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INVESTIGATIONS OF ACID ACTIVATION PRODUCTS OF MONTMORILLONITE BY NMR AND IR SPECTROSCOPIC METHODS

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Abstract. The acid activation product of montmorillonite was investigated by MRJ and IR absorption spectroscopic methods and compared with untreated montmorillonite and synthetic silica gel. It has been found that the second moment M_2 of the MRJ line of the montmorillonite activation product is closed to the M_2 value of silica gel than to M_2 of untreated montmorillonite. The authors presume that this is due to the partial removal of Al and Mg from the octahedral layer during acid activation and to the binding of some protons by oxygen atoms coordinated by Si atoms in the form of Si-OH. This results in an increase of the average proton-proton distances, and therefore in a decrease in the force of their interactions, which is reflected in the M_2 value. The bands ascribed to Si-OH groups (950 and 1420 cm^{-1}) appear in the infrared absorption spectra of activated montmorillonite.

INTRODUCTION

Acid activation of clay minerals, e.g. of montmorillonite, has been studied by several authors (Lopez-Gonzales, Dietz 1952; Mills, Holmes 1950; Osthaus 1956, and others) mainly with a view to defining the structural changes of clay minerals and, consequently, to obtaining products with specified technological properties. Acid activation products of clay minerals find application as catalysts, fuller's earth, plastics fillers, etc. (Mills, Holmes 1950; Grim 1962). Due to those studies, the mechanism of structural transformations of clay minerals, and in their number of montmorillonite, is fairly well known.

The present authors have studied the changes in the mode of proton binding in the successive acid activation products of montmorillonite since the character of proton binding in the activation products defines their acid properties which are essential from the point of view of their utility as, e.g. catalysts. The structure of montmorillonite and of its acid activation products makes it possible for protons to be linked in different ways to the silicon-oxygen bond.

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EXPERIMENTAL

EXPERIMENTAL MATERIAL

The investigations were carried out on an almost monomineral montmorillonite sample separated by sedimentation from bentonite from the Chmielnik deposit, as well as on its activation products. Since the advanced process of acid activation of montmorillonite gives rise to the products which are chemically and structurally close to amorphous silica, comparative studies were carried out simultaneously on synthetic silica gel. Thus, three series of samples were investigated, viz.:

1. Natural Ca-montmorillonite separated from bentonite from Chmielnik. Its chemical and structural properties have been discussed by Tokarski (1953), Kubisz and Stoch (1968), Kłapyta (1975), and others. It is dioctahedral montmorillonite containing mainly Ca^{2+} cations on the exchange positions. The investigations were carried out on an air-dry sample and after heating it at 300°C for 2 and 10 hours.
2. The product of activation of sample 1 with 20% HCl solution for 10 hours at 90°C. The investigations were performed on an air-dry sample and after heating it for 10 hours at 300°C.
3. Synthetic silica gel obtained by precipitation with HCl from potassium silicate solution. It was investigated as an air-dry sample and after heating for 10 hours at 300°C.

EXPERIMENTAL PROCEDURE

The methods of infrared absorption spectroscopy and nuclear magnetic resonance were used to determine the mode of proton binding in the samples discussed.

Infrared absorption spectra were recorded by means of the UR-10 (Zeiss) apparatus. The samples were prepared in the form of KBr disks (about 1 mg of sample +300 mg of KBr).

Derivatives of the proton magnetic resonance spectra were recorded on a home-made broad-line spectrometer at a frequency of 17.45 MHz, using the double modulation technique. Temperature was controlled either by passing cold gaseous nitrogen or by immersing the sample directly in liquid nitrogen in a glass cryostat. Temperature was measured with a copper-constantan thermocouple.

RESULTS

INFRARED SPECTROSCOPIC INVESTIGATIONS

Infrared absorption spectra of untreated montmorillonite, its acid activation product, and of synthetic silica gel are shown in Figure 1.

