To the Problem of the "Capacity" of Layered Silicates in Their Mechanochemical Reactions with Organic Acids

IRINA A. VORSINA, ANTONINA P. BARINOVA and NIKOLAY Z. LYAKHOV

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: grig@solid.nsk.su

Abstract

The "capacity" of layered silicates in mechanochemical neutralization reactions with organic acids has been investigated. It is established that the "capacity" of silicate depends on the nature of the acids and silicate. In reactions with acids readily dissociating in water solutions, the "capacity" of talc is maximum: molar ratio talc : acid = 1 : 2, 1 : 1, and 3 : 2 for unsaturated mono-, bi-, and tribasic acids, respectively. For the same acids, the maximum "capacity" of kaolinite is m. r. kaolinite : acid $\approx$ 1 : 0.5. In the case of saturated monocarboxylic acids, m. r. talc : acid < 1 : 1; for aromatic acids, m. r. talc : acid = 1 : 1, kaolinite : acid $\leq$ 1 : 0.25.

INTRODUCTION

Investigations of mechanical activation for natural layered silicate–organic acid (or salt) systems indicate that neutralization and substitution reactions, respectively, occur during mechanochemical activation. In the products of these reactions (mechanocomposites), the Me ions of the silicate are chemically bound with the acid anions [1–5]. In the case of organic acids mixed with salts, chemical bonds are formed between the cations of the salt and the acidic centers of the silicates, also formed during activation of silicates [5, 6]. Mechanocomposites typically have nanosized particles and high homogeneity. Therefore, using mechanochemical technologies, for example, for drug production can be helpful in solving the problem of the solution rate and consequently of their therapeutic efficiency, and also can help to raise the concentration of the active component in a drug.

The concentration of the active substance is an important question in developing new medical products, both from the viewpoint of their efficiency and safety of treatment.

The purpose of the present work is to study the "capacity" of layered silicates in mechanochemical reactions with organic acids. By the "capacity" of layered silicates in this case we mean the molar ratio (m. r.) silicate : acid such that mechanochemical reaction of neutralization proceeds to completion, *i.e.*, the protons of all carboxyl groups of the acid are involved in the neutralization reaction of the silicate OH groups. This ratio defines the maximum possible concentration of an active substance in the layered composite.

EXPERIMENTAL

The following layered silicates were used in this work: Mg-talc $Mg_3(Si_4O_{10})(OH)_2$; kaolinite $Al_2(Si_2O_5)(OH)_4$. For organic acids we used stearic $C_{17}H_{35}COOH$, lauric $C_{11}H_{23}COOH$, and unsaturated crotonic $CH_3(CH)_2COOH$ (monocarboxylic) acids; suberic $(CH_2)_6(COOH)_2$, glutaric $(CH_2)_3(COOH)_2$, and succinic $(CH_2)_2(COOH)_2$ (dicarboxylic) acids; fumaric and maleic (*cis*-isomer) $(CH_2)_2(COOH)_2$ (unsaturated) acids; tartaric $(CHOH)_2(COOH)_2$ and tribasic citric $C(CH_2)(COOH)_3$ (hydroxyacids); benzoic C_6H_5COOH and salicylic $C_6H_4(OH)COOH$ (aromatic) acids.

The molar ratios of components in silicate : acid mixtures were varied within the range of $1 : 2 \geq$ m. r. $\geq 1 : 0.25$ depending on the basicity of the acid and the nature of the silicate.

