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HYDRONIUM (OXONIUM) ION AS PROBABLE CAUSE OF ACIDITY OF CALCINATED H-FORM OF MONTMORILLONITES

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Abstract. Infrared spectroscopic studies of a series of samples have been carried out obtained by calcination of hydrogen form of montmorillonite in temperature range 20—800°C. The *IR* spectra were recorded using high-temperature vacuum cell. Particular attention was paid to determine the function of proton in calcinated hydrogen form of the mineral under examination.

The analysis of infrared spectra obtained indicates the possibility of existence of positive hydronium ions in crystal lattice of the samples studied, even after their calcination in temperature range 300—650°C. This is manifested by the presence of absorption bands in the region 2400—3550 cm^{-1} (related with ν_3 and ν_1 vibrations) and of maxima 1430 and 1570 cm^{-1} (probably related with ν_1 vibrations).

Polarized water molecules, strongly bound by very active Lewis centres, are important factor contributing to proton acidity of the samples examined since at temperatures higher than 300°C they loose their molecular character due to delocalization of protons in them.

It was also assumed that calcination at temperatures higher than 500°C results in reaction between proton, liberated during deprotonization of hydronium ion, and the crystal lattice of samples in question, leading to the formation of Si-OH groups showing acidic properties.

INTRODUCTION

Acidic properties of clay minerals, determining the course of numerous adsorption and catalytic reactions — both in natural and industrial processes, are actually subjected to large-scale investigations. These properties are conditioned by the presence of acidic centres of Brønsted and Lewis type at the surface of the minerals in question. Surface activity of these substances depends not only on the number of these centres, but also on their strength and distribution as well as on accessibility to reacting molecules.

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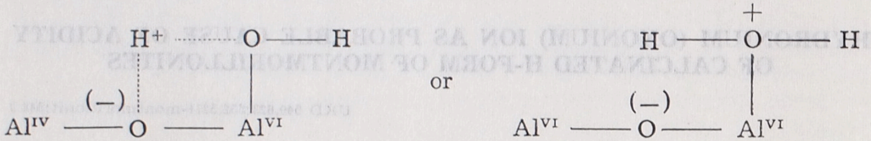
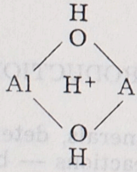
In order to find the cause of, sometimes, strong proton acidity of calcinated hydrogen- and ammonium-forms of dioctahedral smectites, manifested in some catalyctic reactions (Brückman *et al.* 1976), we have to determine precisely the function of protons in these froms of minerals. This problem is still controversial and the state of protons migrating into the interior of layers of H- or NH_4-forms of clay minerals during thermal activation is diversely interpreted by various authors.

On the basis of infrared spectroscopic studies of thermally activated samples of ammonium- and hydrogen-rectorite and of a series of H- and D-forms of smectite, Russel and White (1966) and Russell and Fraser (1971) have found that protons, leaving exchange positions, are locating at oxygens and hydroxyls, showing uncompensated negative charge and coordinated by cations heterovalently substituted in tetrahedral or octahedral layers. Stability of this groupings was explained by assuming the formation of the following arrangements:



The existence of such groupings is manifested by appearance of absorption bands in the *IR* spectra of calcinated hydrogenand ammonium-forms of dioctahedral silicates in the region 3470—3530 cm^{-1} (Russell, White 1966; Russell, Fraser 1971). In these authors opinion, these maxima are due to stretching vibrations of octahedral OH groups perturbed by interaction with protons.

Another interpretation of reaction mechanism between protons and crystal lattice calcinated forms of montmorillonite was proposed by Wright *et al.* (1972). In these authors opinion, absorption bands at ca. 3470 cm^{-1}, appearing after calcination of synthetic ammonium mixed-layer mica/smectite substance, would be due to vibrations of hydroxyl groups perturbed by location of protons in loose tetrahedral space formed by neighbouring (OH, OH) pairs of octahedral layers which can be presented as the following simplified scheme:



Besides, these authors postulate that broad diffused absorption bands appearing in the region 2200—3500 cm^{-1} of the spectrum of calcinated sample studied by them, can be due to translation movements of protons within these tetrahedral spaces.

Another explanation of the function of protons in H-forms of montmorillonite calcinated at temperatures above 300°C was proposed by Vasiliev and Ovcharenko (1975) on the ground of *NMR* studies. The presence of a narrow line ($\Delta H = 0.5\ E$), persisting during thermal activation up to temperature ca. 600°C, is supposed by these authors to be due to the existence of protons not localized in definite electron-donoric centres but freely diffusing within crystal lattice of minerals. However, the mechanism of this peculiar mobility of protons in solid state was not yet explained by these authors.

The essential aim of this study was to establish the factors determining the acidic nature of calcinated hydrogen forms of dioctahedral smectites on the ground of experiments carried out with H-montmorillonites from Chmielnik deposit. It was intended to define the mechanism of interaction between protons and crystal lattice of montmorillonite during its calcination, and to propose a model of acidic from which would be consistent with surface activity of this substance.

EXPERIMENTAL

Hydrogen form of montmorillonite studied was obtained by treating natural washed sample of this mineral, collected from Chmielnik deposit, with 0.05 n solution of hydrochloric acid. Cation exchange ca pacity of the sample examined relative to hydronium ions was found to be 90 mval per 100 g.