Acid activation of montmorillonite results in profound changes of its structure (Grim 1962; Fijał *et al.* 1975a, 1975b). Those changes consist in the replacement of interlayer cations by H_3O^+ ions, the removal of Mg^{2+} and Al^{3+} cations from octahedral sites, and in the structural changes in the tetrahedral layers.

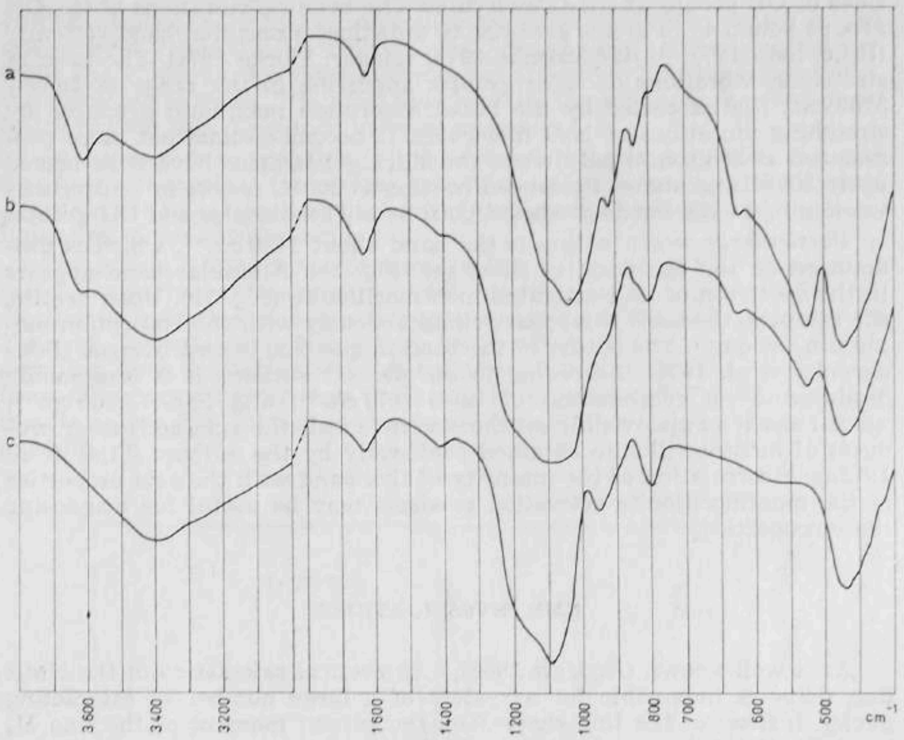

Fig. 1. Infrared absorption spectra
a — untreated montmorillonite (air-dry), *b* — montmorillonite activated with 20% HCl, *c* — silica gel (air-dry)

A comparison of the infrared absorption spectra of untreated (air-dry) sample (Fig. 1*a*) with those of the sample obtained by activation of montmorillonite with 20% HCl solution for 10 hours (Fig. 1*b*) reveals that activation brought about the weakening of the bands 850 and 920 cm^{-1} produced respectively by Mg-OH and Al-OH bending vibrations. Simultaneously, the band 525 cm^{-1} produced by Al-O vibrations is conspicuously weakened. The above observations indicate that Mg^{2+} and Al^{3+} cations are removed from the octahedral layer. At the same time, the spectrum of the activated sample shows a pronounced broadening towards higher wave numbers of the band 1000—1200 cm^{-1} ascribed to ν_3 vibrations of the SiO_4 tetrahedra, and an increase in the intensity of the band 800 cm^{-1} associated with Si-O-Si vibrations. Both these facts evidence that the structure of the tetrahedral layer has been upset and that the process of three-dimensional condensation of SiO_4^{4-} anions leading to the formation of a substance resembling amorphous silica is advancing.