IR absorption spectra were registered on a Specord-75 IR spectrometer; the samples were
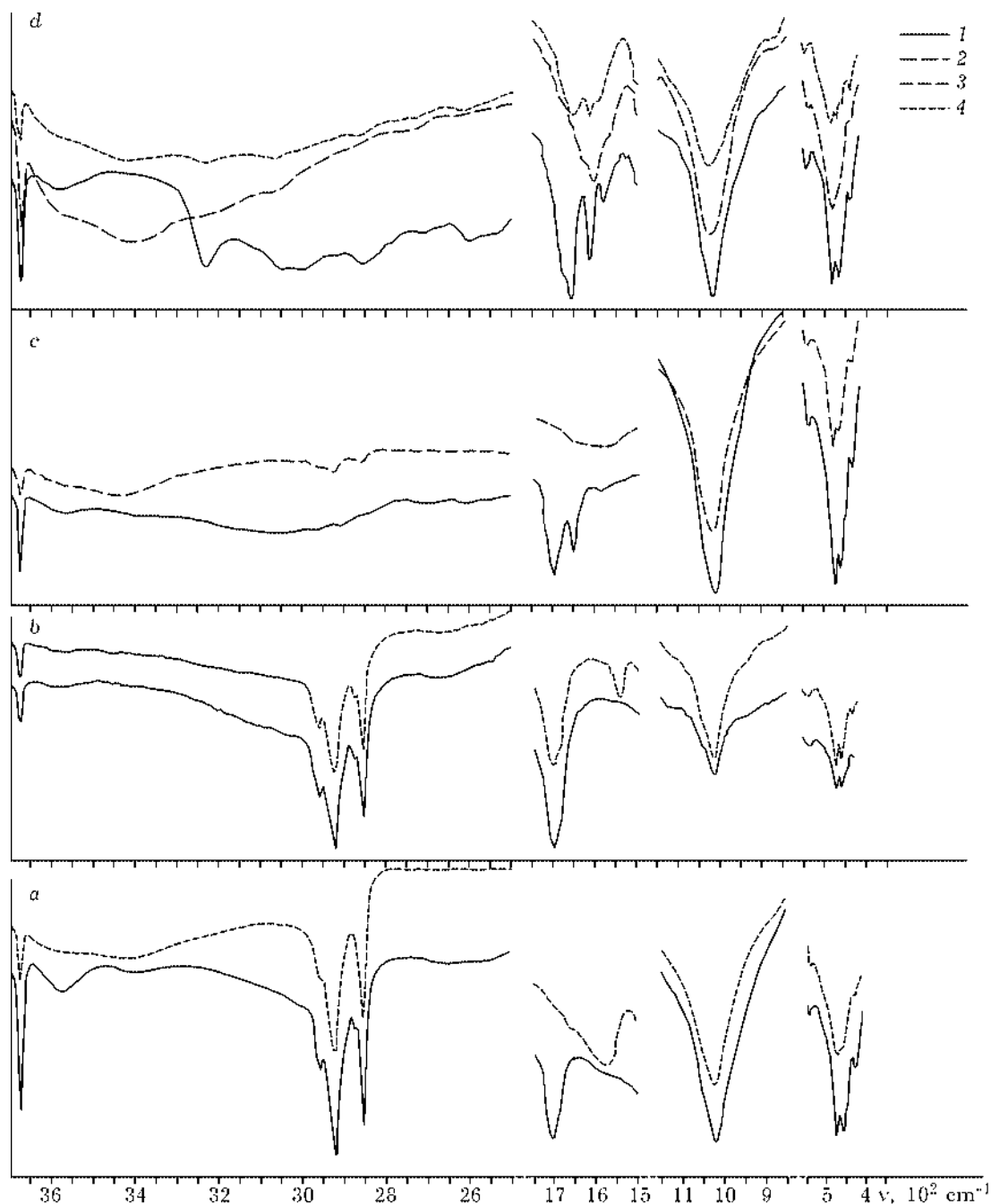
Fig. 1. IR absorption spectra before and after MA of talc mixtures with acids: stearic (*a*), lauric (*b*), crotonic (*c*), and salicylic (*d*) acids. M. r. talc : acid: 1 : 0.5 (*a*), 1 : 2 (*b*), 1 : 2 (*c*), 1 : 1, and 1 : 2 (*d*); activation time τ_a, min: 0 *(1)*, 5 *(2)*, 7 *(3)*, 9 *(4)*.

prepared for spectrum recording in the form of pellets with calcinated KBr. X-ray phase analysis (XRPA) was conducted on a DRON-3M diffractometer (CuK_α radiation). The microstructure of the samples was investigated by means of scanning electronic microscopes JSM-T-20 and JEM-2000 FXII. Mechanical activation (MA) of reaction mixtures was performed in an AGO-2 planetary ball mill [7].

RESULTS AND DISCUSSION

The organic acids used in the experiment have a layered crystal structure [8], which is practically not broken during MA [1–5]. On the contrary, MA of the starting talc and kaolinite results in broken Me—OH bonds and in destruction of networks, with active acidic and basic superficial centers formed inside the layers [9].

MA of organic acids with talc

Monocarboxylic acids. Figure 1 presents the IR absorption spectra of talc mixtures with monocarboxylic acids: stearic, lauric, crotonic, and aromatic salicylic acids before and after MA.

