

Hydrothermal synthesis of montmorillonite containing iron in structure

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A method of hydrothermal synthesis of montmorillonite containing iron in structure was elaborated. The starting substances of this synthesis were gel-like amorphous oxides SiO_2 , Al_2O_3 , MgO , and Fe_2O_3 ($T = 573$ K, $p = 8.8$ MPa, and $t = 6$ days) and the method was verified for 22 different ratios of mass amounts of the starting oxides. It has been found that the atoms of iron are built in layers of mineral and do not occur in exchangeable positions. An occupation of the octahedron centres in structure by the Fe(III) atoms brings about a decrease in temperature of high-temperature transformations of montmorillonite. The exchange capacity for cation equivalents of the synthetic mineral is in the interval $0.96\text{--}1.31$ mol kg^{-1} and besides the Mg^{2+} ions the Al^{3+} cations are also present in exchangeable positions. The value of specific surface is about 800 m^2 g^{-1} .

Разработан метод гидротермического синтеза монтмориллонита, содержащего в своей структуре железо, из геля аморфных окислов SiO_2 , Al_2O_3 , MgO и Fe_2O_3 ($T = 573$ K, $p = 8,8$ МПа и $t = 6$ дней). Этот метод был проверен для 22 различных соотношений по массе индивидуальных исходных окислов в смеси. Обнаружено, что атомы железа заключены в тройных слоях минерала, а не находятся в обменяемых положениях. Занятие центров октаэдров в структуре атомами Fe(III) приводит к снижению теплот высокотемпературных превращений монтмориллонита. Значение обменной емкости по катионным эквивалентам лежит у этого синтетического минерала в интервале от $0,96$ до $1,31$ моль кг^{-1} , причем в обменяемых положениях наряду с ионами Mg^{2+} находятся и катионы Al^{3+} . Величина удельной поверхности равна приблизительно 800 м^2 г^{-1} .

The hydrothermal synthesis in the $\text{SiO}_2\text{--Al}_2\text{O}_3$, $\text{SiO}_2\text{--MgO}$, and $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ systems was studied in detail by *D. M. Roy*, *R. Roy*, and *E. Osborn* [1–3]. It has been revealed by these authors that the hydroaluminosilicate montmorillonite arises at the pressure of 68.8 MPa (this was used for all syntheses) and temperatures under 753 K. As the hydrothermal synthesis of montmorillonite from the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ system was mastered in our laboratory under the conditions: temperature = 573 K, pressure = 8.8 MPa,

reaction time = 6 days [4], we used these conditions for the synthesis of montmorillonite from the $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—MgO—Fe}_2\text{O}_3$ system, too.

We have not found in literature any information about a successful synthesis of montmorillonite containing the Fe atoms in structure though montmorillonites found in majority of localities contain the Fe atoms in the structure [5]. Fe(III) is, to a small extent, substituted for Si(IV) in the centres of tetrahedrons and, to a greater extent, for Al(III) in the centres of octahedrons [5]. The aim of this study was to synthesize a few samples of montmorillonite with increasing content of iron in the structure.

Experimental

In our attempts to synthesize montmorillonite hydrothermally from the $\text{SiO}_2\text{—Al}_2\text{O}_3\text{—MgO—Fe}_2\text{O}_3$ system, we used three methods of preparation of the starting mixture for the synthesis:

1. Amorphous silica was added into an aqueous solution of aluminium, magnesium, and iron(III) nitrates and the mixture was dried and annealed for 2 h at 973 K to yield a mixture of oxides.

2. Amorphous silica was added into an aqueous solution of aluminium and magnesium nitrates. The mixture was dried and annealed at 973 K. Thus we obtained a mixture of amorphous oxides to which hydrated amorphous iron(III) oxide was added (it was prepared by precipitating a solution of iron(III) nitrate with aqueous solution of ammonia and drying the precipitate at 378 K).

3. A suspension of amorphous silica in aqueous solution of aluminium, magnesium, and iron(III) nitrates was subjected to precipitation with ammonia. In this way, the corresponding hydroxides in form of a gel were obtained. This gel was washed with water and used without drying for hydrothermal synthesis.

The syntheses were carried out in closed teflon crucibles which were placed in autoclaves of stainless steel with 0.1 dm^3 internal volume. The autoclaves were put for 6 days at 573 K in an adapted electric drier. The pressure of water vapour at this temperature was 8.8 MPa. The samples were synthesized in five particular series and the mass amount ratios of the starting oxides varied in broad intervals (Table 1).