To obtain comparative data, infrared absorption spectra of air-dry sythetic silica gel were taken (Fig. 1c). Particular attention was paid to the change in the character of the absorption bands produced by vibrations of OH groups and H_2O molecules. The bending vibrations of the OH groups bound to Si atoms give rise to a distinct absorption band 950 cm^{-1} (Hino, Sato 1971 — *fide* Moenke 1974; Langer, Florke 1974). The band of stretching vibrations of these groups, appearing in the range of 3600—3700 cm^{-1}, is concealed by the broad absorption maximum produced by stretching vibrations of H_2O molecules. It becomes somewhat more pronounced at 3640 cm^{-1} only when the silica gel samples have been heated up to 300°C and above. Prolonged heating at 300°C results in conspicuous weakening of the bands produced both by H_2O molecules and OH groups.

Particularly worth noting is the band about 1420 cm^{-1}, which is pronounced on the spectrum of silica gel (Fig. 1*c*). A similar band appears in the spectrum of HCl-activated montmorillonite (Fig. 1*b*). Upon heating the samples, the band disappears simultaneously with the absorption maximum 950 cm^{-1}. The nature of the band in question is controversial (Bondarenko *et al.* 1974). According to the present authors, it is presumably produced by a combination of Si-O (470 cm^{-1}) and Si-OS (950 cm^{-1}) vibrations. It is also visible on the spectra of all the acid activation products of montmorillonite obtained previously by the authors (Fijał *et al.* 1975a). A correlation of the intensity of this band with the acid properties of the montmorillonite activation products may be useful for diagnosing those properties.

NMR INVESTIGATIONS

As is well known (Andrew 1956), a theoretical calculation of the NMR line shape is impossible for a system of a large number of interacting nuclei. Instead of the line shape $f(\omega)$, the second moment of the line M_2 is used for the interpretation of the NMR spectra.

The second moment M_2 of spectrum $f(\omega)$ is defined as

$$M_2 = \int_{-\infty}^{+\infty} (\omega - \omega_0)^2 f(\omega)\, d\omega \qquad [1]$$

where ω_0 is the central resonance frequency of spectrum $f(\omega)$.

For a polycrystalline sample containing two types of nuclei with the spins I and S with nonzero magnetic moments and gyromagnetic ratio γ_I and γ_S, the second moment [1] for I spins is

$$M_2^I = M_2^{II} + M_2^{IS} = \frac{3}{5} \gamma_I^4 h^2 I(I+1) \sum_k \frac{1}{r_{jk}^6} + \frac{4}{15} \gamma_I^2 \gamma_S^2 h^2 S(S+1) \sum_{k'} \frac{1}{r_{jk'}^6} \qquad [2]$$

where $\sum_k$ is the sum over positions of all spins S; j, k — numbers of spins I (e.g. protons); k' — spins S (e.g. ^{27}Al).

For a rigid lattice (at low temperatures), M_2 is the greatest, decreasing with an increase in temperature, which is accompanied by atomic motion in the solid. To obtain information on the structure of the material under study, second moments should be compared for rigid lattices.

In a rigid lattice the nucleus interacts with the local field produced by the magnetic moments of the neighbouring nuclei. If random atomic motion occurs (e.g. diffusion, molecular group reorientation), which is described by a characteristic frequency ν_c, comparable to the rigid lattice NMR line witdh $\Delta\nu$ expressed in frequency ($1 Gs = 4 \cdot 257$ kHz for protons), the spectrum narrows. The local field seen by the nuclei is then averaged by the motion, and the second moment decreases.

As appears from equation [2], the second moment may also decrease due to the changes in the crystal structure, i.e. an increase in the mutual distances of the interacting nuclei (r^{-6} dependence), changes in the configuration of the adjacent nuclei.

The proton NMR spectra of samples *1*, *2*, *3* are shown in Figures 2—4 and 5, respectively. The spectra of the air-dry sample of untrated montmorillonite recorded at room temperature and at 77K are presented in Figure 2. A single narrow line from water absorbed is seen at room temperature; upon cooling it broadens splitting into two lines: a narrow one from OH groups (which has the same width as in the vacuum-heated sample — see Fig. 3*c*) and a broad one from H_2O molecules about 14 *Gs* in width.