It follows from the analysis of the spectra that the capacity of talc in mechanochemical reactions with monocarboxylic acids is m. r. talc : acid ≤ 1 : 1 and is governed by the nature of the acids. This means that only ≤50 % of the hydroxo groups of talc can be involved in mechanochemical interactions with the protons of the carboxyl groups of saturated and aromatic acids. The capacity of talc is maximum for unsaturated crotonic acid, m. r. talc : acid = 1 : 2, i. e., virtually all hydroxo groups of talc are involved in the neutralization reaction with the protons of the carboxyl groups. Indeed the IR spectra of the activated talc mixtures with saturated and aromatic acids when m. r. ≤ 1 : 1 and with an unsaturated acid when m. r. = 1 : 2 do not contain the vibration bands of the carboxyl groups of acids: νOH 3000−2450 cm^{-1}; $\nu C{=}O$ 1800−1650 cm^{-1}, while the bands of the carboxylate ions are present: ν_{as}1650−1550 cm^{-1}, ν_{s}1400−1300 cm^{-1} [1−5]. At the same time, the intensity of the νOH band of talc at 3670 cm^{-1} decreases. The parameters of the characteristic bands of talc in this case do not change significantly except that the band with a peak at 1020 cm^{-1} (νSiO^-; $\nu_{as}Si{-}O{-}Si$) is shifted (see Fig. 1, a−d). The pronounced change in the shape of the deformation vibration band of the layer at 550−440 cm^{-1} points to lattice deformation in the reaction product. The X-ray diffractograms of these mixtures have no reflections corresponding to the acids, while for talc the reflections are broadened and displaced, the shift being no more than by 5 % from the position on the X-ray diffraction pattern of the starting talc (Fig. 2, c, d). According to electronic microscopy data, the reaction product is represented by nanosized platelike particles.

The results presented indicate that the mechanochemical neutralization reaction of the OH groups of talc with the carboxyl protons of acids completed at the indicated values of m. r. and that a new substance has formed − a mechanocomposite with Me ions of silicate chemically bonded to the carboxylate ions of the organic acid [1−4].
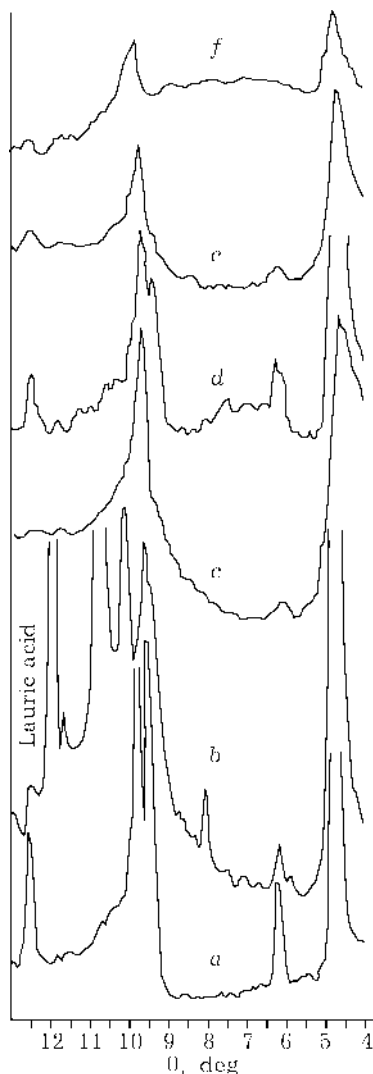

Fig. 2. X-ray diffractograms of the starting talc (a) and of talc mixtures after MA with lauric (b), salicylic (c), crotonic (d), succinic (e), and citric (f) acids. M. r. talc : acid: 1 : 2 (b, d), 1 : 1 (c, e), 3 : 2 (f); τ_a, min: 0 (a), 9 (b), 5 (c, e), 7 (d), 3 (f).

