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THERMAL RESEARCH OF MONTMORILLONITE SYNTHETIZED FROM THE OXIDES $SiO_2-Al_2O_3-MgO-CaO$

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The thermal behaviour of synthetic montmorillonite of relatively simple chemical composition has been studied and interpreted. Montmorillonite was prepared by hydrothermal synthesis at 300° and 8.8 MPa during 165 hours. With the methods of DTA, DTG, TG, X-ray diffraction analysis, infrared spectroscopy and electron microscopy it was proved that the synthetic montmorillonite is a monomineral sample and no differences from natural montmorillonite were observed.

The clay mineral montmorillonite was prepared by a hydrothermal synthesis ($T = 300°$, $p = 8.8$ MPa, $t = 165$ hours) from a mixture of oxides of SiO_2, Al_2O_3, MgO and CaO in a mass ratio of 7.8 : 1.75 : 0.8 : 0.3. The synthesis has previously been described in detail [1].

By a direct method of gradual acid decomposition (6*M* HCl at 98°) the following unit cell formula has been determined:

$$[Si_{7.95}Al_{0.05}]^{IV}\,[Al_{3.42}Mg_{0.58}]^{VI}\,[Ca_{0.21}Mg_{0.11}]\,O_{20}(OH)_4 \cdot nH_2O$$

By the retention of 2-ethoxyethanol a specific surface of 748 m^2/g was found, while washing out the exchangeable cations with a 0.1 *M* solution of aniline hydrochloride led to a cation-exchange capacity of 0.873 mole equiv. per kg of anhydrous mineral [2].

This paper deals with the thermal behaviour of this synthetic montmorillonite of relatively simple chemical composition.

Experimental

The thermoanalytical curves (DTA, DTG and TG) were recorded on a thermoanalyzer derivatograph, type OD 102 (MOM). During the static thermal measurements, the samples were heated for two hours at given temperature in an apparatus for visual DTA, described in detail by Konta [3].

Samples were measured with a Philips vertical X-ray diffractometer (Cu Kα). Infrared spectra were measured on a Spectromaster (Grubb Parsons, England) in the range 8.5–25 μm. Electron micrographs were taken with a Tesla electron microscope, type BS 242 (acceleration potential 60 kV). The direct enlargement was 2500 times; the final enlargement (7000 times) was obtained by photographic means.

Prior to measurements on the derivatograph, the samples were homogenized in an agate mortar and sieved through a 16 900 mesh/cm^2 sieve. The water content was standardized by placing the samples into a desiccator above a saturated solution of calcium nitrate at a temperature of 20° after being dried at 110° for 7 hours. Conditions of measurements: weight of samples 1000 mg, heating rate 10°/min, atmosphere static air, reference material α-Al_2O_3, sample holders Pt crucibles, sensitivity DTA 1/5, DTG 1/3, TG 500 mg.

DTA, DTG and TG curves of the montmorillonite in the temperature range from 20 to 1200° are given in Fig. 1.

In the temperature interval 50—350° there is a double endothermic peak caused by dehydration of the mineral. The symmetric endothermic peak with maximum at 740° corresponds to dehydroxylation of the montmorillonite. Destruction of the crystal structure is associated with a small endothermic peak with a maximum at 1015°, followed by the first exothermic peak. This peak, with maximum at 1060°, corresponds to the occurrence of high-temperature phases.

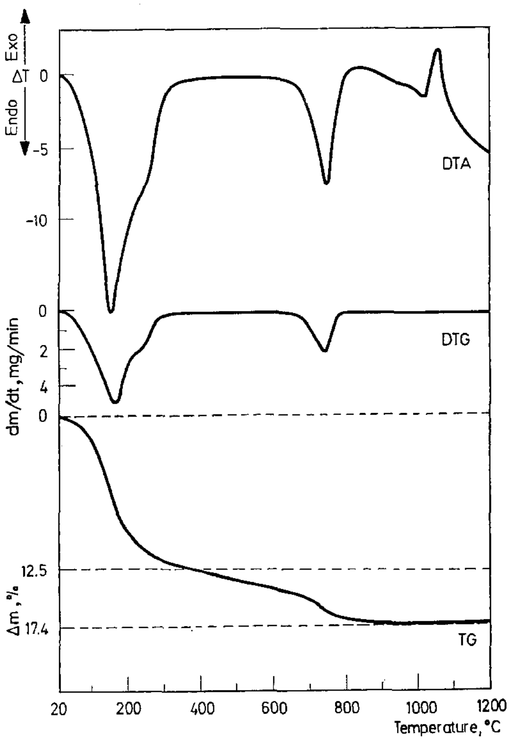

Fig. 1. DTA, DTG and TG curves of synthetic montmorillonite

In the DTG curve the double peak with maxima at 175 and 240° corresponds to the release of water bonded in a molecular form to the surface of the montmorillonite and coordinating the exchangeable Mg^{2+} and Ca^{2+} cations. The third, considerably smaller peak corresponds to the release of water bonded in the form of OH groups in the structure of the mineral. The destruction of the crystal structure of the montmorillonite is not accompanied by mass changes.