Infrared absorption spectra of the samples examined were recorded using *UR-10* (C. Zeiss Jena) spectrophotometer. The specimens were prepared as films sedimented on aluminium foil and pressed at 1000 kG/cm^2. The films thus obtained were placed in a vacuum cell allowing to get spectra in temperature range 20—650°C. The vacuum of approx. 10^{-3} tor was applied. Selected samples were subjected to the action of H_2O, D_2O and pyridine vapours. Samples treated at 700 and 800°C were preliminarily heated for 2 h in electric furnace and subsequently calcinated in vacuum cell at 600°C under lowered pressure.

RESULTS

Infrared absorption spectra for samples of H-montmorillonite from Chmielnik obtained by thermal activation in temperature range 25—800°C using vacuum absorption cell are presented in Figures 1 (*a*—*h*). They display some specific features, characteristic only of hydrogen or ammonium calcinated forms of dioctahedral smectites. Broad diffused band in the region 2400—3500 cm^{-1} occurs within wide temperature range. It disappears but at activation temperatures approx. 700°C (Fig. 1*g*, *h*).

Dehydroxylation process results in a decrease of intensity of this band due to stretching vibration of octahedral OH groups at 3630 cm^{-1}. Partly dehydroxylized forms of sample studied are characterized by fine structure of this band in the region 3600—3700 cm^{-1} (maxima at 3620 and 3670°C) as well as by distinct asymmetry of this band, its diffusion towards lower wave numbers in the region 3450—3600 cm^{-1} (Fig. 1 *d*—*g*). Besides, in the *IR* spectrum of the H- form there appears maxima at 1430 and 1570 cm^{-1} of medium intensity. The latter is fairly distinct at temperatures 260—300°C after considerable dehydration of sample. These maxima disappear at temperatures 600—700°C i.e. simultaneously with disappearance of the plateau in the region 2400—3500 cm^{-1} (Fig. 1).

Another diagnostic feature of the H- form of montmorillonite is its hydratation, persisting till high temperatures (up to ca. 550°C) despite evacuation of vapours at the pressure of ca. 10^{-3} mm Hg. Absorption resulting from deformation of H_2O molecules occurs at 1630 cm^{-1}. Corresponding stretching vibrations represent a component of the wide plateau in the region 3000—3500 cm^{-1}. It should be emphasized that spectra recorded at temperatures higher than 300°C display lack of maxima resulting deformational vibrations of H_2O as well as distinct diminishing of the absorption plateau, particularly in the region 3000—3500 cm^{-1} (Fig. 2 *a—e*).

IR spectra of calcinated samples show the presence of a band at 3750 cm^{-1} which is getting more distinct and intense after nearly complete dehydration of octahedral OH groups (Fig. 1 *f—h*). It is assigned to stretching vibrations of OH in silanol groups. Absolute evaluation of intensity changes of this band within wide temperature range is difficult because of variation of background line in the region approx. 3700 cm^{-1} caused by dehydroxylation of octahedral OH groups.

IR spectra presented in Figure 3 are documenting the changes in absorption caused by sorption of pyridine vapours on Lewis and Brønsted centres. The former results in appearance of 1445, 1470, 1495 and 1598 cm^{-1} maxima whilst the latter of the 1455, 1495, 1550 and 1635 cm^{-1} ones. Besides, this adsorption is the cause of occurrence of some variations in the course of bands characteristic of acidic form of montmorillonite. We observe a distinct increase of intensity of bands resulting from stretching vibrations of octahedral hydroxyl. Besides, it looses, to some extent, the formerly mantioned fine structure and is getting more sharp, showing a maximum at 3760 cm^{-1}. Moreover, asymmetry of this band in the region 3450—3600 cm^{-1} also disappears. Depending on the conditions of adsorption of pyridine, the shape and intensity of 2400—3500 cm^{-1} band is slightly different. It seems that adsorption of pyridine vapours also causes some increase of intensity of bands resulting from vibrations of H_2O

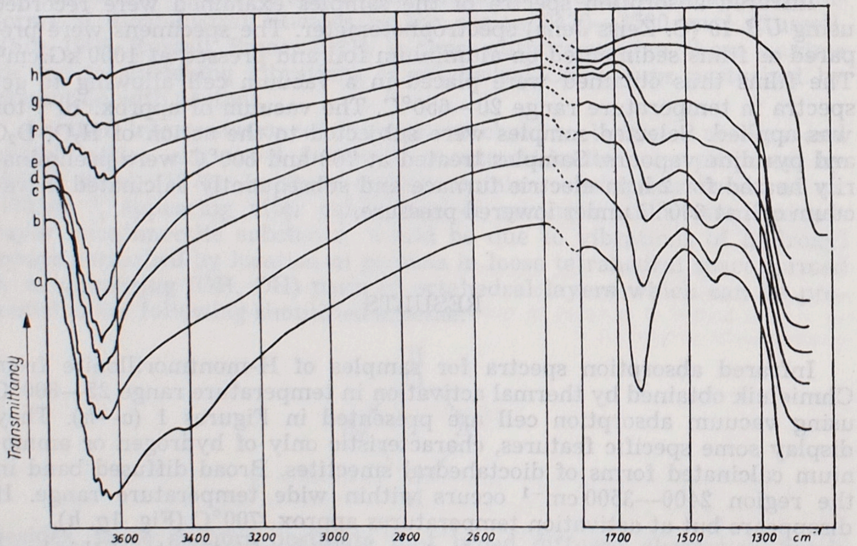


Fig. 1. *IR*-spectra of H-montmorillonite samples representing various degrees of calcination

