665 cm⁻¹, ν₁ C=O related to the carboxylic groups of the acid decreases substantially, 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 with two maxima appears: at ~ 1615 cm⁻¹ and a more distinct one at 1595 cm⁻¹. Similarly to the mixture of aerosil with mono- and polycarboxylic acids, the IR spectra of the mixture exhibit the shift of the bands ν₁, ν₂, ν₃ of SiO₄⁻ - aerosil tetrahedrons. However, unlike for the examples considered above, band ρ H₂O as a shoulder of band ν₃ SiO₄⁻, in the region of 850-950 cm⁻¹ is only barely seen (Fig. 6).
Because of this, taking into account the features of the chemical bonds of aromatic hydroxy acids, we may assume that the mechanochemical interaction with aerosil is participated by the carboxylic groups and the phenol groups of salicylic acid. Phenol (alcohol) hydroxyl groups of acids, similarly to the hydroxy groups of hydroxy acids, interact mechanochemically with acid centres on the surface of SiO₂ forming water. Carboxylic groups of the acid interact with aerosil during MA, similarly to the interaction of mono- and polycarboxylic acids (Scheme 1), that is, through hydrogen bonds between the hydroxyl groups of carboxylic fragments in monomer acid molecules and water molecules that are in turn bound with rather strong hydrogen bonds with basic centres on the surface of aerosil. The position of the maximum of band ν C=С (1615 cm⁻¹) in the IR spectra of aromatic compounds depends on the presence and nature of substituents [24, 25]. That is why the maximum of band ν C=C in the IR spectrum of the product of MA of the mixture aerosil / salicylic acid shifts to lower frequencies: 1615 cm⁻¹ → 1595 cm⁻¹. The reflections of the acid are absent from the diffraction patterns of the activated mixture of aerosil with the acid.

**Aerosil + monoaminoacids**

Changes of the characteristic bands of aerosil in the IR spectra of activated mixtures of aerosil with e.g. glycine are similar to the spectra of all the above-considered activated systems. Thus, in the IR spectra of the mixtures aerosil / glycine, mr. = 8 : 1 (Fig. 7), after MA for 3 min the bands characteristic of stretching and bending vibrations of NH₃⁺ groups disappear; the corresponding regions: 3400-2300, 2200-2050 and 1550-1450 cm⁻¹, as well as the band νₘ COO-, 1700-1550 cm⁻¹ [24, 25]. Instead of the indicated bands, some new ones appear: a broad diffuse band with barely seen maxima at 3650 and 3250 cm⁻¹ in the region 3700-2700 cm⁻¹ and a broad one with the maximum at 1635 cm⁻¹. However, unlike for the IR spectra of activated mixtures of aerosil with aromatic acids, in this case the band of the out-of-plane bending vibrations ρ H₂O of «bound» water is almost unseen; the region is 950-850 cm⁻¹ (Fig. 7).

Similar changes of the bands related to the vibrations of NH₃⁺ and COO⁻ groups of amino acids were observed by the authors of [26] studying MA of leucine with talc and phenyl alanine with kaolin, talc, SiO₂ and α-, γ-Al₂O₃ [8]. They sup-
posed that leucine and phenyl alanine are present in the products of activation as \( \text{NH}_2\text{CHRCOO}^- \), with nitrogen and oxygen atoms bound with the support. On the basis of the above, and taking into account the fact that the band \( \rho \text{H}_2\text{O} \) of water molecules bound with the dioxide is almost unseen in the IR spectra of activated mixtures of aerosil with glycine, we assume that the interaction of aerosil with glycine proceeds without the participation of water molecules, and the amino groups of the acid in the resulting composite material interact with the basic centres on the surface of the support, while the carboxylic groups interact with its acid centres.

Fig. 7. IR spectra of the mixture of aerosil with aminoacetic acid before (1) and after MA for 3 min (2), 5 min (3). Aerosil to acid mass ratio \( \text{mr} = 8 : 1 \)

In the IR spectrum of the mixture of glycine with aerosil after MA, the band in the region of \( 3700-2700 \text{ cm}^{-1} \) belongs to the stretching vibrations of \( \text{NH}_2 \) groups and water molecules that may be bound with glycine anion and aerosil [21, 24, 26]. The band with the maximum at \( 1635 \text{ cm}^{-1} \) should be assigned to several vibrations: antisymmetric stretching vibrations of \( \text{COO}^- \) groups of glycine [24, 25], water molecules [21-23] and bending vibrations of \( \text{NH}_2 \) groups [24, 25]. Overlapping makes it impossible to determine the position of each band. Reflections of aminoacetic acid are absent from the diffraction patterns of these samples.

**CONCLUSIONS**

1. Mechanochemical interaction of non-calcined aerosil with biologically active organic acids was studied by means of IR spectroscopy and XRD. The formation of the chemical bond between the components of composite materials aerosil/BAS was established.

2. It was demonstrated that in the case of mono- and polycarboxylic acids the molecules of water adsorbed on aerosil are the binding link between the support and monomer acid molecules: aerosil – absorbed water – acid. Water molecules form hydrogen bonds with the basic surface centres of aerosil and with the hydroxyls of carboxylic groups of the 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 both by basic surface centres of aerosil and acidic ones: hydroxy (phenol) groups interact with acidic centres, while hydroxyls of COOH groups of acids formed H-bonds with molecules of absorbed water fixed by H-bonds with basic centres on surface of aerosil.
4. It was established that amino-groups of mono-basic mono-amino-acids get partially deprotonated during the interaction with the basic active centres of aerosil on its surface, while COO groups interact with its acidic centres.

REFERENCES