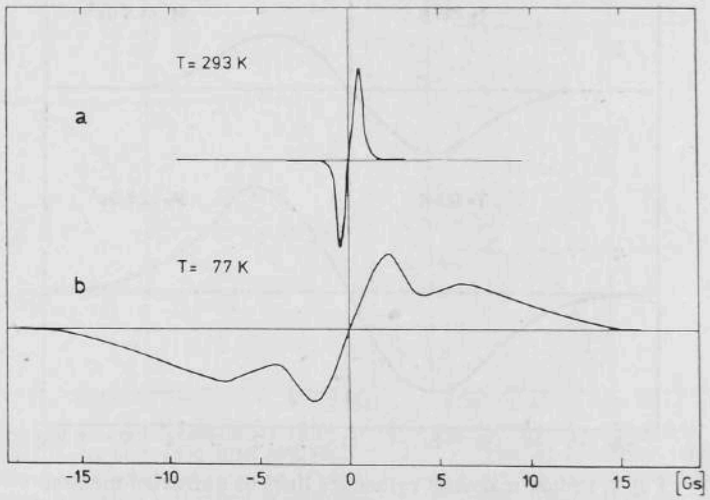

Fig. 2. Proton magnetic resonance lines of untreated montmorillonite
a — air-dry sample (spectrum recorded at room temperature), *b* — air-dry sample ($T = 77K$)

Figure 3 shows the NMR spectra of untreated montmorillonite dried by heating at 300°C for 2 hours (*a*) and 10 hours (*b*). Spectrum (*c*) corresponds to the sample vacuum-dried at 300°C. Spectra *a* — *b* were recorded at room temperature, *c* — at 123K. As anticipated, the narrow line corresponding to H_2O molecules disappears upon drying. There remains, however, the broad line, about 4 *Gs* wide, i.e. similar to that observed in the spectrum of the air-dry sample recorded at liquid nitrogen temperature (Fig. 2*b*).

Activation of montmorillonite (Fig. 4) results in a substantial narrowing of the resonance line, down to width of 1.5 *Gs*. In its shape and width, the line becomes similar to that of silica gel (Fig. 5).

Values of the second moments of the lines are presented in Table 1.

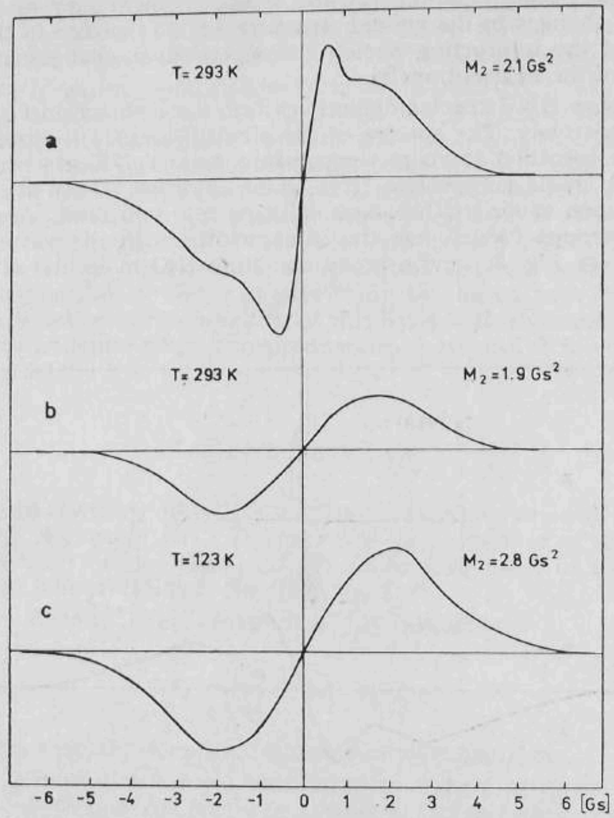

Fig. 3. Proton magnetic resonance lines of untreated montmorillonite

a — dried by heating at 300°C for 2 hours (spectrum recorded at room temperature), *b* — dried by heating at 300°C for 10 hours (room temperature), *c* — vacuum-dried at 300°C for 10 hours (T = 123K)