a — room temperature, *b* — 200°C, *c* — 300°C, *d* — 400°C, *e* — 500°C, *f* — 600°C, *g* — 700°C, *h* — 800°C. During the experiment samples were dehydrated by evacuation to 10^{-3} mm Hg in quartz vacuum cell. Spectra were recorded at room temperature. Samples treated at 700 (*g*) and 800°C (*h*) were preliminarily heated for 2 h in electric furnace and subsequently calcinated in vacuum cell at 600°C under lowered pressure. Sample prepared in the form of thin selfsupporting film

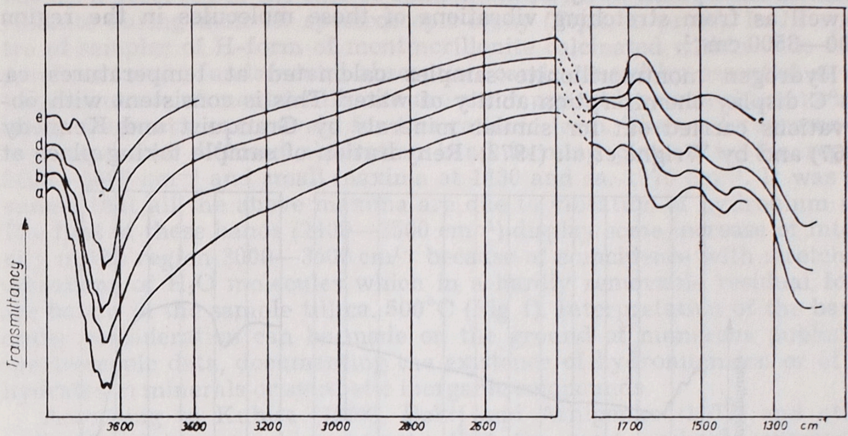


Fig. 2. *IR*-spectra of montmorillonite samples recorded et elevated temperatures

a — 200°C, *b* — 300°C, *c* — 400°C, *d* — 500°C, *e* — 580°C. Spectra were recorded under pressure lowered to 10^{-3} mm Hg in quartz vacuum cell. Sample prepared in the form of thin selfsupporting film

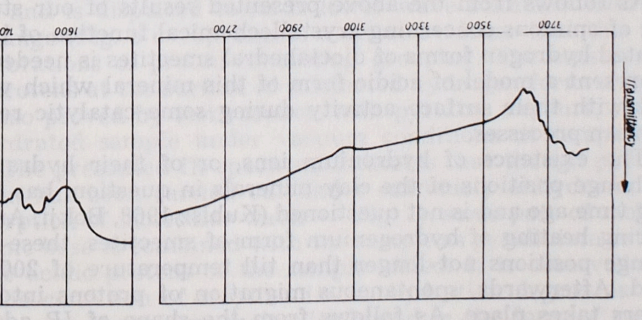


Fig. 3. *IR*-spectrum of H-montmorillonite sample (calcinated at 600°C) after pyridine adsorption (room temperature vapour pressure for 12 h at 150°C followed by 1 h evacuation at 180°C)

Spectrum were recorded in vacuum cell at 25°C; sample prepared in the form of thin selfsupporting film molecules and particularly those from deformational ones — ca. 1600 cm^{-1} as well as from stretching vibrations of these molecules in the region 3000—3500 cm^{-1}.

Hydrogen montmorillonite samples calcinated at temperatures ca. 700°C display chemisorption ability of water. This is consistent with observations carried out for similar minerals by Granquist and Kennedy (1967) and by Wright *et al.* (1972). Rehydration of sample taking place at temperature 25°C and relative humidity of air 40% leads to the results presented in Figure 4. Besides, we observe an increase of intensity at 3670 cm^{-1} band resulting from stretching vibrations of structural hydroxyls and, particularly, in the region above 3000 cm^{-1} as well as an increase of intensity of 1630 cm^{-1} band caused by deformational vibrations of water molecules.

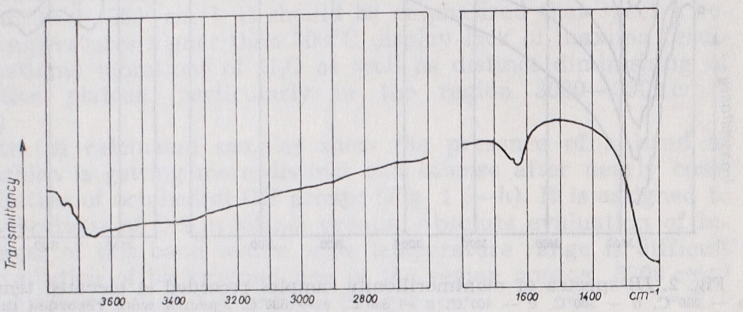


Fig. 4. *IR*-spectrum of H-montmorillonite sample (calcinated at 600°C) after rehydration in ambient conditions during 3 days (humidity 40%)
Sample in the form of selfsupporting film

DISCUSSION

As follows from the above presented results of our study, some revision of opinions concerning crystallochemical function of hydrogen in calcinated hydrogen forms of dioctahedral smectites is needed. It is necessary to present a model of acidic form of this mineral which would be consistent with their surface activity during some catalytic reactions and adsorption precesses.