From the TG curve it follows that in the temperature range 30–350° a double stage release of water takes place. The weight loss is 12.5%. Dehydroxylation is accompanied by a weight loss of 4.9%. With respect to the fact that the theoretical loss of water molecules from one unit cell of the investigated montmorillonite is 4.92%, the course of the TG curve is in very good agreement with the generally accepted model of the structure of this mineral, with four OH groups per unit cell.

The DTA curve has a typical montmorillonitic character [4]. According to the high-temperature classification by Grim and Kulbicki [5], the sample is apparently of Wyoming type. The high-temperature phases are described in [6].

The results of X-ray measurements of the synthetic montmorillonite gradually heated up to the temperature of crystal structure destruction are given in Table 1. The intensity of the (001) reflection decreases with increasing temperature, in contrast to the intensity of the (003) reflection.

The values of the interplanar spacings of the synthetic montmorillonite are in good agreement with those published for natural montmorillonites from different localities. As can be seen from the results, the synthetic mineral contains at 20°

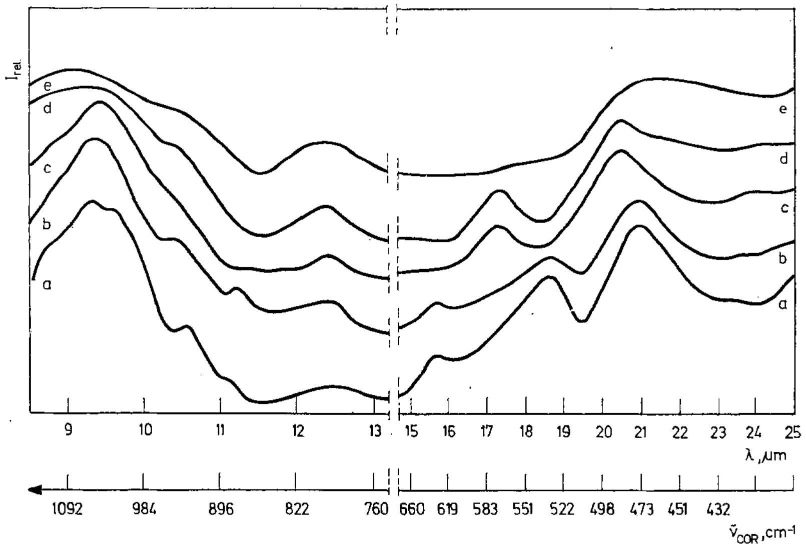

Fig. 2. Infrared spectra of synthetic montmorillonite (a) and the same montmorillonite heated for two hours at 600 °C (b), 700 °C (c), 800 °C (d) and 900 °C (e)

a bimolecular layer of water in the interlayer space. After dehydroxylation the values of *b* were distinctly increased.

Infrared spectra of samples of the synthetic montmorillonite are shown in Fig. 2. The spectrum of the untreated montmorillonite is characterized by three intense absorption bands centered at 1050, 470 and 530 cm^{-1}. The first absorption band is generally assigned to stretching vibrations of Si–O bonds and is typical for all clay minerals [7]. The second one is assigned to deformation vibrations of these bonds, and the third (with maximum at 530 cm^{-1}) is assumed to correspond to vibrations of Si–O–Al bonds [8]. In the infrared spectrum there are also absorption bands with maxima at 1115 cm^{-1}, is typical for all clay minerals [7], the second corresponds to vibrations of Al–OH bonds [8°, the third belongs to different modifications of SiO_2 [8] and the fourth to vibrations of (Mg, Al)–OH bonds [9].

In the spectrum of montmorillonite that had been heated for two hours at 600° no essential changes were observed. The intensity of the absorption band assigned to vibrations of the Si–O–Al bonds was decreased, and the absorption band corresponding to the Al–OH bonds was shifted (from 930 to 945 cm^{-1}).