Three of the prepared samples did not contain any Fe_2O_3 , but their content of MgO varied. Among the other 22 samples, sample 5 exhibited the maximum content of Fe_2O_3 . In this case, the mass of Fe_2O_3 represented 21.5% of the starting oxides. After the synthesis the samples were dried at 378 K and thoroughly homogenized in a mortar.

The products were identified by means of X-ray phase analysis and thermal analysis. The X-ray measurements were performed on a vertical goniometer (Philips) using the lamp with Cu anticathode (voltage 35 kV, current 20 mA, Ni filter). The thermoanalytical measurements were carried out on a thermoanalyzer Derivatograph (MOM, Budapest) up to 1373 K (heating rate 10 K min^{-1} , weight of sample 300 mg, $\alpha\text{-Al}_2\text{O}_3$ as reference material, static atmosphere—air).

Table 1

Mass amount ratios of the starting oxides $n(\text{SiO}_2) : n(\text{Al}_2\text{O}_3) : n(\text{MgO}) : n(\text{Fe}_2\text{O}_3)$

Sample	$\frac{n(\text{SiO}_2)}{\text{mol}}$	$\frac{n(\text{Al}_2\text{O}_3)}{\text{mol}}$	$\frac{n(\text{MgO})}{\text{mol}}$	$\frac{n(\text{Fe}_2\text{O}_3)}{\text{mol}}$	Synthesis
1	4	1	0.3	0	1
2	4	0.9	0.3	0.1	
3	4	0.8	0.3	0.2	
4	4	0.7	0.3	0.3	
5	4	1	0.2	0.6	2
6	4	1	0.3	0.5	
7	4	1	0.4	0.4	
8	4	1	0.5	0.3	
9	4	1	0.6	0.2	
10	4	1	0.7	0.1	
11	4	1	0.8	0	
12	4	1	0.70	0	3
13	4	1	0.65	0.05	
14	4	1	0.60	0.10	
15	4	1	0.55	0.15	
16	4	1	0.7	0.10	4
17	4	1	0.6	0.10	
18	4	1	0.5	0.10	
19	4	1	0.4	0.10	
20	4	0.9	0.7	0.10	5
21	4	0.9	0.7	0.15	
22	4	0.8	0.7	0.15	
23	4	0.8	0.7	0.20	
24	4	0.9	0.6	0.15	
25	4	0.8	0.6	0.20	

The values of cation exchange capacity and specific surface were determined for selected samples. The exchangeable cations were estimated after displacement with aniline hydrochloride (120 cm³ of solution with concentration 0.1 mol dm⁻³ for 0.5 g of sample) [6]. The magnesium was determined complexometrically by using eriochrome black T as indicator while xylenol orange was used for complexometric determination of aluminium. The iron(III) was determined photometrically by using sulfosalicylic acid (absorbance at the wavelength 440 nm).

Before determining the specific surface, the investigated samples were treated with the CaCl₂ solution of 1 mol dm⁻³ concentration for obtaining monoionic Ca-montmorillonites. The specific surface was determined by the method of gradual desorption of 2-ethoxyethanol in vacuum at 298 K. This method enables to determine the surface density of 2-ethoxyethanol which forms a monomolecular layer. As the value of this

quantity is equal to 0.326 mg m^{-2} [7] for Ca-montmorillonite, the corresponding specific surface can be easily calculated.

Results and discussion

The X-ray diffraction patterns of the samples which had been hydrothermally synthesized from a mixture of oxides (SiO_2 , Al_2O_3 , MgO , Fe_2O_3) according to the first method contained the diffraction lines of montmorillonite and the two most intensive lines of Fe_2O_3 diffractions corresponding to interplanar distances of 0.269 nm and 0.251 nm. The intensities of montmorillonite diffractions decreased and the background of X-ray diffraction patterns increased with increasing proportion of iron(III).

The DTA and TG curves of the products of synthesis exhibited a course typical of montmorillonite. The water sorbed in samples was released at temperatures below 620 K while the water bound in the form of the OH groups escaped in proximity of 973 K. The collapse of the crystalline structure of the mineral manifested itself on the DTA curves by an endothermic peak and the subsequent crystallization of high-temperature phases gave rise to an exothermic peak. The last two processes do not affect the course of the TG curves.

