# Changes in the surface and microstructure of montmorillonites after thermal treatment

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The changes in the microstructure and specific surface of three samples of the Ca forms of dioctahedral smectites due to thermal treatment have been investigated. The measurements of external surface area by the BET method, total surface area by the method of retention of the ethylene glycol monoethyl ether and the distribution of pore sizes obtained from the adsorption isotherms of argon have shown that the changes in external surface area in the heating region up to 400°C are significantly affected by the residual molecular water film as well as residual negative charge of the three-layer of smectite. From 500°C, the total as well as external surface of the investigated smectites starts to decrease considerably owing to dehydroxylation and this process is finished in the temperature region under 900°C.

It appears that plenty of cavities and transport canals remain preserved up to 800°C. Through these canals, the gaseous aqueous phase may escape during dehydroxylation or conversely, a gaseous reagent can penetrate to accessible surface in adsorption or in catalytic processes.

Были исследованы изменения микроструктуры и удельных поверхностей трех образцов диоктаэдрических смектитов в Са-форме после их термической обработки. На основании измерений внешних удельных поверхностей методом БЭТ, общих удельных поверхностей методом удержания моноэтилового эфира этиленгликоля и распределения величины поров по изотермам адсорбции аргона было показано, что изменения внешних удельных поверхностей в области нагрева до 400°С в значительной степени подвержены влиянию остаточной пленки воды, а также избыточным отрицательным зарядом тройного слоя смектита. Начиная с 500°С, как внешние, так и общие удельные поверхности изученных смектитов сильно понижаются вследствие дегидроксилирования, которое заканчивается до 900°С.

Оказалось, что при нагреве до 800°С в смектитах остаются достаточные пространства и транзитные проходы, через которые может газообразная водная фаза в ходе дегидроксилирования улетучиваться или же газообразный реагент при адсорбционных и каталитических процессах входить в свободно доступную поверхность.

For investigations of catalytic activity and sorption processes, it is important to find out the possible passages through which the reagent penetrates the surface of smectite or the reaction products escape. The investigation of the kinetics of dehydration or dehydroxylation also necessitates the disclosure of canals and passages through which the water released in these processes could escape.

In these cases, the problem in question is to reveal the behaviour and transformations of the solid phase from the view-point of transport phenomena after heating to higher temperatures.

One of the characteristic properties of smectites is their specific surface. According to possible access of different molecules, the surface area is to be divided into

a) external surface which is represented by external area of the leaf crystals of which the grains of mineral are composed, *i.e.* the sum of their upper and lower areas as well as sidewalls;

b) internal surface which is represented by the sum of all surfaces of particular three-layers in the crystal. It is obvious that this surface many times exceeds the external surface because one crystal may contain several tens or hundreds of individual three-layers.

The surface area of montmorillonite in relation to the changes produced by its heating has not been studied in more detail as yet.

### Experimental

#### *Materials and methods*

For investigations, three pure monomineral montmorillonites of different provenance were used: Polkville (USA), Askangel' (USSR), and Jelšový Potok (ČSSR). The preparation of pure monomineral samples and their transformation into the Ca form was carried out by the method described in [1].

The samples were isothermally heated at a given temperature for 1 h in platinum crucibles in a muffle furnace in air atmosphere.

The external surface area was calculated by the BET method [2] from the adsorption isotherms of argon which were determined with a volumetric apparatus modified by *Daneš* [3]. The adsorption of Ar was determined at 77.3 K.

The distribution of micropores was evaluated from the adsorption isotherms of argon of the samples of montmorillonite Polkville by the MP method according to [4].

The total surface area was calculated from retention of the ethylene glycol monoethyl ether according to [5].

### Results and discussion

The structure of montmorillonite is laminated. The individual fundamental three-layers are bound to each other by relatively weak attractive forces owing to

which the polar water molecules can easily penetrate between three-layers. Water is adsorbed on internal surface of individual three-layers, *i.e.* on the planes of oxygen atoms of the tetrahedral network and furthermore, it forms hydration spheres about individual exchangeable cations which compensate for the excess negative charge of three-layer. Besides, owing to texture arrangement, there are vacancies — pores — between the leaf-shaped crystals of montmorillonite where the capillary forces can produce the condensation of water vapour from the atmosphere.

The water molecules form an adsorption film in the interlayer, the width of which varies with external conditions (temperature, relative humidity, pressure, *etc.*) and kind of the exchangeable cation. In air-dry samples of the Ca montmorillonites the width of this film is about 0.4—0.5 nm [6].

