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Figure 1

Figure 1: Figure 1

Abstract

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STUDY OF THE THERMAL DEHYDRATION OF PALYGORSKITE BY INFRARED SPECTROSCOPY

Palygorskite (1-4) contains two forms of bound water: water located in the zeolitic channels of the structure and in the porous space of the packets into which the needlelike particles of the mineral aggregate (zeolitic water), and water molecules removed at a higher temperature (300-350°), bound (3) to octahedral Mg^{2+}, Fe^{3+}, or Al^{3+} ions on the side walls of the channels.

Fig. 1. Absorption spectra of K-palygorskite in the region of O—H stretching vibrations at different dehydration temperatures: 1 —20; 2 —65; 3 —120; 4 —150; 5 —210; 6 —250; 7 —300; 8 —350°.

To obtain direct information on the mechanism of the adsorption interaction of these forms of moisture with the surface of the mineral, we used the method of infrared (IR) spectroscopy. A fluorite plate with a thin layer (15-20 μ) of sample deposited on it was placed either in a special thermal cuvette, allowing spectra to be recorded in the temperature range 20-350°, or in a glass vacuum cuvette with fluorite windows, of a design somewhat modified in comparison with that described earlier (5). The cuvette made it possible to record spectra both of a sample with water adsorbed on it and of water vapor itself without changing any experimental conditions. The spectra were recorded on an IKS-14 instrument in the ranges 3800-2700 and 1700-1300 cm^{-1}, with a temperature interval of 20-40° after 1.5 hours had elapsed following attainment of the required temperature in the case of the thermal cuvette. When recording in vacuum, the sample placed in the sealed end of a tube was evacuated at the corresponding temperature for 2 hours at a vacuum of $5 \cdot 10^{-2} \div 10^{-2}$ mm Hg. Under these conditions the spectra had the same appearance. However, under heating with simultaneous evacuation, removal of one or another type of water, judging from the change

Fig. 2. Absorption spectra of K-palygorskite in the region of deformation O-H vibrations of H_2O molecules at different dehydration temperatures: 1 –20; 2 –35; 3 –50; 4 –65; 5 –95; 6 –110; 7 –160; 8 –190; 9 –230; 10 –280; 11 –330°

Figure 2: Fig. 2. Absorption spectra of K-palygorskite in the region of deformation O-H vibrations of H_2O molecules at different dehydration temperatures: 1 –20; 2 –35; 3 –50; 4 –65; 5 –95; 6 –110; 7 –160; 8 –190; 9 –230; 10 –280; 11 –330°

in intensity of the corresponding absorption bands, occurs 30-40° earlier than in the case of thermal treatment alone.

To determine the influence of exchange ions, the Li^+-, K^+-, Ca^{2+}-, Cu^{2+}-, Co^{2+}-, Zn^{2+}-, Al^{3+}-, and Fe^{3+}-forms of palygorskite were investigated. For the Cu^{2+}-, Co^{2+}-, Zn^{2+}-, Al^{3+}-, and Fe^{3+}-modifications, weak single or double bands were found in the region 1430-1470 cm^{-1}, decreasing somewhat in intensity only after 250-280°. Similar bands were also found for the corresponding cation-substituted forms of montmorillonite and kaolinite. They are absent in the Li-, K-, and Ca-forms. We have assigned these maxima to deformation vibrations of OH groups of the hydroxides of the corresponding metals, small amounts of which are probably formed during preparation of the samples. Valence vibrations of OH groups of hydroxides do not appear in the spectrum of palygorskite.*

The literature data on hydroxide spectra (6-9) confirm this assignment of the frequencies. In other respects, the IR spectra of the previously listed cation-substituted forms of the mineral and their changes as a result of heating are identical; therefore, Figs. 1 and 2 show the absorption curves in the region of stretching and deformation vibrations of OH groups, recorded in a thermal cuvette at different temperatures only for one sample—K-palygorskite.