The IR spectra of the activated mixtures of talc with monocarboxylic saturated and aromatic acids when m. r. > 1 : 1 and 1 : 2 have vibration bands of the carboxylate ion, ν_{as} and $\nu_s COO^-$, as well as the bands characteristic for the carboxyl group: $\nu C{=}O$ and νOH, and also νOH of talc (see Fig. 1, b, d). The X-ray diffractograms of these samples contain reflections that are due to talc and mechanocomposite, and reasonably intense reflections of the unchanged acid (see Fig. 2, b). These facts suggest that mechanochemical reaction for these mixtures does not proceed to completion even though the activation time τ_a increased to 10 min and more.
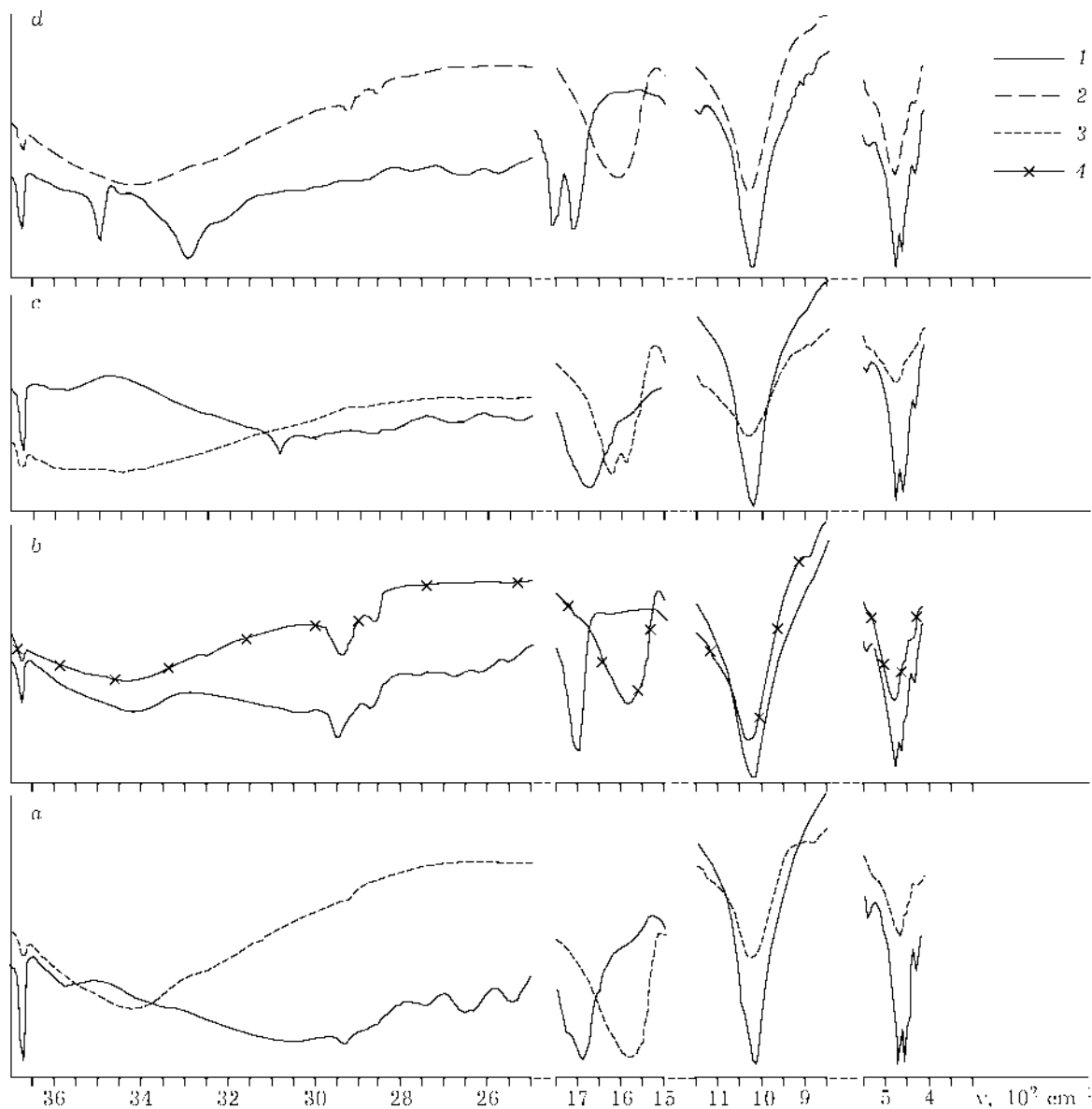
Fig. 3. IR absorption spectra before and after MA of talc mixtures with succinic (*a*), suberic (*b*), fumaric (*c*), and citric (*d*) acids. M. r. talc : acid = 1 : 1, for citric acid, 3 : 2; τ_a, min: 0 *(1)*, 3 *(2)*, 5 *(3)*, 13 *(4)*.

Dicarboxylic acids. Irrespective of their nature (saturated, unsaturated, or hydroxyacids), dicarboxylic acids interact with talc at m. r. = 1 : 1, *i. e.*, at such m. r. when the number of hydroxy groups of $Mg_3(Si_4O_{10})(OH)_2$ equals that of carboxyl groups of $R(COOH)_2$. For tribasic citric acid $(OH)C(CH_2)_2(COOH)_3$, a similar interaction with talc takes place when m. r. = 3 : 2. Indeed, the IR spectra of the activated mixtures (Fig. 3) do not contain the vibration bands of the carboxyl group of the acid vOH $3250-2450$ cm^{-1} and vC=O $1800-1650$ см$^{-1}$, and the stretching vibration band of the hydroxyl group of talc, vOH 3670 см$^{-1}$, also vanishes. In

the IR spectra of the product of the mechanochemical interaction of talc with a polybasic acid, one can observe the bands of the carboxylate ion, $v_{as}COO^-$ $1650-1550$ cm^{-1} and v_sCOO^- $1400-1300$ cm^{-1}; the bands that are due to the stretching vibrations of the $Si-O^-$ and $Si-O-Si$ bonds of talc (the 1020 cm^{-1} band, the shoulder at 1040 cm^{-1}, and the 670 cm^{-1} band, respectively) are somewhat broadened, and their maxima are displaced by $10-15$ cm^{-1}. Apparently, the involvement of slightly acidic $Si-OH$ groups of talc along with $Mg-OH$ groups in neutralization reactions with polybasic acids strengthens the $Si-O^-$ bonds and weakens the

Si−O−Si bonds and, accordingly, leads to an obvious shift of the νSi−O and ν_{as}Si−O−Si bands to the high-frequency range, and to a shift of ν_sSi−O−Si to the low-frequency range.