By heating of montmorillonite, the pore water and physically bound unstable water is liberated first. Water escapes from the pores of grains under static conditions at temperatures of about 100°C. The interlayer water, *i.e.* water bound at interlayers of the smectites by sorption forces as well as the coordination water forming the solvation spheres of exchangeable cations is continuously released up to the temperature of 400—450°C. Over this temperature, a dehydroxylation, *i.e.* mutual reaction of the structural hydroxyl groups, sets in and gives water vapour which is released from the solid phase while the whole structure is simultaneously reorganized.

### Surface area and texture of thermally nontreated montmorillonites

By evacuating at 20°C (needed for determination of the argon isotherm), a substantial portion of the water present in pores among the particles escapes. The water occurring on the surface of flake-shaped particles of montmorillonite also escapes. However, some places on the surface remain covered with a residual water film. That has been shown by the investigations of adsorption performed by *Mooney et al.* [7], *Barshad* [8], and *Johansen* and *Dunning* [9]. These views are also confirmed by our investigations of the size distribution of microcavities (Fig. 1). The distribution curve of microcavity sizes of montmorillonite Polkville evacuated at 20°C exhibits two distinct maxima. The first one, in the range of wall distances under 0.55 nm, indicates the presence of microcavities which permit, at the maximum, the formation of a monomolecular layer of adsorbate between two neighbouring surfaces. That is likely to concern the cavities arisen at the external surface of particles and crystals after escape of the monomolecular water film. The residue of the water film forms the supports preventing an approach and tight adhesion of external surfaces of the crystals. The second broader maximum occurring in the region over 1 nm corresponds to the presence of vacancies where the supports consist of the thinnest leaves of montmorillonite represented only by single three-layer unit [10].
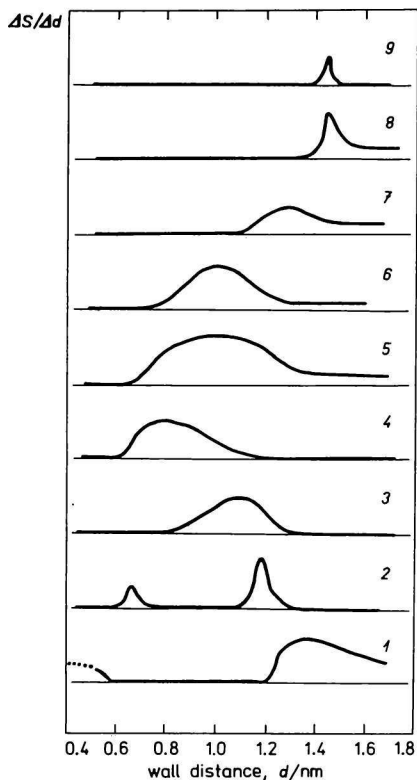
Fig. 1. Distribution curves of the pore sizes for montmorillonite Polkville.
1. 20°C; 2. 100°C; 3. 200°C; 4. 300°C;
5. 400°C; 6. 500°C; 7. 600°C; 8. 700°C;
9. 800°C.

The observations of *Barrer* and *McLeod* [11], *Brooks* [12], and *Aylmore et al.* [13] suggest that the sorption of a nonpolar gas which has practically access only to external surfaces and sides of crystals of the smectite and the value of external surface area depends on kind of the evacuation used. Moreover, *Green-Kelly* [14] and *Knudson* and *McAtee* [15] ascertained the influence of arrangement and orientation of the crystals.

A verification of the effect of incomplete removal of water is documented for samples of Polkville and Askangel' in Fig. 2. The residual water is calculated within the constituent weight of a sample evacuated at 300°C and at the pressure of 1 Pa. As obvious, the presence of water significantly influences the external surface area of samples. Even after longer evacuation over $P_4O_{10}$, a certain amount of water remains in samples. This amount of water may be removed only by a substantial temperature increase and simultaneous evacuation which results in higher values of external surface areas owing to the fact that some sites in the surface previously blocked by water molecules get free.

The external surface areas of the investigated original montmorillonites (20°C) are in the range 38—50 $m^2 g^{-1}$, which is in good agreement with the data published [14—16].
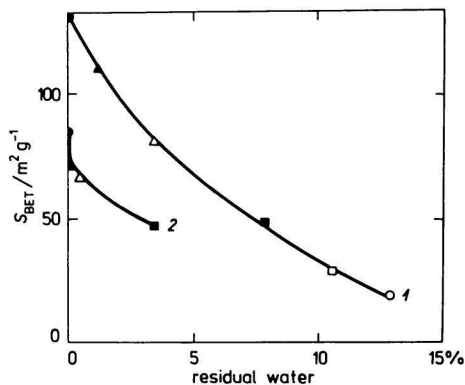
Fig. 2. Influence of residual humidity on determination of the external surface area.
1. Montmorillonite Polkville; 2. montmorillonite Askangel'.
○ 30 min outgassing at 20°C; □ 120 min outgassing at 20°C; ■ 18 h outgassing over $P_4O_{10}$ at 20°C; △ 30 min outgassing at 110°C; ▲ 30 min outgassing at 205°C; ● 30 min outgassing at 310°C.