To understand the phenomenon of the line narrowing in the NMR spectra of the acid activation products of montmorillonite, experiments were carried out at 123K and 77K. As shown in Table 1, the second moments increase with a decrease in temperature. Hence, from the point of view of NMR, the materials under study represent rigid lattices at temperatures not higher than 77K. Therefore, the spectra at 77K are determined by the distribution of protons and ^{27}Al nuclei in the structure of the activation products.

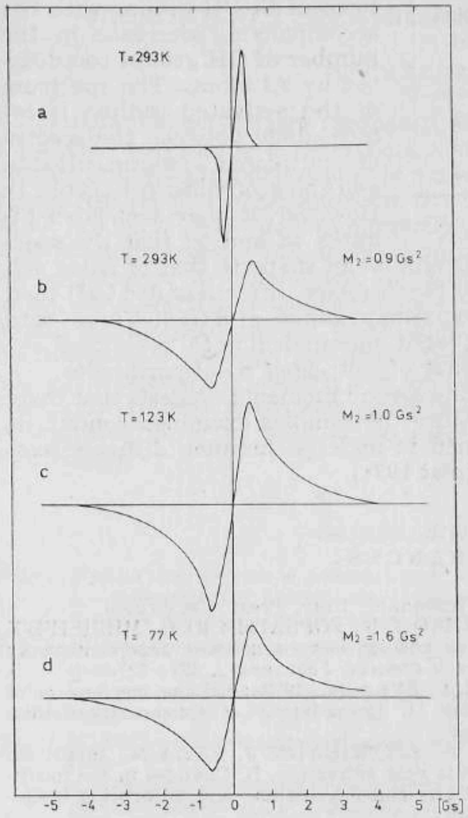

Fig. 4. Proton magnetic resonance lines of montmorillonite activated with 20% HCl

a — air-dry sample (spectrum recorded at room temperature), *b* — dried by heating at 300°C for 10 hours (room temperature), *c* — dried at 300°C for 10 hours (T = 123K), *d* — dried at 300°C for 10 hours (T = 77K)

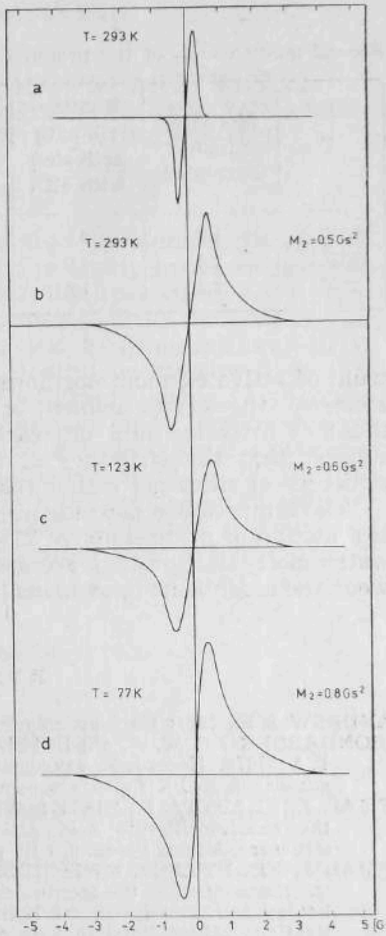

Fig. 5. Proton magnetic resonance line of synthetic silica gel

a — air-dry sample (spectrum recorded at room temperature), *b* — dried by heating at 300°C for 10 hours (room temperature), *c* — dried at 300°C for 10 hours (T = 123K), *d* — dried at 300°C for 10 hours (T = 77K)

The NMR spectrum of untreated montmorillonite containing no interlayer water is determined by the interaction between protons in OH groups in the octahedral layer and, to a lesser extent, by the interaction between protons and ^{27}Al nuclei. The contribution to the second moment from the interaction ^{1}H — ^{27}Al is about 1/3 of that from ^{1}H — ^{1}H.