The existence of hydronium ions, or of their hydrates, localized in exchange positions of the clay minerals in question, has beeen evidenced long time ago and is not questioned (Kubisz 1968, Bokji, Arkhipenko 1977). During heating of hydrogenium form of smectites, these ions occupy exchange positions not longer than till temperature of 200—300°C is reached. Afterwards, spontaneous migration of protons into the interior of layers takes place. As follows from the shape of *IR* adsorption spectra (presented in Fig. 1), no matter of increasing activation temperature above 300°C and up to ca. 650°C with simultaneous evacuation of water vapour, the substance under examination preserves diagnostic features characteristic of hydronium ion from spectra (Fig. 1 *c*—*g*). Analogical behaviour has been observed in the case of ammonium forms of fluorinated montmorillonite during their *IR* spectroscopic study (Fijał, in press). In *IR* spectra of samples of H-form of montmorillonite calcinated within wide temperature range, fundamental absorption bands caused by essential structural elements of montmorillonite are accompanied by some characteristic bands diagnostic exclusively for this cationic form. They are represented by: broad and diffused absorption band forming plateau in the region 2400—3500 cm^{-1} and small maxima at 1430 and ca. 1570 cm^{-1}. It was assumed that all the above maxima are due to vibration of hydronium ion. The first of these bands (2400—3500 cm^{-1}) display some increase of intensity in the region 3000—3500 cm^{1-} because of coincidence with stretching vibrations of H_2O molecules which in a hardly removable residual form are bound in the sample till ca. 500°C (Fig 1). Interpretation of the bands under consideration can be made on the ground of numerous published spectroscopic data, documenting the existence of hydronium ion or of its hydrates in minerals or synthetic inorganic compounds.

According to Kubisz (1968), Bokij and Arhipenko (1977) and other authors opinions we may assume that the most probable absorption regions in *IR* spectra connected with vibrations within this complex ions are as follows:

1. 2400—3550 cm^{-1} bands corresponding to wholly symmetric vibrations ν_1 of A_1 class and to streatching degenerated ones of E class. In the above authors opinion, these bands should be distinctly broad and diffused.
2. 1255—1705 cm^{-1} vibrations ν_4 of E class.
3. 785—1175 cm^{-1} — vibrations ν_2 of the A_1 class.

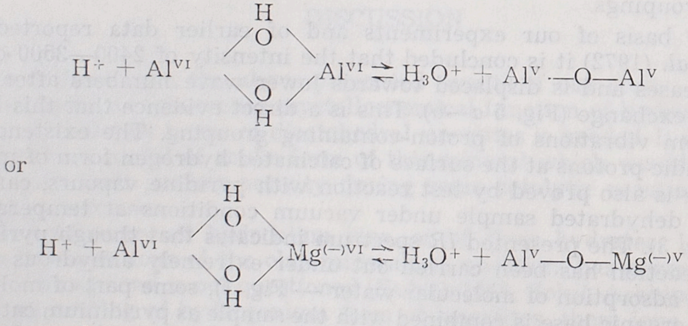
Consequently, the bands in the region 2400—3500 cm^{-1} (ν_1, ν_3) and at 1430 and 1570 cm^{-1} (probably ν_4) can be accepted as spectroscopic evidence of existence of complex hydronium ion in calcinated hydrogen form of montmorillonite. The region of ν_2 vibrations is not diagnostic because of coincidence with very intense bands resulting from vibrations of silica--oxygen groupings.

On the basis of our experiments and of earlier data reported by Wright *et al.* (1972) it is concluded that the intensity of 2400—3500 cm^{-1} band decreases and is displaced towards lower wave numbers after isotopic H/D exchange (Fig. 5 *a*—*b*). This is a direct evidence that this band results from vibrations of proton-containing grouping. The existence of mobile, acidic protons at the surface of calcinated hydrogen form of montmorillonite is also proved by test reaction with pyridine vapours, carried out using dehydrated sample under vacuum conditions at temperature 600°C (Fig. 3). The presented *IR* spectrum indicates that though pyridine sorption reaction has been carried out under extremely anhydrous conditions (no adsorption of molecular water — Fig. 1), some part of molecules of this organic base is combined with the sample as pyridinium cations, containing some acidic protons of the sample tested. It is observed that, depending on the condition of sorption i.e. on hydration degree or temperature, the amount of pyridine molecules bound in the form of pyridinium ions is different. This is caused by competition for protons between adsorbed substance and the layers of acidic form of clay mineral (Yariv, Heller-Kallai 1973) and only strong bases are capable to keep the majority of protons when samples are heated under vacuum conditions.