Since the deformation vibrations of the silicon-oxygen layer are modified by lattice vibrations [10], changes in the parameters of the corresponding bands (in the range 550−400 cm^{-1}) are also more significant, indicating that the talc lattice in the mechanocomposite undergoes deformation.

On the X-ray diffractogram of these samples (see Fig. 2, *e, f)*, reflections of acids are absent, while the reflections of talc are considerably broadened and displaced (depending on the nature of the acid), the shift being up to 4 % from their position for the starting talc. A similar pattern is obtained for the mixture of talc with crotonic acid where m. r. = 1 : 2. The data obtained suggest that a mechanocomposite formed, which "inherited" the type of the crystal structure of the starting talc (see Fig. 3). This assumption is verified by the results of high-resolution electron microscopy, showing that the composite of talc and succinic acid is represented by agglomerates of plate-like particles [5].

Differences between talc interactions with mono- and polybasic acids in the course of their combined activation can be understood if we consider the following. Talc is a layered silicate of 2 : 1 type containing only one sort of OH group, namely, intralayer hydroxy groups (slightly acidic Si−OH and basic Mg−OH groups located only on the lateral faces and edges of the platelike particles). Note that under certain medium conditions, namely, at pH < 2, Si−OH can act as basic groups [11]. Taking into consideration the data of [11] and the fact that molecular water forms during combined activation of talc with organic acids [1−5], one can assume that dissociation of polybasic and monobasic unsaturated acids leads to pH < 2. As a consequence, Si−OH can be involved in neutralization as basic groups when m. r. talc : acid = 1 : 2, 1 : 1, and 3: 2, respectively, for monobasic unsaturated and for bi- and tribasic acids, *i. e.*, when the number of hydroxy groups of talc equals that of COOH groups of acids. For this reason, the νOH bands of the stretching vibrations of talc (3670 cm^{-1})

and acids (3250−2450 cm^{-1}) are absent from the IR spectra of the reaction products. Instead, the spectra contain a wide band in the region 3700−3000 cm^{-1} having no distinct maxima and belonging to the νOH vibrations of molecular water [12] and to the alcohol groups of hydroxyacids, forming various types of hydrogen bond in the mechanocomposite, including those with water molecules. The alcohol hydroxy groups of acids, which are typical ol groups, are not involved in the mechanochemical reactions of neutralization with talc, since the IR spectrum of the reaction product has the νOH bands of unchanged talc when m. r. talc : acid > 1 : 1 and 3 : 2 for tartaric and citric acids, respectively. The time τ_a of mechanochemical interaction of talc with carboxylic acids is governed by the nature of the acid: τ_a = 3 min for readily soluble tartaric and citric acids, 5 min for succinic acid, 7 min for crotonic and glutaric acids, and 13 min for sparingly soluble suberic acid.

Mechanochemical interaction of organic acids with kaolinite

Unlike talc, kaolinite − an octahedral mineral of 1 : 1 type − has at least four kinds of OH group, represented by four νOH bands in the ranges of vibrations 3695 cm^{-1} (intralayer OH groups), and 3670, 3650, and 3620 cm^{-1} (OH groups of the external network of the layer). These groups form hydrogen bonds (differing in energy) with the oxygen atoms of the adjacent layer [13].

Unlike talc, both basic Al−OH and acidic Si−OH groups are located not only on the lateral, but also on the basal (001) faces. It is very important that the lateral faces amount to only 10−15 % of the total surface depending on particle dispersity; hence, the basal faces of kaolinite contain more than 80 % of all OH groups [11].