The couple consisting of endothermic and exothermic peaks on the DTA curves shifted to lower temperatures with increasing content of Fe_2O_3 in samples. This couple of peaks was shifted to lower temperatures quite significantly when compared with the records obtained for the samples synthesized without Fe_2O_3 (samples 1, 11, and 12 in Table 1).

We have verified that an addition of Fe_2O_3 to the samples of montmorillonite which were synthesized only from the SiO_2 — Al_2O_3 — MgO system does not produce such shift. The DTA curves in the temperature interval 1073—1373 K of sample 1 without iron atoms, of sample 1 with admixture of hydrated Fe_2O_3 (corresponding to the Fe_2O_3 content in sample 3), and of sample 3 with iron atoms in the structure of synthetic montmorillonite are represented in Fig. 1. It results from these facts that the iron atoms partially get built in the crystal structure of montmorillonite during the syntheses according to the first method, but a part of them does not react in this manner and remains in the form of a particular phase of iron(III) oxide. The unreacted portion of Fe_2O_3 does not affect the course of the DTA and TG curves, but manifests itself by brown-red colour and especially by two diffractions of Fe_2O_3 in the X-ray diffraction patterns.

The products of hydrothermal syntheses according to the second method (synthesis from a mixture of annealed oxides (SiO_2 , Al_2O_3 , MgO , and hydrated Fe_2O_3)) gave diffractions of montmorillonite as well as the two above-mentioned

diffractions of Fe_2O_3 in the X-ray diffraction patterns. The presence of the unreacted portion of Fe_2O_3 was not reflected in the course of the DTA and TG curves, but it manifested itself by red colour of all samples.

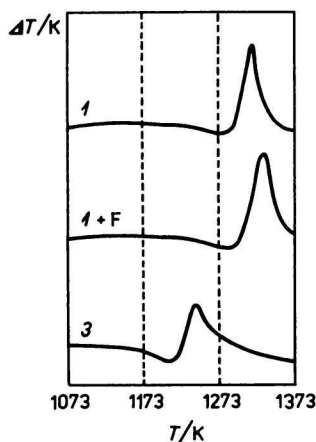


Fig. 1. DTA curves of synthetic montmorillonites. Sample 1 without Fe(III) in structure; 1 + F — sample 1 with admixture of hydrated Fe_2O_3 ; sample 3 containing Fe(III) in structure.

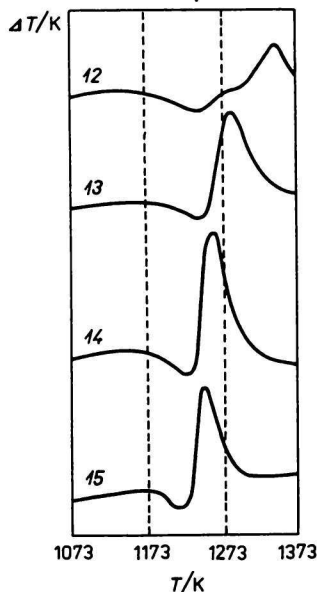


Fig. 2. High-temperature region of the DTA curves of synthetic montmorillonites. Samples 12—15 according to Table 1.

For both methods of synthesis of montmorillonite a part of iron atoms remained nonbuilt in the layers of mineral and formed a particular phase of Fe_2O_3 . The cause of unsatisfactory results probably consists in imperfect homogeneity of the starting mixture prepared by the both methods.

The products of hydrothermal synthesis according to the third method (synthesis from the gel of hydrated oxides) differed by colour from the preceding ones. The original red or even brown-red colour of the starting mixture was quite suppressed.

The diffraction lines of Fe_2O_3 did not appear in the X-ray diffraction patterns even in a single case though the crystalline Fe_2O_3 arises from the gel of hydrated oxide by hydrothermal action ($T = 573 \text{ K}$, $p = 8.8 \text{ MPa}$, $t = 6 \text{ days}$). The DTA curves of all samples exhibited the course typical of montmorillonite. The sorbed water and the water forming the hydration sphere of exchangeable cations was released from samples below 620 K. The endothermic peak with the

maximum in the temperature interval 963—1008 K corresponds to the release of the water bound in the form of the OH groups in octahedral sheets of montmorillonite. The collapse of the layer and the formation of crystalline high-temperature phases manifests itself by two peaks in vicinity of the temperature of 273 K. A considerable difference between the samples without and with the Fe(III) atoms is observed. Provided the Fe(III) atoms are present in the structure of montmorillonite, this couple of peaks on the DTA curve shifts largely towards lower temperatures [8].