In the case under consideration, adsorption of pyridine at the surface of sample is followed by a complex of reactions taking place within the acidic form which can be documented by spectroscopic studies. So e.g. there occurs an increase of intensity of stretching vibrations of OH ions. This band is getting more sharp with a maximum at 3675 cm^{-1} and does not show diffusion in the region 3450—3600 cm^{-1} characteristic of so called perturbed hydroxyls. When comparing the spectra of the sample studied before and after adsorption of pyridine (Fig. 1 *f* and 3) we observe a distinctincrease of absorption in the region 3000—3550 cm^{-1} caused by sorption of organic base. We have, however, to take into account (to subtract) adsorption caused by C-H vibrations of pyridine in the region 3000—3250 cm^{-1}. Besides, sorption of pyridine causes a decrease of asymmetry of the band, showing maximum at 1575 cm^{-1}, assigned to ν_4 vibrations of hydronium ion in the region of lower wave numbers and an increase of intensity at 1600 cm^{-1} caused, to some extent only, to C-C vibrations of pyridine.

On the ground of the above data it is assumed that migration of some acidic protons of hydronium complex to the molecules of organic base results in the formation of equivalent amount of molecular H_2O, causing absorption due to stretching and deformational vibrations of H_2O in the region 3000—3500 cm^{-1} and ca. 1600 cm^{-1}. Moreover, sorption of pyridine causes a change of shape of the band resulting from stretching O-H vibrations within silanol groups at 3745 cm^{-1}. Consequently, we observe considerably lower intensity and some broadening of this band (Fig. 3). So, the Si-OH groups are an additional source of acidic protons in calcinated samples of hydrogen form of montmorillonite.

The possibility of formation of complex, positive hydronium ions in thermally activated montmorillonite is, most probably, due to reactions of protons, migrating towards the interior of layers (in temperature range 200—300°C) together with hydroxyls of octahedral sheet according to the following scheme:



(I)

$$H^{+} + Al^{VI}\begin{matrix}H\\O\\ \\O\\H\end{matrix}Al^{VI} \rightleftarrows H_3O^{+} + Al^{V}—O—Al^{V}$$

or

$$H^{+} + Al^{VI}\begin{matrix}H\\O\\ \\O\\H\end{matrix}Mg^{(-)VI} \rightleftarrows H_3O^{+} + Al^{V}—O—Mg^{(-)V}$$

Consequently, migration of protons into the interior of layers could initiate dehydroxylation of octahedral OH groups, in accordance with earlier observations of Russel and White (1966). This dehydroxylation should be accompanied by a change in coordination of octahedral cations which, following Wright *et al.* (1972) opinion, are getting coordination number 5.

Since, because of disappearance of interlayer spacing and collapsing of the crystal lattice, we cannot fix the sites of hydronium ions thus formed in exchange positions, it is advised to localize them either in hexagonal free spaces of tetrahedral layers or in analogical vacances of octahedral ones. Direct interaction of protons with hydroxys of octahedral layers, manifested by appearance of bands connected with perturbed OH groups in the region 3470—3600 cm^{-1}, reported in earlier papers (Russell, White 1966, Russell, Fraser 1971, Wright *et al.* 1972) and observed in this study (Fig. 1), suggests localization of complex hydronium ions in free octahedral positions within partly dehydroxylized crystal lattice of clay mineral.

Thermal stability of hydronium ions in crystal lattice of calcinated smectite is determined by several factors, conditioned both by crystallochemical properities of this ion and by its position in free spaces of crystal lattice of the silicate under examination. This ion shows high energy of total hydration, ranging from 270 to 415 kcal/mol (on the average 300 kcal/mol — Kubisz 1968). Besides, protons of this ion display distinct tendency to form strong hydrogen bonds. So e.g. the bond energy of H_3O^+ ion with water molecules in its trihydrate amounts to 44 — 49 kcal/mol for each water molecule. Consequently, we have to assume hydrogen interaction with oxygens surrounding hydronium ions, additionally increasing its thermal stability and causing perturbance of O-H bond length in hydroxyl groups.

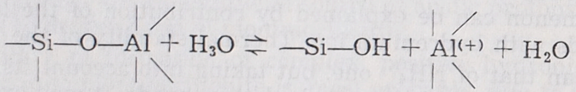
The data presented in earlier publications (Russell, White 1966, Wright *et al.* 1972) and in this paper (Fig. 1 *f*, *g*) indicate higher stability of so called perturbed octahedral hydroxyls relative to the remaining OH ions. This phenomenon can be explained by contribution of the latters to hydrogen bonds with hydronium ion. Thermal stability of the latter should be lower than that of NH_4^+ one, but taking into account its stabilization in vacances of octahedral layer by hydrogen bonds, it may exceed the stability of ammonium. So e. g. the presence of maximum at 1420 cm^{-1} (characteristic of NH_4^+ ion) in *IR* spectrum of ammonium form of montmorillonite from Chmielnik was found to occur (under identical temperature conditions) till 580°C. An additional factor, increasing temperature stability of the complex hydrogen ion, are diffusion barriers acting during removal of H_2O originated during deprotonation of H_3O^+ ions and the fact that hydronium ion is quadrupol in character.

The postulated existence of hydronium ion in calcinated products of the discussed sheet silicates can be the basis of explanation of their, sometimes distinct, acidic properties. Their particular activity e. g. in cracking processes (Brückman *et al.* 1976, Fijał 1977, 1978 - in press) can be explained by high mobility of proton of hydronium ion, especially in systems where hydrogen bonds occur. Proton intrabond jumps along hydrogen bonds formed between these ions and hydroxyl groups of octahedral, oxygen atoms and H_2O molecules may explain (following Eigen *et al.* 1962, Kubisz 1968 and other authors suggestions) acidic nature of the substances examined.