From the analysis of the IR spectra of the starting and activated mixtures of kaolinite with carboxylic acids it follows that mechanochemical neutralization of kaolinite OH groups with the COOH protons of acids takes place for saturated monocarboxylic and aromatic acids when m. r. kaolinite : acid ≤ 1 : 0.25; for tri-, bi-, and monobasic unsaturated acids,
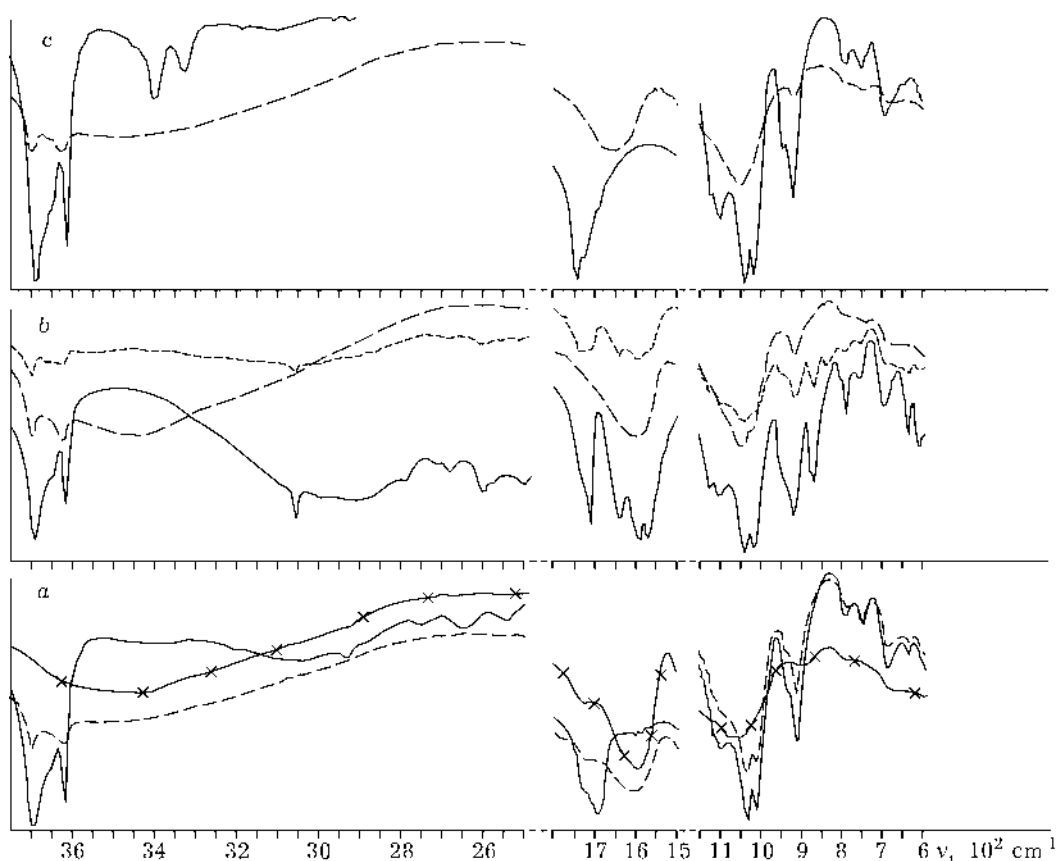
Fig. 4. IR absorption spectra of kaolinite mixtures with succinic (*a*), maleic (*b*), tartaric (*c*), lauric (*d*), crotonic (*e*), and benzoic (*f*) acids before and after MA. M. r. kaolinite : acid = 1 : 1 and 1 : 0.5 (*a*), 1 : 0.25 and 1 : 2 (*b*), 1 : 0.75 (*c*), 1 : 0.25 (*d, f*), 1 : 0.5 (*e*); τ_a, min: 0 *(1)*, 1 *(2)*, 3 *(3)*, 5 *(4)*, 7 *(5)*.
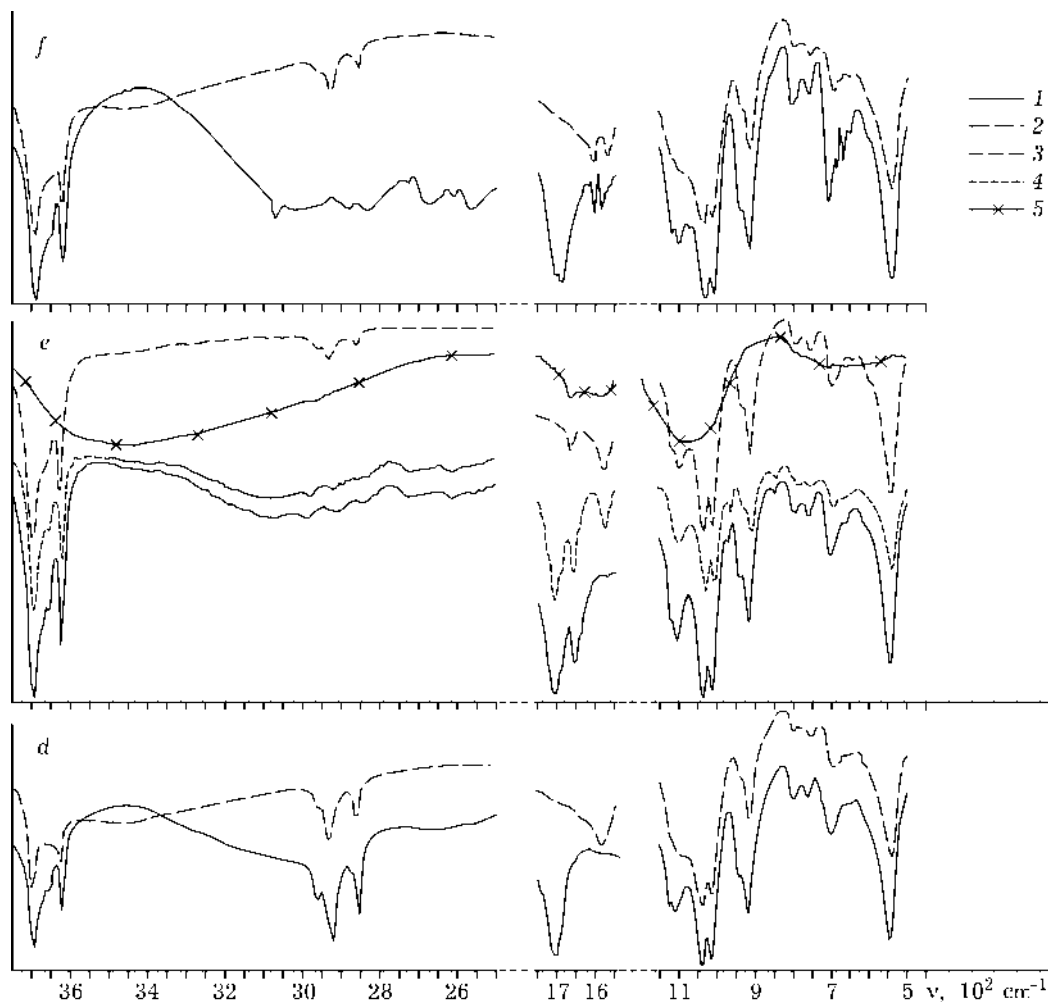
when m. r. $\leq$ 1 : 0.5. This is indicated by the absence of bands characteristic of the carboxyl group in the IR spectra of the reaction products: νOH 3400–2450 cm^{-1}, $\nu C=O$ 1800–1650 cm^{-1}, and the presence of the carboxylate ion bands: ν_{as} 1620–1550 cm^{-1}, ν_s 1450–1300 cm^{-1}, along with νOH 3700–3000 cm^{-1} of molecular water. At the same time, the intensity of the νOH and δOH bands of kaolinite decreases appreciably, and their shape changes (ranges 3750–3600 and 950–900 cm^{-1}, respectively). The intensity and shape of the bands in the regions 1150–950 and 850–750 cm^{-1} that are due to the stretching vibrations of the Si–O–Si, SiO$^-$ and Si–O–(Al) bonds [10] change drastically. The greatest changes in the parameters of these bands, including the displacements of maxima, take place for hydroxoacids (Fig. 4).