More distinct changes were caused by heating of the montmorillonite at 700°. The absorption maxima assigned to vibrations of the Si–O bonds remained at 1120, 1045, 795 and 480 cm^{-1}, but the bands with maxima at 930 (or 945), 880 and 635 cm^{-1} disappeared completely, which confirms a total dehydroxylation of the mineral. The shift of the absorption band from 530 cm^{-1} to 565 cm^{-1} can be explained as a result of a change of the octahedral coordination of Al to tetrahedral during the process of montmorillonite dehydroxylation [8]; this is also connected with the observed increase in the value of *b* in the diffraction patterns (Table 1).

Further heating at 800° caused other changes in the character of the infrared spectrum. Only three absorption bands, with maxima at 1060, 800 and 485 cm^{-1},

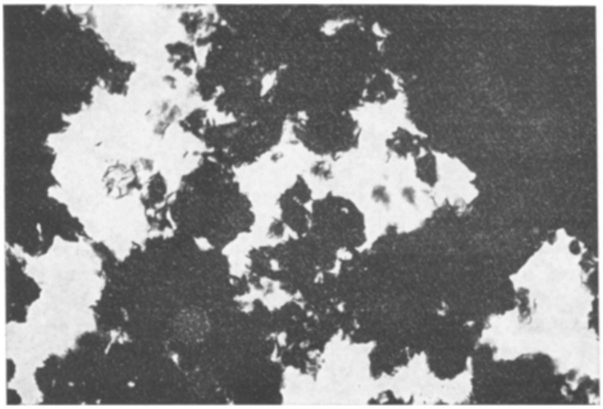

Fig. 3. Electron micrographs of a sample of synthetic montmorillonite; magnification 7000×

Table 1

Interplanar spacings d_{hkl} (nm) of synthetic montmorillonite heated at different temperatures for two hours

hkl	d_{hkl}, 20°	d_{hkl}, 600°	d_{hkl}, 700°	d_{hkl}, 800°	d_{hkl}, 900°
001	1.532	0.958	1.030	1.020	—
002	—	0.473	0.491	—	—
003	0.510	0.316	0.325	0.324	—
110 020	0.443	0.444	0.448	0.447	—
005	0.308	—	—	—	—
130 200	0.254	0.254	0.257	—	—
220 040	0.223	—	0.225	—	—
240 310	0.1684	0.1682	0.1677	—	—
330 060	0.1493	0.1491	0.1513	—	—

corresponding to Si – O vibrations in SiO_4 tetrahedra, and the already interpreted band with maximum at 570 cm^{-1}, were observed in the infrared spectrum. The tendency towards decreasing of the absorption band intensities and increasing of their widths is a manifestation of the gradual "amorphization" of the sample [8], which was also confirmed by X-ray measurements.

A considerably wide and rather indistinct absorption band with maximum at about 1090 cm^{-1}, as well as the further course of the infrared spectrum of the sample heated at 900°, indicate that the SiO_4 tetrahedra are linked together through all four corners [8, 10].

The purity of the synthetic montmorillonite was verified by electron microscopy. In Fig. 3 there can be seen particles of a clay mineral of size 1 to 1.5 μm. Some of

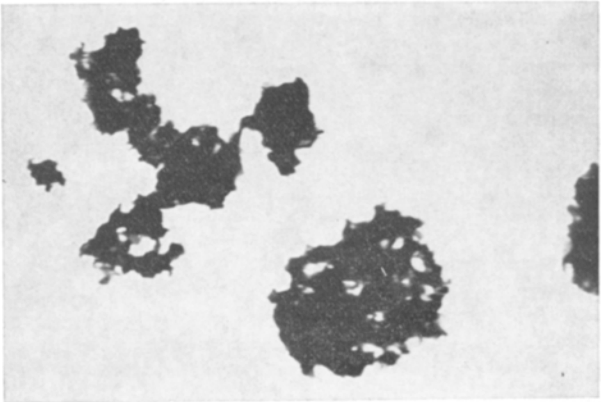

Fig. 4. Electron micrographs of a sample of synthetic montmorillonite after heating at 700 °C; magnification 7000×

them have diffused edges and others have their edges sharp and twisted. It is possible to distinguish clusters of particles which are compact and impenetrable for an electron beam. These aggregates are as large as 10 μm. By its morphology the sample represents a monomineral, well crystallized montmorillonite [11].

Heating of the sample at 600° did not cause any more distinct changes in the morphology of its particles. Only after the sample was heated at 700° could a certain agglomeration of smaller aggregates with irregular and distinct boundaries be observed (Fig. 4). In the agglomerates of particles, spherical cavities in the form of bubbles were observed.