## Surface area and microtexture of thermally treated montmorillonites

Fig. 3 represents the change in external specific surfaces of the investigated montmorillonites as a function of heating temperature. In respect of different loss of water in thermal treatment, the quoted surface areas are related to a unified weight of samples dried at 100°C.

By heating to 100°C, the surface area of some smectites decreases. It is interesting that montmorillonite with the largest specific surface (Polkville) exhibits no decrease whereas the greatest decrease appears with montmorillonite Askangel' exhibiting the lowest temperature course of changes.

The decrease in surface areas accompanying the heating to 100°C is likely to be due to rests of the adsorbed water molecules on external surfaces between particles which form islets of aqueous film and can be removed only by heating to 100°C. This process permits a tight agglomeration of the leaf- and plate-shaped crystals to each other from which a lower value of the external surface area results. The remains of the aqueous film functioned as prop aparts and allowed the molecules of nonpolar gas, *i.e.* argon, to penetrate to the external surface of the crystals [13]. It cannot be excluded that a resorption of water vapour from the atmosphere takes place during handling with the samples. This resorption could, as evident from Fig. 2, significantly affect the determination of the external surface area of particles.

A temperature increase from 100 to 400°C brings about a successive loss of interlayer water. As shown by *Rowland et al.* [6] and *Warshaw et al.* [17], the heating in·this temperature range should not produce any structural changes in Ca montmorillonites except a gradual reduction of the interlayer distance from 1.4—1.5 nm at 20°C to 0.96 nm at 250°C owing to the escape of interlayer water.

It ensues from the results represented in Fig. 3 that the external surface areas of the investigated montmorillonites in some cases quite distinctly increase in the temperature interval of 100—400°C while the subsequent falling wave appears as
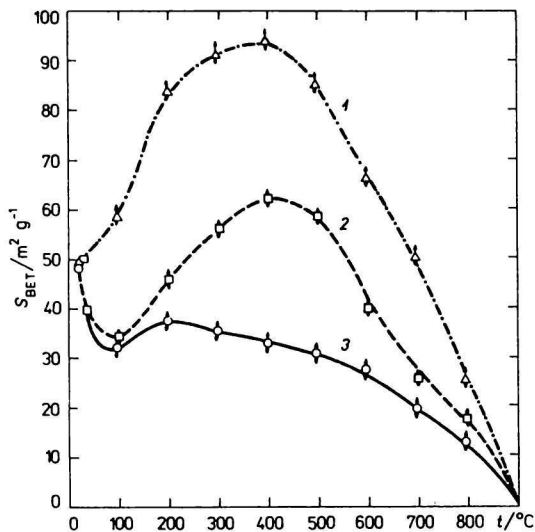
*Fig. 3.* Changes in external surface area of the smectites after heating.
*1.* Montmorillonite Polkville; *2.* montmorillonite Jelšový Potok; *3.* montmorillonite Askangel'.
Arrows at individual points indicate the mean deviation of individual determinations of surface area.

far as above 400°C because of degradation of the montmorillonite structure by dehydroxylation. The surface area increase in that temperature range is to be explained again by the presence of water, in this case of the interlayer water which forms a coordination sphere of the exchangeable cation and blocks the surface of interlayer. A successive escape of this water liberates the interlayer space where argon can penetrate most probably at the edges of crystallites because of attenuation of the attractive forces of layers by edge faults and breakage bonds, which is reflected in an increased value of the surface area. Thus argon cannot, to a greater extent, penetrate into the interlayer because of a generally small ability of nonpolar gases to overcome the attractive forces binding individual three-layers of the smectites to each other [13].

A comparison of the surface areas of the samples subjected only to heating with the corresponding samples which have been also evacuated suggests that the heating and simultaneous evacuation enable us to obtain higher values of the external surface areas.

It is characteristic that the value of the maximum specific surface obtained on the curve of temperature dependence decreases in the order Polkville > Jelšový Potok > Askangel'. As for the sample Askangel', the increase in surface area is insignificant and the maximum is reached at 200°C. Assuming the course of surface change and the height of the maximum of surface area after heating depend on magnitude of the mutual attractive forces of three-layers of individual montmoril-

lonites, the external surface area obtained should be in relation with the residual negative charge of three-layer of a given montmorillonite. The values of negative layer charge found for the investigated samples of montmorillonites are in excellent agreement [18]. Montmorillonite Polkville (0.22 charge per unit cell) has the lowest value of residual negative charge and, in conformity with the above assumption, offers the smallest resistance to overcoming the attractive forces of layers, which manifests itself in the course of temperature dependence by high values of the external surface area. As for montmorillonite Jelšový Potok (residual charge 1.09 per unit cell), the increase in surface area is much lower while montmorillonite Askangel' (residual charge 1.30 per unit cell) offers such a great resistance to the penetration of argon that it cannot practically penetrate into interlayer.