The X-ray diffractograms of the activated mixtures of kaolinite and monobasic carboxylic acids, as well as saturated and aromatic acids with m. r. $\leq$ 1 : 0.25, contain only kaolinite reflections (see Fig. 4, *c*). In the case of kaolinite mixtures with unsaturated monocarboxylic and polybasic acids, the reflections of the acids are missing when m. r. $\approx$ 1 : 0.5, while for kaolinite the intensities decrease drastically, and the reflections are shifted and broadened (see Fig. 4, *d, e*).

In this context, one can assume the following. During mechanical activation of kaolinite with saturated and aromatic monocarboxylic acids, neutralization with acid protons takes place for only Al–OH groups on the lateral faces of the silicate. The hydroxyl groups of the basal faces are typical ol groups [14] and are therefore not involved in mechanochemical neutralizations.

During combined activation with kaolinite, the acidity of the medium becomes other than neutral as a result of dissociation of the monoba-

sic unsaturated and polybasic carboxylic acids and due to water formation during the mechanochemical reaction (a similar phenomenon takes place in mechanical activation of the stated acids with talc). Therefore, it is believed [11] that Al—OH groups from not only (hk0), but also (001) faces of kaolinite are involved in the mechanochemical neutralization reactions with monobasic unsaturated and polybasic acids. In this case, m. r. kaolinite : acid ≈ 1 : 0.5. The possibility of Al—OH groups from basal faces to be involved in exchange reactions is supported by the data of [14—16].

