

Properties of the OH groups in the Mg-montmorillonite structure

^aI. HORVÁTH, ^bE. S. SAN'KO, ^bE. A. PAUKSHTIS, and ^bE. N. YURCHENKO

^a*Institute of Inorganic Chemistry, Centre of Chemical Research,
Slovak Academy of Sciences, 842 36 Bratislava*

^b*Institute of Catalysis, Siberian Branch of the U.S.S.R. Academy of Sciences,
630 090 Novosibirsk*

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Thermal decomposition and the acid-base properties of hydroxyl groups in Mg-montmorillonite were studied by thermoanalytical methods and i.r. spectroscopy. In the temperature range 200—700°C the OH groups of montmorillonite structure were characterized by five absorption bands with $\bar{\nu}(\text{OH})/\text{cm}^{-1} = 3740, 3710, 3675, 3640, \text{ and } 3595$.

Thermally most stable were the OH groups with $\bar{\nu}(\text{OH}) = 3675$ and 3595 cm^{-1} , the least stable those with $\bar{\nu}(\text{OH}) = 3710 \text{ cm}^{-1}$.

Acid-base properties of the OH groups were investigated by the adsorption of pyridine, deuterated ammonia, and benzonitrile vapours. It was found that on the surfaces of the investigated samples (heated at various temperatures in the interval 200—700°C) strong protonic centres are absent, or unattainable for larger molecules. Only the most stable OH groups of the structure in configurations Al—OH—Al and Al—OH—Mg manifested a certain acidity, sufficient for the protonization of ammonia.

The formation of pyridine and benzonitrile donor-acceptor complexes took place *via* surface Mg^{2+} ions mainly after the heat treatment at 500—600°C.

Методами термогравиметрического анализа и ИК спектроскопии изучалось термическое разложение и кислотноосновные свойства гидроксильных групп Mg-монтмориллонита. В температурном интервале 200—700°C в структуре монтмориллонита OH группы характеризуются пятью полосами поглощения $\bar{\nu}(\text{OH})/\text{cm}^{-1} = 3740, 3710, 3675, 3640$ и 3595 .

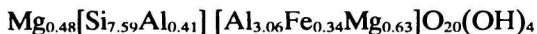
Термически наиболее устойчивыми оказались OH группы с $\bar{\nu}(\text{OH}) = 3675$ и 3595 cm^{-1} , а мало устойчивыми OH группы с $\bar{\nu}(\text{OH}) = 3710 \text{ cm}^{-1}$.

Кислотноосновные свойства OH групп изучались поглощением насыщенных паров пиридина, дейтерированного аммиака и бензонитрила. Установилось, что на поверхностях изучаемых образцов (выжигаемых при различных температурах в температурном интервале 200—700°C) отсутствуют сильно протонные центры или же для больших молекул они

неприступны. Определенную кислотность (достаточную для протонизации аммиака) проявляли только термически наиболее устойчивые OH группы, находящиеся в структуре как группировки Al—OH—Al или же Al—OH—Mg.

Образование донорно-акцепторных комплексов с пиридином и бензонитрилом осуществлялось посредством Mg^{2+} ионов, особенно после выжигания образцов при 500—600°C.

The water from the magnesian form of montmorillonite of the crystallochemical formula



is released in four temperature regions (Fig. 1): 30—130°C (5.9 mass %), 150—260°C (1.6 mass %), 260—370°C (1.2 mass %), and 400—750°C (4.3 mass %). Escaping water comes either from the adsorbed water molecules situated mostly in interlayer spaces of the structure, as well as from hydration shells of Mg^{2+} cations or is produced by the interaction of OH groups during dehydroxylation [1].

In the montmorillonite structure it is possible to distinguish: the OH groups forming octahedral coordination of central atoms (in this case Al, Mg, and Fe), further the OH groups of H_2O molecules from hydration shells of the exchangeable cations (Mg^{2+}), and finally a little part represent the OH groups situated on the crystal edges (also in the form of Si—OH bonds).