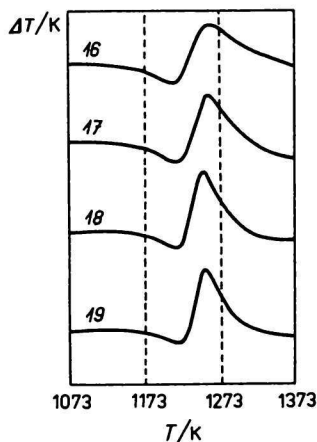


Fig. 3. DTA curves of synthetic montmorillonites with gradually decreasing content of MgO. Samples 16—19 according to Table 1.

The samples with high contents of the magnesium are montmorillonites of the Cheto type the exothermic peak on the DTA curve of which is distinctly separated from the preceding endothermic peak. As for these samples, the shift of the mentioned couple of peaks is not so conspicuous. The DTA curves (in high-temperature region) of sample 12 with maximum 7.5% content of MgO and samples 13—15 with gradually increasing content of Fe₂O₃ and decreasing content of MgO are represented in Fig. 2. The shift in the couple of peaks towards lower temperatures by the effect of Fe₂O₃ is evident. The transition of montmorillonite of the Wyoming type to montmorillonite of the Cheto type (increased content of MgO) is described in papers [9—11].

The DTA curves of samples 16—19 in which the content of Fe₂O₃ was in principle constant, but the content of MgO continuously decreased give evidence that the observed shift towards lower temperatures is not caused by decreasing content of MgO in the samples (Fig. 3, Table 1). As obvious, the temperature corresponding to the maximum of the exothermic peak remains constant in this case.

After transformation of samples 11—25 into Ca-montmorillonites, we determined the specific surfaces. The obtained values varied within the interval 785 — $832 \text{ m}^2\text{g}^{-1}$. However, no direct dependence on content of the Fe(III) atoms in the structure of minerals could be observed. The total specific surface of natural montmorillonites calculated from the parameters of the unit cell and results of chemical analysis corresponds approximately to 750 — $800 \text{ m}^2\text{g}^{-1}$ [12].

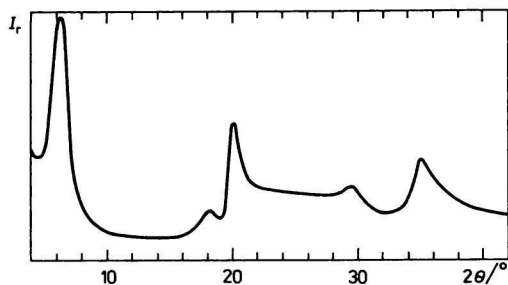


Fig. 4. X-Ray diffraction pattern of synthetic montmorillonite containing the Fe(III) atoms in structure. Sample 14 (Table 1).

Cation exchange capacity was determined for samples 12—14 and 20—25. It appears that iron did not occur in exchangeable positions and all samples were Mg—Al-montmorillonites. The value of the exchange capacity for cation equivalents varied within the interval 0.96 — 1.31 mol kg^{-1} while aluminium the ions

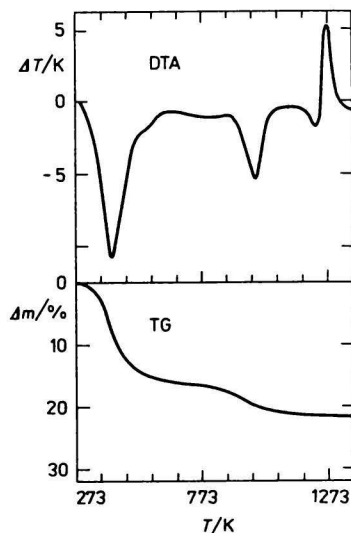


Fig. 5. DTA and TG curves of sample 14 consisting of synthetic montmorillonite (heating rate 10 K min^{-1} , weight of sample 300 mg).

of which were displaced from exchangeable positions in all investigated samples represented about one fifth of the capacity. Thus the ion exchange ability of the samples of synthetic montmorillonite corresponded to the ion exchange ability of natural mineral.

For better clearness and documentation of the obtained results, we present the X-ray diffraction pattern of sample 14 (Table 1) in Fig. 4 and the DTA and TG curves of this sample up to the temperature of 1373 K in Fig. 5. The course of the DTA curve is characteristic of montmorillonite of the high-temperature Wyoming type.

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