Fig. 5. Electron micrographs of a sample of synthetic montmorillonite after heating at 800 °C; magnification 7000×

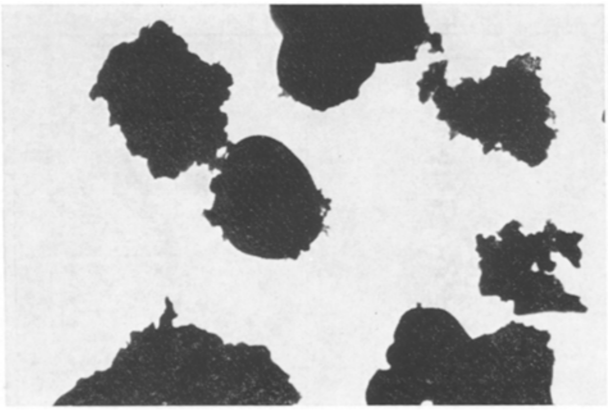

Fig. 6. Electron micrographs of a sample of synthetic montmorillonite after heating at 900 °C; magnification 7000×

Heating of the synthetic montmorillonite at 800° caused the sintering of a considerable proportion of the aggregates (Fig. 5). The aggregates still contain cavities. The great number of electron micrographs made from each sample indicated no presence of other minerals as admixtures.

After heating at 900° the process (sintering) was complete. No unsintered particles were observed in the electron micrographs. The sample consists of distinct glass-like formations with partially spherical character. From the point of view of the morphology it is no longer montmorillonite (Fig. 6).

Discussion

It was proved by the methods of thermal and X-ray diffraction analysis, infrared spectroscopy and electron microscopy that the investigated synthetic montmorillonite of relatively simple chemical composition represents a monomineral sample. The methods used revealed no differences from natural montmorillonite.

In response to increasing temperature the water molecules bonded in the form of bimolecular layers in the interlayer space of the synthetic montmorillonite are gradually released. After dehydration the basal spacing d_{001} is reduced to 0.958 nm, but the morphology of the montmorillonite is not markedly changed.

Heating of the sample for two hours at 700° results in its complete dehydroxylation. Two water molecules that were originally bonded in the form of OH groups to octahedrally coordinated atoms are released from each unit cell. The infrared spectrum indicate formation of $Si-O-Al^{IV}$ bonds instead of the original $Si-O-Al^{VI}$. The electron micrographs show the formation of spherical cavities in the middle of the agglomeration of particles. This allows us to suppose that dehydroxylation of the synthetic montmorillonite is not a homogeneous process [12]: Reorganization of the structure of an octahedral layer of the mineral results in the formation of tetrahedra of AlO_4 in the acceptor regions and in the escape from the donor regions of the water molecules formed. With respect to the fact that one Mg^{2+} ion in the octahedral layer of the ensuing mineral corresponds to approximately seven Al^{3+} ions, it can be assumed that the migration of octahedral atoms (as well as the formation and escape of water molecules) proceeds easily, while the reorganization of the oxygen layer occurs only with certain difficulties; thus, within a relatively wide temperature range an anhydride of montmorillonite appears as an intermediate metastable phase.

The destruction of the crystal structure of the anhydride of montmorillonite at 900° is apparent not only from X-ray measurments (Table 1) but also from the infrared spectrum (Fig. 2), which confirms a linkage of SiO_4 tetrahedra through all four oxygen atoms. Corresponding morphological changes are shown in the electron micrographs (Fig. 6).

In the high-temperature part of the DTA curve (Fig. 1) the exothermic peak follows the endothermic one. This is due to the crystallization of high-temperature phases of the synthetic montmorillonite, which is described in paper [6].

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ZUSAMMENFASSUNG — Das thermische Verhalten synthetischer Montmorillonite verhältnismässig einfacher chemischer Zusammensetzung wurde untersucht und gedeutet. Montmorillonit wurde durch hydrothermische Synthese bei 300 °C und 8.8 MPa in 165 Stunden hergestellt. Durch die Methoden der DTA, DTG, TG, Röntgendiffraktionsanalyse, Infrarotspektroskopie und Elektronenmikroskopie wurde erwiesen, daß synthetische Montmorillonit eine monominerale Probe ist und keine Abweichungen von natürlichem Montmorillonit beobachtet werden konnten.

Резюме — Изучено и объяснено термическое поведение синтетического монтмориллонита относительно простого химического состава. Монтмориллонит был плучен гидротермическим синтезом в течении 165 часов при 300° и давлении 8.8 МПа. Методами ДТА, ДТГ, ТГ, рентгенодифракционного анализа, ИК спектроскопии и электронной микроскопии доказано, что синтетический монтмориллонит является мономинералом и не отличается от природного.