By removing the prevailing part of the molecular H_2O and by lowering the OH group concentration in the montmorillonite structure the proton donating centres

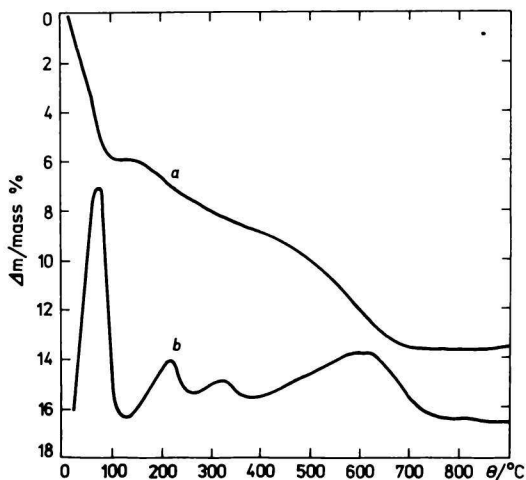


Fig. 1. TG (a) and DTG (b) curves of Mg-montmorillonite.

Thermoanalyzer DuPont 990, heating rate $10^{\circ}C\ min^{-1}$, sample weight 19.38 mg, N_2 flow $1\ cm^3\ s^{-1}$.

can be formed which are important in heterogeneous catalysis [2—4]. The surfaces of Mg-montmorillonite were shown to have acidic properties by *e.g.* Farmer and Russel [5].

The aim of this work is to study the individual types of the OH groups in montmorillonite from the viewpoint of their thermal stability (using mainly methods of i.r. spectroscopy) and to search for a correlation between thermal stability of the OH groups and their acid-base properties.

Experimental

The sample of montmorillonite Jelšovský Potok (separated from the bentonite from the locality of the same name in central Slovakia) was used as starting material in our experiments. The Mg form of this mineral was prepared by repeated saturation with 0.5 M-MgCl₂ solution (until the Ca²⁺ ions disappeared in the interlayer space).

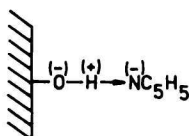
Samples for i.r. spectroscopy were prepared (by isothermal heating in static air atmosphere with 2 h duration) at selected temperatures corresponding to distinct dehydration and dehydroxylation steps: 200°C — desorption of interlayer water; 350°C — removal of the substantial part of water from the hydration shells of the exchangeable Mg²⁺ ions; 500°C — termination of the dehydration and the beginning of the dehydroxylation; 600 and 700°C — advanced dehydroxylation and termination of the dehydroxylation, respectively. Heated specimens were stored in an exsiccator over P₂O₅ to avoid their rehydration.

The specimens of ignited montmorillonite were pressed with CaF₂ to tablets 1 cm in diameter containing 2.3—5.1 mg of the investigated material per 1 cm² of tablet area. The tablets were degassed for 2 h at 1.3 × 10⁻² Pa and then spectra were registered in a UR-20 spectrometer at room temperature. The concentration of OH groups was evaluated on the basis of the relative integral band intensities with the help of a curve synthesizer, taking into account the content of montmorillonite in a tablet.

Acid-base properties were estimated from the adsorption of pyridine, deuterated ammonia ND₃, and benzonitrile.

The adsorption of pyridine vapours saturated at room temperature took place in a specially adapted chamber in the spectrometer at 150°C for 15 min (experimental details were described in [6]). Unadsorbed pyridine was exhausted at the same temperature for 30 min. Deuterated ammonia was adsorbed in two stages, at 25°C and 13 × 10² Pa for 15 min and at 150°C for 15 min. Saturated benzonitrile vapours were adsorbed at room temperature for 15 min.

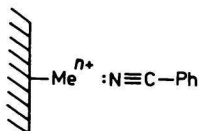
In the i.r. spectra of pyridine after its adsorption, absorption bands near 1545 cm⁻¹ [7] with strong protonic centres can be expected on the solid phase surface due to the formation of a hydrogen bond between the surface OH group and pyridine (Scheme 1)



Scheme 1

Protonic centres are indicated also by the formation of ND_4^+ during adsorption of ND_3 .