It is well known that hydronium ion and its hydrates do not show rigid structure. Excessive mobile proton forms definite configurations of complex hydrogen-oxygen ions in any short time intervals. Dynamics of this model can be characterized by assuming statistical in time and space probability of distribution of this ion in crystal lattice of the solid (Kubisz 1968). It should be remembered that depending on local structural conditions and on the field exerted by cations in montmorillonite crystal lattice, hydronium ion can be modified to different degree i. e. to show a transitional character between H_2O and H_3O^+.

As follows from the above data, the presence of mobile protons, not localized after calcination at 600°C (suggested by Vasiliev and Ovcharenko 1975 on the ground of *NMR* spectra of H-montmorillonite) can easily be explained by assuming the possibility of existence of hydronium ions in crystal lattice of a solid. It seems that the occurrence of hydronium ions in the structure under consideration is limited by thermal stability of the system formed by coupling between hydrogen-bond protons and hydroxyl groups of octahedra. Particular thermal stability of perturbed hydroxyls has been already emphasized. Deprotonation of hydronium ions probably causes reaction of protons with neighbouring (OH, OH) pairs, with which they were bound earlier (according to scheme I), leading to dehydroxylation of octahedral hydroxyles. As follows from presented data, further increase of temperature causes subsequent reaction of protons with crystal lattice of montmorillonite resulting in the formation of additional silanol groups (Fig. 1*f*, *g*, *h*). This is manifested by an increase of intensity of 3470 cm^{-1} band observed in temperature range 500—700°C. It is well known that thermal stability of silanol groups is higher than that of octahedral hydroxyls. Consequently their absorption bands occur even in *IR* spectra of samples heated at 800°C (Fig. 1*h*). Reaction leading to the formation of these groups can proceed as follows:

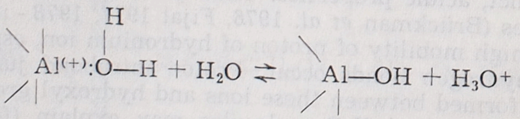
(II)



$$-Si-O-Al + H_3O \rightleftharpoons -Si-OH + Al^{(+)} + H_2O$$

The mechanism of this reaction also suggests the possibility of formation of strong acidic Lewis centres. They would be represented by positively charged AL^{3+} ions, showing no coordinational saturation and thus displaying ability of partial rehydration and rehydroxylation, similarly as H-montmorillonites calcinated at 700—800°C (Fig. 4). When treated with H_2O or D_2O vapours and, particularly, at higher temperatures, the hydroxyl groups connected with octahedral cations are regenerated. This is manifested by reappearance of adsorption band in the region 2400—3550 cm^{-1} (Fig. 5 *a*, *b* and Fig. 4). This reaction would be presented schematically as follows:

(III)



$$Al^{(+)}{:}\overset{H}{O}-H + H_2O \rightleftharpoons Al-OH + H_3O^+$$

Consequently, the reaction I—III represent experimentally evidenced variability of surface properties and, particularly, of acidic ones, depending on the mode of activation of sample — calcination temperature, accessibility to water vapours etc.

Another factor determining proton (Brønsted) acidity of the samples studied is their ability to bind strongly the H_2O molecules, even at high temperatures — up to ca. 550°C. This is manifested by the presence of absorption bands in the region 1600—1650 cm^{-1} due to deformational vibrations of these molecules even in *IR* spectra of calcinated samples at 500°C (Fig. 1 *a*). Stretching O-H vibrations of water molecules are superposing on the band assigned to vibration of hydronium ions causing adsorption in the region 3000—3500 cm^{-1}.

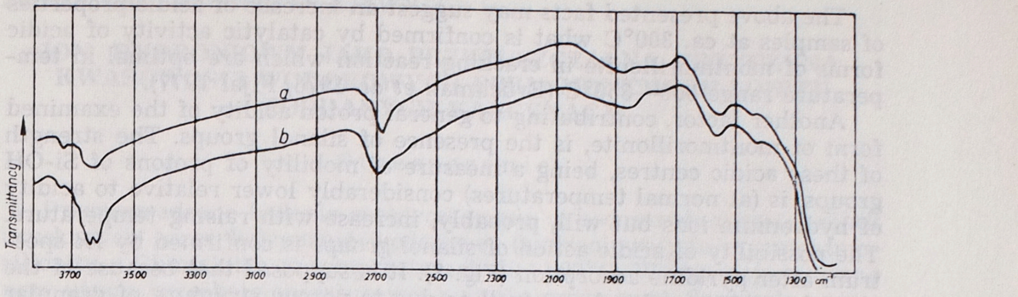


Fig. 5. *IR*-spectra of H-montmorillonite samples heated preliminarily at 600°C and subsequently deuterated using D_2O vapour at 25°C, then calcinated

a — spectrum of H/D-montmorillonite sample evacuated at 200°C, *b* — spectrum of H/D-montmorillonite sample evacuated at 600°C. *IR*-spectra were recorded in vacuum cell at 25°C. Sample prepared in the form of thin selfsupporting film