Fig. 2. Absorption spectra of K-palygorskite in the region of deformation O-H vibrations of H_2O molecules at different dehydration temperatures: **1** –20; **2** –35; **3** –50; **4** –65; **5** –95; **6** –110; **7** –160; **8** –190; **9** –230; **10** –280; **11** –330°.

In the spectrum of the water-saturated sample in the region of stretching O-H vibrations (Fig. 1), a whole series of bands is observed, the intensities of which change in different ways as the temperature increases. The bands 3390 ± 20 and 3284 ± 20 cm^{-1} were assigned by us, by analogy with the bands of liquid water (10), respectively, to the antisymmetric (ν_3) and first overtone of the deformation ($2\nu_2$) vibrations of the OH groups of zeolitic water molecules. The high intensity of the 3284 cm^{-1} band, as in the case of liquid water (10), can be explained by Fermi resonance between the vibrations ν_1 and $2\nu_2$ (11). The deformation O-H vibration of water molecules of this type corresponds to the band 1654 ± 5 cm^{-1} (Fig. 2), which is very intense at 20° and disappears rapidly upon heating.

The narrow and intense band 3590 ± 20 cm^{-1} (Fig. 1), located in the region of vibrations of unbound OH groups (12) and decreasing in intensity from 210-250°, belongs to the hydroxyl groups of the mineral, which, according to structural data ([1], [2]), are located in the central part of the octahedral layer. The absence of any changes in the position of this band indicates that the structural OH groups of palygorskite are inaccessible to adsorbed water molecules ([13]). The decrease in the intensity of this band at 210-350° indicates that dehydroxylation of the mineral begins before dehydration is complete.

* These bands are clearly visible in the spectra of the corresponding samples of monomontmorillonite, recorded at high temperatures (150-350°).

Of interest is the behavior of the band 3546 ± 20 cm^{-1} upon heating. At first (65°) it splits into weakly resolved bands at 3554 and 3538 cm^{-1}. At the same time, the intensity of the band 3620 ± 20 cm^{-1}, which exists in the spectrum of the initial sample as a shoulder on the peak at 3590 cm^{-1}, increases. With further heating (110°), the band at 3554 cm^{-1} disappears and the intensity of the band at 3620 cm^{-1} increases further. Simultaneously, a weak maximum at 3234 ± 20 cm^{-1} appears in the spectrum. In the region of deformation O—H vibrations at these temperatures, the band 1642 ± 5 cm^{-1} appears and then disappears, while the intensity of the band 1620 ± 5 cm^{-1} increases. Beginning at 150°, the intensity of the bands at 3620, 3538, 3234, and 1620 cm^{-1} decreases, with the maximum of the first band shifting to 3640 cm^{-1}. Undoubtedly, all these bands belong to O—H vibrations of water molecules coordinated by octahedral ions. This assignment is supported by the fact that similar bands have been found in the IR spectra of zeolites ([14–16]), as well as by the lower-frequency position, in comparison with liquid water, of the ν_2 vibration band, as also in the spectra of crystalline hydrates ([17]). Thus, the removal of water coordinated by octahedral ions in palygorskite begins at 150°. At 300-350° this water is still present in the mineral (Figs. 1 and 2).