Donor-acceptor properties of surfaces were evaluated after adsorption of pyridine and benzonitrile on samples. When pyridine complexes are formed intensive absorption bands at 1450 and 1610 cm^{-1} [7] arise, benzonitrile complexes render an absorption band $\tilde{\nu}(\text{CN})$ in the region of $2240\text{--}2290\text{ cm}^{-1}$. The value $\tilde{\nu}(\text{CN})$ depends on the character of the surface cation Me^{n+} , which reacts with benzonitrile (Scheme 2)



Scheme 2

where Ph represents the phenol ring.

Results

Thermal stability of OH groups

Infrared spectra of the montmorillonite samples after thermal treatment in the region of $3500\text{--}3750\text{ cm}^{-1}$ are shown in Fig. 2. Five absorption bands can be

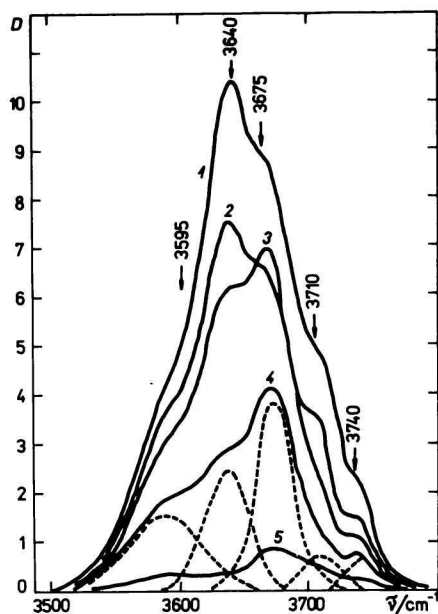


Fig. 2. IR spectra of the OH groups in samples 1—5, according to Table 1.

Dashed lines represent the profiles of the individual bands for sample No. 4. Summarized profiles are correlated for a tablet containing 10 mg of montmorillonite per 1 cm^2 .

distinguished in the spectrum with $\tilde{\nu}(\text{OH})=3740, 3710, 3675, 3640,$ and 3595 cm^{-1} . Corresponding relative intensities of the bands are evaluated in Table 1.

Table 1

Relative intensities* of absorption bands due to OH groups in montmorillonite

Sample No.	Temperature of heating $\theta/^\circ\text{C}$	$\tilde{\nu}(\text{OH})/\text{cm}^{-1}$	3595	3640	3675	3710	3740
		Half-width	70	44	40	35	24
		cm	$\tilde{\nu}(\text{OD})/\text{cm}^{-1}$	2650	2690	2715	2740
1	200		34.2	57.5	35.9	18.5	4.8
2	350		31.3	40.9	29.0	9.3	3.6
3	500		25.3	31.6	33.8	5.9	2.9
4	600		17.0	13.3	21.2	2.7	2.3
5	700		3.6	1.2	4.9	1.6	0.6

* The values of the relative integral intensities were recalculated taking into account the content of montmorillonite in the tablet.

The results indicate that the intensity of individual bands decreases with an unequal rate. The intensity of bands with $\tilde{\nu}(\text{OH})=3675$ and 3595 cm^{-1} which belong to the thermally most stable OH groups is not essentially changed up to 500°C . Less stable are OH groups with $\tilde{\nu}(\text{OH})=3740 \text{ cm}^{-1}$ and the least stable those producing the band with $\tilde{\nu}(\text{OH})=3710 \text{ cm}^{-1}$ (the intensity of the latter decreases steeply and almost linearly with the temperature of heating). The OH groups characterized by absorption band $\tilde{\nu}(\text{OH})=3640 \text{ cm}^{-1}$ escape during the heating to 500°C approximately twice so quickly as the thermally most stable OH groups. The concentration of the latter groups is lowered in the interval $500\text{--}700^\circ\text{C}$ 26 times, while the concentration of the former only 5—7 times.

Acid-base properties of the OH groups

The analysis of the i.r. spectra of all samples after pyridine adsorption showed the absence of the absorption band $\tilde{\nu}(\text{CN})=1540 \text{ cm}^{-1}$. Thus, the acidic OH groups (with $\text{p}K_a \leq -5$) do not occur on the surface of the investigated samples or such centres are unattainable for pyridine molecules.