There are several causes of considerable stability of H_2O in calcinated samples of the hydrogen form in question. The existence of broken bonds at the edges of layers and the resulting presence of coordinationally not saturated Al and Mg atoms favour the binding of water molecules at these centres. It seems, however, that water liberated during dehydroxylation is not immediately expulsed through free space of montmorillonite lattice, but its removal requires overcoming diffusion barriers and delivering sufficient activation energy. Migration of these molecules, even at elevated temperatures and continuous evacuation of vapours for several hours, is a slow process. This phenomenon is also due to possible stabilization of cations in octahedral layers which after dehydroxylation show coordination number 5. Moreover, hydrogen interaction with hydronium ions and coordination by means of Lewis centres render difficult rapid diffusion of these molecules at temperatures lower than 500°C.

Strong polarization of water molecules situated in Lewis centres (its presence is confirmed by pyridine test) results in delocalization of protons in these molecules causing, in turn, an increase of Brønsted acidity of the sample studied. In fact, *IR* absorption spectra of hydrogen form examined at various temperatures (Fig. 2 *a*—*e*) document disappearance of molecular properties of water above 300°C. As follows from comparison of the spectra recorded at 200 and 300°C, at temperatures approx. 300°C the band in the region 1600—1650 cm^{-1} (corresponding to deformational vibrations of H_2O) become diffused and disappear, similarly as those in the region 3000—3500 cm^{-1} resulting from stretching vibrations. This phenomen is due to delocalization of protons. We may, thus, assume that water molecules bound by calcinated hydrogen forms of montmorillonite display instability of chemical character at elevated temperatures, showing tendency to liberate protons and pass into an intermediate stage between H_2O and H_3O^+.

The above presented facts may suggest an increase of acidic properties of samples at ca. 300°C what is confirmed by catalytic activity of acidic forms of montmorillonite in cracking reaction which are optimal in temperature range 300—350°C (Brückman *et al.* 1976, Fijał 1977).

Another factor, contributing to general proton acidity of the examined form of montmorillonite, is the presence of silanol groups. The strength of these acidic centres, being a measure of mobility of protons of Si-OH groups, is (at normal temperatures) considerably lower relative to acidity of hydronium ions but will, probably, increase with raising temperature. The possibility of acidic action of silanol groups is confirmed by *IR* spectrum after pyridine adsorption (Fig. 3). It is supposed that because of the size of pyridine molecule, as well as due to porous structure of granular aggregates of calcinated forms of montmorillonite, participation of all the Si-OH groups in reactions with organic base molecules is not possible.

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JON HYDRONIOWY JAKO PRZYPUSZCZALNA PRZYCZYNA KWASOWOŚCI WODOROWYCH FORM MONTMORILLONITU PODDANYCH KALCYNACJI

Streszczenie

Przeprowadzono badania spektroskopowe w podczerwieni serii próbek uzyskanych przez kalcynację wodorowej (hydroniowej) formy montmorillonitu z Chmielnika w temperaturach 20—800°C. Widma rejestrowano przy użyciu wysokotemperaturowej kiuwety próżniowej. Szczególną uwagę zwrócono na ustalenie funkcji protonu w wodorowych formach badanego minerału poddanych kalcynacji.

Na podstawie analizy spektrogramów przyjęto możliwość istnienia kompleksowych, dodatnich jonów wodorowo-tlenowych (hydroniowych) w sieci krystalicznej montmorillonitu, także po kalcynacji w temperaturach 300—650°C. Spektroskopowym przejawem egzystencji jonu hydroniowego w kalcynowanych substancjach jest obecność pasm absorpcji: 2400—3550 cm^{-1} (od drgań ν_3 i ν_1) oraz maksimów 1430 i 1570 cm^{-1} (prawdopodobnie od drgań ν_4).

Ważnym czynnikiem uczestniczącym w kwasowości protonowej badanych próbek są silnie związane przez mocne centra Lewisa, spolaryzowane drobiny H_2O, które w temperaturach 300°C i wyższych zatracają drobinowy charakter w wyniku delokalizacji protonu tych cząsteczek.

Przyjęto także, iż wynikiem kalcynacji w temperaturach powyżej 500°C jest reakcja protonu, wyzwalanego w trakcie deprotonacji jonu hydroniowego, z siecią krystaliczną badanej próbki, co prowadzi do utworzenia grup Si-OH o własnościach kwasowych.

OBJAŚNIENIA FIGUR

Fig. 1. Spektrogramy próbek reprezentujących różne stadia kalcynacji H-formy montmorillonitu z Chmielnika, rejestrowane w kiuwecie próżniowej pod ciśnieniem 10^{-3} mm Hg. Temperatura kalcynacji
a — pokojowa, *b* — 200°C, *c* — 300°C, *d* — 400°C, *e* — 500°C, *f* — 600°C, *g* — 700°C, *h* — 800°C. Widma *g—h* odpowiadają próbkom wygrzewanym wstępnie przez 2 h, w piecu elektrycznym, a następnie kalcynowanym w kiuwecie próżniowej pod obniżonym ciśnieniem w temperaturze 600°C. Preparat sporządzono w formie cienkiej błonki