The course of the distribution curves of pore sizes is also an argument which supports the mechanism of Ar adsorption (Fig. 1). By heating to 100°C, the range of microcavities (under 0.55 nm) shifts to higher values (about 0.7 nm) at a simultaneous contraction of the distribution of pore sizes in the region of 1 nm with a tendency to a gradual shift into the region of smaller sizes (0.6 nm) during further heating, which may be explained by the existence of fissures (along edges of crystallites) arisen by a side penetration of the Ar molecules. The width of these cavities corresponds to a monomolecular layer of Ar on opposing sides of wall, *i.e.* to two monomolecular layers altogether. At temperatures above 500°C, the size of cavities increases and their occurrence simultaneously decreases. Later on, in the temperature interval 700—800°C, a contraction of the distribution of these cavities appears which is due to structural changes after dehydroxylation. A certain amount of cavities with a mean size of about 1.45 nm is still present at 800°C but it disappears below 900°C and the external surface area approaches zero as well.

The investigation of total surface areas is represented in Fig. 4. The determination is based on the assumption that the ethylene glycol monoethyl ether as a polar substance penetrates into interlayer of the smectite and forms a monomolecular film on its surface, which enables us to determine the total, *i.e.* both internal and external surface area.

At the beginning of heating, a slight increase in total surface area appears. It culminates in the values of 830—860 m$^2$ g$^{-1}$ at 200°C. The increase in total surface area in this temperature interval is evidently due to escape of the physical water and, to a certain extent, the interlayer water which has blocked some part of surface. Above 200°C, the total surface areas of the investigated smectites decrease. Initially — to 400°C approximately — this decrease is slight probably owing to an initial irreversible collapse of internal surfaces of interlayers. Over 400°C, the total surface area of samples rapidly decreases, which indicates the dehydroxylation of montmorillonites. In the temperature interval of 600—800°C, this decrease temporarily slows down obviously due to the presence of residual
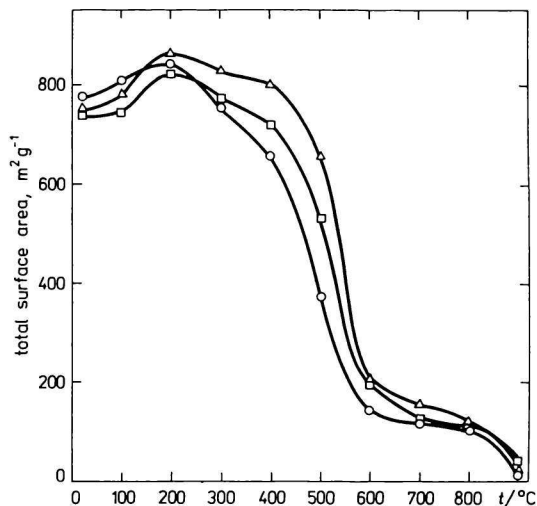
*Fig. 4.* Changes in total surface area of the smectites after heating.
△ Montmorillonite Polkville ; □ montmorillonite Jelšový Potok ; ○ montmorillonite Askangel'.

parts of the original structure and its total destruction manifesting itself in the bend of curve finished at about 900°C, which is in agreement with other investigated parameters. It may be stated that the character of the curves expressing total surface areas is practically equal for all investigated samples.

It results from all above investigations that vacancies large enough occur in the texture mass of the smectite during dehydroxylation, *i.e.* in the temperature region of 500—700°C. The product of dehydroxylation, *i.e.* water vapour can easily escape through these vacancies. They may be characterized as transition canals through which the water vapour, after releasing the three-layer where it has arisen, escapes from a grain or crystal into environs. The external surface area of the solid phase is large enough and accessible (practically comparable with original smectite) to ensure a connection with these transition canals.

In the crystal itself or inside basic three-layer a certain barrier could exist. This barrier would prevent the passage of the water arisen by dehydroxylation to the external surface from where a free escape is possible. It might be the cause that the initial stage of water escape would be controlled by the diffusion through coherent three-layers to the nearest external surface of crystal.

From the view-point of sorption processes and catalytic properties of the thermally treated smectites, it appears that their surface is large enough and accessible up to relatively high temperatures (800°C) so that no observable retardation or blocking of these reactions exists. This is valid if the molecules of sorption medium have such dimensions and configuration that any effect of steric factors is out of question, *i.e.* their width must not be larger than the diameter of the entrance holes of transition canals.

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