After adsorption of deuterated ammonia on samples ignited at 200 and 350°C a wide absorption band near 2400 cm^{-1} arises in the i.r. spectra (persisting also after the sucking off the ammonia at 25°C) indicating the presence of chemisorbed ND_3 molecules. The occurrence of OH groups causing the protonization of

ammonia on the surface of samples can be concluded from this result (their pK_a need not exceed 0).

Besides the mentioned band around 2400 cm^{-1} bands with $\tilde{\nu}(\text{OD})$ at 2760 and 2740 cm^{-1} appear in all samples and, after longer treatment with ND_3 arise also bands with $\tilde{\nu}(\text{OD}) = 2715, 2690, \text{ and } 2650\text{ cm}^{-1}$. Their intensity increased with the time of ND_3 treatment whereas the intensities of corresponding $\tilde{\nu}(\text{OH})$ bands at $3675, 3640, \text{ and } 3595\text{ cm}^{-1}$ decreased. The deuterization of these bands took place with different rate. The isotopic exchange H—D of OH groups with $\tilde{\nu}(\text{OH}) = 3675\text{ cm}^{-1}$ took place with the highest rate and of those characterized by $\tilde{\nu}(\text{OH}) = 3595\text{ cm}^{-1}$ with the lowest rate. In the same order the half-width of the band (the width of the band in the half of its height) was increased (Table 1). The morphology of the absorption band depends on the forces displayed by neighbouring atoms on OH groups. In the case of "Y" type zeolites the half-width of the $\tilde{\nu}(\text{OH})$ band renders the information about structural cavities, which are occupied by OH groups [8]. The less is the cavity, the greater is the half-width of the band.

In the course of ND_3 adsorption the OH groups with $\tilde{\nu}(\text{OH}) = 3740$ and 3710 cm^{-1} were readily converted to OD groups (absorption bands $\tilde{\nu}(\text{OD}) = 2760$ and 2740 cm^{-1} , respectively). The absence of the acidic behaviour can be concluded from this result.

Although the presence of stronger proton donating centres was not shown on the surfaces by the adsorption of pyridine (the absorption band at $\tilde{\nu}(\text{CN}) = 1545\text{ cm}^{-1}$ was absent), the formation of donor-acceptor complexes was found to be characterized by bands at 1453 and 1615 cm^{-1} . Similar complexes were formed also during adsorption of benzonitrile (absorption band $\tilde{\nu}(\text{CN}) = 2270\text{ cm}^{-1}$ [9]).

Relative intensity of the band $\tilde{\nu}(\text{CN}) = 1545\text{ cm}^{-1}$ in the spectra of pyridine adsorbed by the studied samples acquired the values: 0.2, 0.3, 0.9, 0.96, 0.32 in dependence on the heating temperature of the samples — 200, 350, 500, 600, and 700°C , respectively.

Discussion

The results of thermogravimetric analysis (Fig. 1) and i.r. spectroscopy (Fig. 2) indicate that the bonds of the OH groups in montmorillonite structure are energetically inhomogeneous.

The i.r. spectrum of a material reveals its structural and chemical character. In the spectrum of pyrophyllite, the crystal structure of which is closely related to that of montmorillonite a typical vibration band of OH groups $\tilde{\nu}(\text{OH}) = 3675\text{ cm}^{-1}$ was observed [10]. Each OH group in the octahedral network in the crystal structure of pyrophyllite is coordinated by two Al atoms in Al—OH—Al combination. With increasing tetrahedral substitution of Si for Al and Al for Mg or Fe in octahedra, as

it occurs mainly in montmorillonites, the forces acting by surrounding atoms on OH groups are changed. The absorption band corresponding to vibrations of OH groups widens and splits. The most significant shifts to lower wavenumbers are due to Fe presence in octahedra [11].