Fig. 2. Spektrogramy H-montmorillonitu rejestrowane w temperaturach podwyższonych
a — 200°C, *b* — 300°C, *c* — 400°C, *d* — 500°C, *e* — 580°C. Widma rejestrowano w kiuwecie próżniowej pod ciśnieniem 10^{-3} mm Hg. Preparat sporządzono w formie cienkiej błonki

Fig. 3. Spektrogram H-formy montmorillonitu (prażonej w 600°C), na której sorbowano pary pirydyny w temperaturze 150°C przez okres 12 h (prężność par pirydyny odpowiadała temperaturze pokojowej)
Nadmiar pirydyny ewakuowano w temperaturze 180°C przez okres 1 h. Stosowano kiuwetę próżniową; preparat w formie cienkiej błonki

Fig. 4. Spektrogram H-formy montmorillonitu (kalcynowanej w 600°C), poddanej hydratacji na powietrzu o wilgotności względnej 40%, przez 3 dni
Preparat w postaci cienkiej błonki

Fig. 5. Spektrogramy H-formy montmorillonitu (kalcynowanej w 600°C) traktowanej parami D_2O przez okres 24 h

a — spektrogram H/D-formy po ewakuacji par w 200°C, *b* — spektrogram H/D-formy wygrzewanej w 600°C. Widma rejestrowano w temperaturze 25°C, w kiuwecie próżniowej pod ciśnieniem 10^{-3} mm Hg. Preparat wykonano w formie cienkiej błonki

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Ежи ФИЯЛ, Станислав ОЛЬКЕВИЧ

ИОН ОКСОНИЯ КАК ВЕРОЯТНАЯ ПРИЧИНА ВОДОРОДНЫХ ФОРМ МОНТМОРИЛЛОНИТА, КОТОРЫЕ ПОДВЕРГАЛИСЬ КАЛЬЦИНАЦИИ

Резюме

Были проведены ИК спектроскопические исследования среди образцов, полученных путём кальцинации водородной (оксониевой) формы монтмориллонита при температуре 20—800°C. Спектры были регистированы путём использования высокотемпературной кюветы. Особенное внимание уделялось установлению функции протона в водородных формах изучаемого минерала, которые подвергались кальцинации.

На основании анализа спектограмм принято возможность существования комплексных, положительных водородно-кислородных ионов (оксониевых) в кристаллической решётке монтмориллонита, тоже после кальцинации при температурах в 300—650°C. Спектральным признаком существования охониевого иона в кальцинованных веществах является присутствие полос поглощения: 2400—3550 см$^{-1}$ (из-за колебаний ν_3 и ν_1) и максимумов 1430 и 1570 см$^{-1}$ (предположительно из-за колебаний ν_4).

Очень важным фактором, который принимает участие в протонной кислотности образцов, являются сильно связанные мощными центрами левиса поляризованные молекулы H_2O, которые при температурах в 300°C и выше утрачивают молекулярный характер из-за дилокализации протона этих молекул.

Было принято тоже, что следствием кальцинации при температурах выше 500°C является реакция протона, освобождающегося во время депротонирования охониевого иона, с кристаллической решёткой изучаемо образца, что приводит к образованию групп Si-OH с кислотными свойствами.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. ИК-спектры образцов представляющих различные стадии кальцинации H-формы монтмориллонита из Хмельника, регистрированные в вакуумной кювете при давлении 10^{-3} Hg. Температуры кальцинации

a — комнатная, *b* — 200°C, *c* — 300°C, *d* — 400°C, *e* — 500°C, *f* — 600°C *g* — 700°C, *h* — 800°C. Спектры *g*—*h* соответствуют образцам предварительно прогреваемым 2 h в электропечи, а потом кальцинованным в вакуумной кювете при сниженном давлении и температуре в 600°C. Препарат был приготовлен в форме тонкой плёнки

Фиг. 2. ИК-спектры H-формы монтмориллонита, регистрированные в повышенных температурах

a — 200°C, *b* — 300°C, *c* — 400°C, *d* — 500°C, *e* — 580°C. Спектры были регистрированы в вакуумной кювете при давлении в 10^{-3} мм Hg. Препарат был приготовлен в форме тонкой плёнки

Фиг. 3. ИК-спектр H-формы монтмориллонита (кальцинированной при температуре 600°C), на которой были сорбированы пиридиновые пары при температуре в 150°C в течение 12 h (давление пара пиридина соответствовало комнатной температуре). Излишнее количество пиридина было удалено при температуре в 180°C в течение 1 h

Применялась вакуумная кювета; препарат был приготовлен в форме тонкой плёнки

Фиг. 4. ИК-спектр H-формы монтмориллонита (кальцинированной при температуре в 600°C), которая подвергалась гидратации на воздухе с относительной влажностью 40% в течение 3 дней. Препарат был приготовлен в форме тонкой плёнки

Фиг. 5. ИК-спектры H-формы монтмориллонита (кальцинированной при температуре в 600°C), которая подвергалась воздействию паров D_2O в течение 24 h

a — спектрограмма H/D-формы после удаления паров при температуре в 200°C, *b* — спектрограмма H/D-формы монтмориллонита кальцинированного при температуре в 600°C. Спектры были регистрированы при температуре в 25°C в вакуумной кювете при давлении в 10^{-3} мм Hg. Препарат был приготовлен в форме тонкой плёнки