The acidic Si—OH groups cannot become basic groups as they do in the case of talc, because of the differences in the crystal structure of talc and kaolinite, availability of four types of hydroxyl groups in the structure of kaolinite, strong hydrogen bonds differing in energy, and disposition of the acidic and basic OH groups not only on the edges and lateral faces (~ 10-15 %), but also on the basal planes (more than 80 %) [11]. Therefore, the maximum capacity of kaolinite, m. r. kaolinite : acid ≈ 1 : 0.5, is observed even in the case of MA with readily dissociating polybasic acids. Indeed, in spite of increased activation time ($\tau_a > 7$ min), the IR spectra of the activated mixtures of kaolinite with acids, for example, crotonic, succinic, and tartaric acids (m. r. > 1 : 1), lauric and benzoic acids (m. r. > 1 : 0.5) contain distinct bands characteristic of the carboxyl group, $\nu C=O$ 1680−1720 cm^{-1} and νOH 3400−2400 cm^{-1}, along with the bands of the carboxylate ion ν_{as} 1650−1550 cm^{-1} and ν_s 1400−1300 cm^{-1} (see Fig. 4). The X-ray diffraction patterns of these mixtures contain reflections of both kaolinite and unchanged acids (see Fig. 5, b). Further increase in the activation time to $\tau_a = 15$ min leads only to kaolinite amorphization and supposedly to partial separation of amorphous Al_2O_3 and SiO_2 [14]. This is evidenced
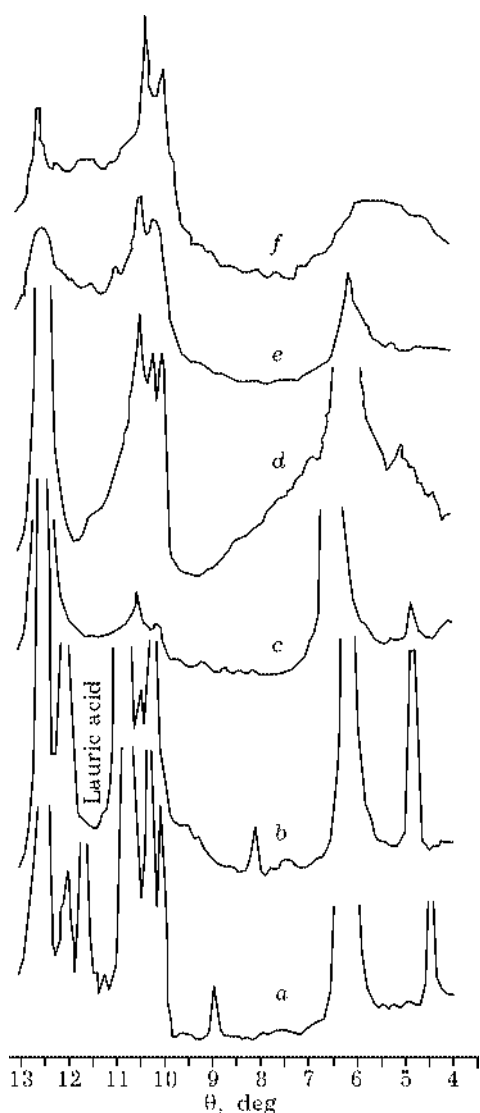
Fig. 5. X-ray diffractograms of the starting kaolinite (*a*) and mixtures with lauric (*b, c*), crotonic (*d*), succinic (*e*), and tartaric (*f*) acids after MA. M. r. kaolinite : acid: 1 : 1 (*b*), 1 : 0.25 (*c*), 1 : 0.5 (*d*), 1 : 0.5 (*e*), 1 : 1 (*f*); τ_a, min: 10 (*b*), 5 (*c*), 3 (*d*), 1 (*e*), 3 (*f*).

by the broadening, changed shape, and displacement of the band peaks, which are due to the vibrations of the SiO_4^- tetrahedron of kaolinite. This is also indicated by the emergence of a wide band having no distinct maxima in the range $820-550$ cm^{-1}, which was attributed [17] to the stretching vibrations of the Al−O bonds of aluminum oxide (see Fig. 4, *a*, *b*, curves *5*). The X-ray diffractograms of these samples contain no reflections of acids or basal planes of kaolinite, but contain a halo in the θ ranges $14-9°$ and $7-4°$ (see Fig. 5, *f*).

CONCLUSIONS

1. In mechanochemical neutralization reactions with acids dissociating in solutions and melts, the capacity of talc is m. r. talc : acid = 1 : 2, 1 : 1, and 3 : 2 for the monobasic unsaturated acid and for bi- and tribasic acids, respectively. This indicates that the reactions involve all hydroxyl groups of talc (not only basic Mg−OH groups, but also acidic Si−OH groups). Dissociation of acids and formation of molecular water as a reaction product create the necessary conditions for the Si−OH groups to be involved in such reactions (pH < 2).

2. In the mechanochemical reactions of neutralization with saturated and aromatic monobasic carboxylic acids, the capacity of talc is m. r. talc : acid ≤ 1 : 1 because only Mg−OH groups are involved in the reaction.

3. The Al−OH groups of only lateral faces are involved in the mechanochemical reactions of kaolinite with saturated and aromatic monocarboxylic acids, which proceed when m. r. kaolinite : acid ≤ 1 : 0.25.

4. The maximum capacity of kaolinite in the mechanochemical reactions of neutralization with unsaturated monocarboxylic and polybasic acids is m. r. kaolinite : acid ≈ 1 : 0.5, indicating that Al−OH groups not only from the lateral, but also from the basal faces are involved in the mechanochemical interaction.

5. The alcohol OH groups of hydroxyacids are not involved in the mechanochemical reactions of neutralization with talc and kaolinite. They form various types of hydrogen bond in the reaction product (mechanocomposite), including those with water molecules.

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