The analyses showed that the absorption bands with wavenumbers $\tilde{\nu}(\text{OH}) = 3640, 3675, \text{ and } 3595 \text{ cm}^{-1}$ are thermally the most stable components of the vibration spectrum in the region of $3400\text{--}3750 \text{ cm}^{-1}$. This triplet characterizes OH groups in octahedral network of the mineral structure. The splitting of $\tilde{\nu}(\text{OH})$ band probably corresponds to the occupation of central atoms in octahedra by three atomic species (there are 76% Al, 16% Mg, and 8% Fe in octahedra according to crystallochemical formula). The most frequent combinations occurring in the octahedra of dioctahedral minerals are: Al—Al—vacancy, Al—Fe—vacancy, and Al—Mg—vacancy [12]. From the viewpoint of the relative intensities of the absorption bands (Table 1) the band with $\tilde{\nu}(\text{OH}) = 3640 \text{ cm}^{-1}$ can be assigned to the OH group occurring between two Al atoms (combination Al—OH—Al). The shift of this vibration to lower frequencies in comparison with pyrophyllite can be explained by the force action of a negative charge localized on the oxygen atoms in tetrahedral network (due to Si—Al exchange) [13]. The absorption bands at $3675 \text{ and } 3595 \text{ cm}^{-1}$ are probably produced by the vibration of OH groups in combinations Al—OH—Mg and Al—OH—Fe.

The absorption band at 3710 cm^{-1} can be assigned to OH groups of strongly dissociated water molecules forming the relicts of hydration shells of Mg^{2+} ions. This band correlates with two extremes on the DTG curve in the region of $150\text{--}350^\circ\text{C}$ (Fig. 1). The rests of water molecules occupying interlayer spaces are presumably responsible for this effect.

The absorption band with $\tilde{\nu}(\text{OH}) = 3740 \text{ cm}^{-1}$ showing the lowest relative intensity belongs obviously to OH groups localized on the edges of montmorillonite crystals. Its $\tilde{\nu}(\text{OH})$ value is close to $\tilde{\nu}(\text{Si—OH})$ value of colloidal silica, therefore an occurrence of $\equiv\text{Si—OH}$ groups in the investigated samples can be assumed in this case. This hypothesis is supported by the fact that OH groups with $\tilde{\nu}(\text{OH}) = 3740 \text{ cm}^{-1}$ are very quickly transformed to OD groups.

The acidic properties were manifested only by certain thermally stable OH groups occupying positions in the octahedral network of the structure. Their acidity is not strong ($\text{p}K_a \approx 0$) and, moreover unfavourable steric factors play a role.

With pyridine and benzonitrile a formation of the donor-acceptor complexes took place. During adsorption of pyridine the intensity of the absorption band corresponding to the complex was found to grow with the temperature of thermal treatment from 200 to 600°C and it dropped substantially for a sample heated at 700°C . The formation of donor-acceptor complexes is connected in this case with the occurrence of Mg^{2+} ions in the structure and on the surface of samples. Their activity is gradually increased by removing of molecular water (hydration shells) as

well as of OH groups bound to Mg^{2+} ions. When a stage of advanced dehydroxylation as well as that of a full dehydroxylation is attained, small Mg^{2+} ions migrate into positions which are unsuitable for the formation of donor-acceptor complexes [14].

Conclusion

There are 5 types of energetically differently bound OH groups in a sample of Mg-montmorillonite dehydrated at 200°C. Thermally most stable are the OH groups occurring in the octahedral network of the mineral structure in configurations Al—OH—Al, Al—OH—Mg, and Al—OH—Fe. In the i.r. spectra it is possible to distinguish the OH groups coming from the rests of hydration shells of the exchangeable Mg^{2+} ions and those localized on the edges of montmorillonite crystals (often as $\equiv Si-OH$ groups).

Testing of proton donating properties of the OH groups showed that in the structure of thermally treated montmorillonite samples there do not occur OH groups with strong acidic properties. However, it is possible that in this case the results are influenced by unfavourable steric factors and thus the protonic centre is not accessible for the organic molecule.

A donor-acceptor behaviour of Mg^{2+} ions was observed mainly after thermal treatment of samples at 500 and 600°C. At higher temperatures of heating this ability of the Mg^{2+} ions is distinctly diminished.

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