The complex change in the bands at 3620, 3554, 3546, 3538, 3234, 1642, and 1620 cm^{-1} in frequency and intensity with increasing temperature indicates that the type of bonding of the water removed from the mineral at the higher temperature to the surface of the channels depends on the presence in the latter of molecules of zeolitic water. Let us consider in somewhat greater detail the model of the adsorption complex in palygorskite. Consider the case corresponding to the temperature interval 110-350°, i.e., when the molecules of zeolitic water have been removed from the channels. Three pathways are possible, according to which adsorption of molecules of the second type may occur: a) interaction of the lone pairs of the molecule with the octahedral cation (ion-dipole interaction), both hydrogens being free; b) ion-dipole interaction with cations and simultaneous bonding of one hydrogen to the oxygen surface of the zeolitic channels, the other hydrogen being free; c) ion-dipole interaction and simultaneous bonding of two hydrogens to the oxide surface of the channels. In the first case, with two free hydrogens, two sharp bands should be observed in the high-frequency region of the spectrum (3700-3600 cm^{-1}), corresponding to the symmetric and antisymmetric vibrations of free OH groups, similar to those observed in dilute solutions of water in nonpolar solvents ([18]). In adsorption according to scheme b), there should occur a disruption of the interaction between the stretching vibrations ν_1 and ν_3, which should split into two isolated vibrations: the vibration of nonassociated OH groups with frequency $\nu_{\text{free}} = 3720\text{-}3600$ cm^{-1} and the vibration of associated groups (ν_{assoc}) with a lower frequency (^{10,19})*. In the third case, the absorption bands should be shifted into the low-frequency region of the spectrum (3400-3200 cm^{-1}), similar to the bands of water molecules in various crystalline hydrates (^{17,21}). The presence in the spectrum of intense bands at 3640 and 3538 cm^{-1} supports the mechanism of adsorption interaction according to the second scheme; here $\nu_{\text{free}} = 3640$ cm^{-1}, $\nu_{\text{assoc}} = 3538$ cm^{-1}. The bands at 3234 and 1620 cm^{-1} belong, respectively, to the first overtone of the deformation vibration and to the deformation vibrations of molecules of this type of water.

Resolution at high temperatures of a weak complex band with a maximum at 3390 cm^{-1} also indicates the possibility of bonding according to the third scheme. Thus, we have a definite dynamic equilibrium between two types of adsorption complexes, shifted, however, as follows from comparison of the intensities of the corresponding absorption bands, toward the second type of bond.

* Recently A. N. Sidorov (^{20}) proposed a somewhat different interpretation of the absorption bands of H_2O molecules for this case.

The presence in the mineral channels of molecules of low-temperature zeolitic water leads to interaction of the free hydrogen with the oxygens of these molecules through a hydrogen bond. This corresponds to the appearance in the spectra at temperatures of 35-65° of bands at 3554 and 1642 cm^{-1}, which are assigned to the stretching and deformation vibrations of OH groups of water molecules coordinated by octahedral ions and simultaneously bonded by hydrogen bonds to the surface oxygens of the channels and to the oxygens of zeolitic-water molecules, the latter bond evidently being weak. When the sample is saturated with water, the bands at 3554 and 3538 merge into one intense band with a maximum at 3546 cm^{-1}. On the basis of this interpretation, it is clear that the increase in the intensity of the bands at 3620 and 1620 cm^{-1} when the temperature is raised to 110° is the result of an increase in the number of water molecules bound to the surface of the zeolitic channels according to the second scheme, i.e., with one free hydrogen.

As for the mechanism of the adsorption interaction of molecules of zeolitic water with the surface, from an analysis similar to that given above it follows that they will be oriented with two H atoms in the direction of the surface oxygens of the aluminosilicate lattice of the mineral; moreover, in the channels the oxygens of these molecules are additionally bonded by a hydrogen bond to the hydrogens of molecules coordinated by octahedral ions. Comparison of the frequencies ν_3 and ν_2 of the O—H vibrations of zeolitic-water molecules obtained in our study with the corresponding frequencies for liquid water—3425 and 1645 cm^{-1} (^{10})—indicates that the bond energy zeolitic water—surface oxygens is greater than the interaction energy in liquid water. This should be explained by the loosening action of surface oxygens, which carry an excess negative charge as a result of nonstoichiometric substitution chiefly of Si^{4+} by Al^{3+} in the tetrahedra.

The presence, even in a water-saturated sample (Fig. 1), of an intense band at 3620 cm^{-1} leads to the conclusion that the molecules of zeolitic water are arranged discretely in the mineral channels, as a result of which high-temperature water can be bonded to the channel surface according to the scheme with one free hydrogen (scheme b), even when the sample is fully saturated with water.

Finally, two weak maxima at 2934 and 2865 cm^{-1} have been found in the spectrum of palygorskite; in accordance with the works ([22,23]), these may provisionally be assigned to stretching vibrations of hydroxyl groups of the hydroxonium ion. For a more reliable assignment of these frequencies, experimental verification at low temperatures is necessary.

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