During the process of acid activation of montmorillonite, considerable amounts of Al are removed, and the average distance between the neigh-

Table 1

Second moments M_2 of the proton lines (Gs^2)

T	Montmorillonite (untreated)	Montmorillonite activated with HCl	Silica gel
293K	1.9	0.9	0.5
123K	2.8	1.0	0.6
77K	3.4	1.6	0.8

bouring protons increases. This is probably due to the binding of some protons to oxygens coordinated by Si atoms in the form of Si-OH groups with the accompanying decrease in the number of OH groups coordinated by Al atoms. The spectrum of the activated sample is intermediate between the spectra of untreated montmorillonite and those of silica gel (Table 1). However, it is evident from Figures 4*d* and 5*d* that the spectrum of activated montmorillonite is similar in shape to that of silica gel. Moreover the second moment of the two samples differ less (0.8 Gs^2) than those of activated and untreated montmorillonite (1.8 Gs^2). These data suggest that the structure of activated montmorillonite resembles the structure of silica gel rather than that of untreated montmorillonite.

The temperature dependence of the second moments suggests that there is a motion of protons above 77K. Since the samples examined contain no water molecules, protons are assumed to undergo jumping diffusion between the neighbouring oxygens (Fripiat 1971).

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WYNIKI BADAŃ PRODUKTÓW KWASOWEJ AKTYWIZACJI MONTMORILLONITU METODĄ MAGNETYCZNEGO REZONANSU JĄDROWEGO I SPEKTROSKOPII W PODCZERWIENI

Streszczenie

Metodą magnetycznego rezonansu jądrowego (protonowego) i spektroskopii absorpcyjnej w podczerwieni zbadano produkty kwasowej aktywacji montmorillonitu porównując je z montmorillonitem wyjściowym i syntetycznym żelem krzemionkowym. Stwierdzono, że drugi moment M_2 linii MRJ produktu aktywacji montmorillonitu jest bardziej zbliżony do M_2 żelu krzemionkowego niż do M_2 montmorillonitu nieaktywowanego. Autorzy tłumaczą to usuwaniem w procesie aktywacji kwasowej znacznej części Al z warstw oktaedrycznych i związaniem części protonów przez atomy tlenu koordynowane wokół atomów Si w formie Si-OH. Powoduje to zwiększenie średnich odległości proton—proton a zatem zmniejszenie siły ich wzajemnych oddziaływań, co znajduje swój wyraz w wartości M_2. Pasma związane z obecnością grup Si-OH (950, 1420 cm^{-1}) pojawiają się w widmach absorpcyjnych w podczerwieni produktów aktywacji montmorillonitu.

OBJAŚNIENIA FIGUR

Fig. 1. Widma absorpcyjne w podczerwieni

a — montmorillonit nieaktywowany (powietrznie suchy), *b* — montmorillonit aktywowany 20% HCl, c — żel krzemionkowy (powietrznie suchy)

Fig. 2. Widma magnetycznego rezonansu protonowego montmorillonitu nieaktywowanego

a — próbka powietrznie sucha (widmo rejestrowane w temperaturze pokojowej), *b* — próbka powietrznie sucha ($T = 77K$)

Fig. 3. Widma magnetycznego rezonansu protonowego montmorillonitu nieaktywowanego

a — osuszany przez ogrzewanie w 300°C w ciągu 2 godzin (widmo rejestrowane w temperaturze pokojowej), *b* — osuszany przez ogrzewanie w 300°C w ciągu 10 godzin (temperatura pokojowa), c — osuszany w 300°C z odpróżnianiem, w ciągu 10 godzin ($T = 123K$)

Fig. 4. Widma magnetycznego rezonansu protonowego montmorillonitu aktywowanego 20% HCl

a — próbka powietrznie sucha (widmo rejestrowane w temperaturze pokojowej), *b* — próbka osuszana przez ogrzewanie w 300°C w ciągu 10 godzin (temperatura pokojowa), c — próbka osuszana w 300°C w ciągu 10 godzin ($T = 123K$), *d* — próbka osuszana w 300°C w ciągu 10 godzin ($T = 77K$)

Fig. 5. Widma magnetycznego rezonansu protonowego syntetycznego żelu krzemionkowego

a — próbka powietrznie sucha (widmo rejestrowane w temperaturze pokojowej), *b* — próbka osuszana w 300°C w ciągu 10 godzin (temperatura pokojowa), c — próbka osuszana w 300°C przez 10 godzin ($T = 123K$), *d* — próbka osuszana w 300°C w ciągu 10 godzin ($T = 77K$)

Ежи ФИЯЛ, Анджей ЯСИНЬСКИ, Витольд ЖАБИНЬСКИ

РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЙ ПРОДУКТОВ КИСЛОТНОЙ АКТИВАЦИИ МОНТМОРИЛЛОНИТА МЕТОДОМ ЯДЕРНОГО МАГНИТНОГО РЕЗОНАНСА И ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ

Резюме

Продукты кислотной обработки монтмориллонита изучено методом ядерного (протонного) магнитного резонанса и абсорбционной инфракрасной спектроскопии, сравнивая их с исходным монтмориллонитом и синтетическим кремнистым гелем. Обнаружено, что второй момент M_2 линии ЯМР продукта активации монтмориллонита наиболей похож на M_2 кремнистого геля чем на M_2 неактивированного монтмориллонита. Авторы объясняют это удалением в процессе кислотной активации значительного количества Al из октаэдрических слоев и связыванием части протонов атомами кислорода координированными вокруг атомов Si в форме Si-OH. Это вызывает увеличение средних расстояний между протонами и, следовательно, уменьшение силы их взаимодействия, что отражается в значении M_2. В инфракрасных спектрах продуктов активации монтмориллонита появляются полосы поглащения связанные с присутствием групп Si-OH (950, 1420 cm^{-1}).

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Инфракрасные спектры

a — необработанный монтмориллонит (воздушно сухой), *b* — монтмориллонит активированный 20% HCl, *c* — кремнистый гель (воздушно сухой)

Фиг. 2. Спектры протонного магнитного резонанса обработанного монтмориллонита

a — образец воздушно сухой (спектр полученный в комнатной температуре), *b* — образец воздушно сухой ($T = 77$ K)

Фиг. 3. Спектры протонного магнитного резонанса необработанного монтмориллонита

a — просушен нагреванием в температуре 300°C в течение 2 часов (спектр полученный в комнатной температуре), *b* — просушен нагреванием в температуре 300°C в течение 10 часов (комнатная температура), *c* — просушен в температуре 300°C в вакуум в течение 10 часов ($T = 123$ K)

Фиг. 4. Спектры протонного магнитного резонанса монтмориллонита активированного 20% HCl

a — образец воздушно сухой (спектр полученный в комнатной температуре), *b* — образец просушен подогреванием в температуре 300°C в течение 10 часов (комнатная температура), *c* — образец просушен в температуре 300°C в течение 10 часов ($T = 123$ K), *d* — образец просушен в температуре 300°C в течение 10 часов ($T = 77$ K)

Фиг. 5. Спектры протонного магнитного резонанса синтетического кремнистого геля

a — образец воздушно сухой (спектр полученный в комнатной температуре), *b* — образец просушен в температуре 300°C в течение 10 часов (комнатная температура), *c* — образец просушен в температуре 300°C в течение 10 часов ($T = 123$ K), *d* — образец просушен в температуре 300°C в течение 10 часов ($T = 77$ K)