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SIGNIFICANCE OF STRUCTURAL FACTORS IN DEHYDROXYLATION OF KAOLINITE POLYTYPES

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The relations between the perfection of the structure, the size of the crystals and the course of dehydroxylation of kaolinite polytypes, as revealed by DTA and DTG curves, are discussed. The dehydroxylation of kaolinites is a peculiar type of homogeneous, intracrystal thermal dissociation. The kinetics of this process are dependent on the rate of removal of water vapour from the structure and its pressure in the structural domains.

Systematic investigations of the decomposition of simple substances such as carbonates, sulphates, hydroxides and some hydrates, carried out during the past few decades by many authors, showed that the reactions of thermal decomposition of solids have a specific character, which distinguishes them from reactions in homogeneous, gaseous or liquid systems. The factors affecting their kinetics are different.

The rates of isothermal reactions in homogeneous systems are determined exclusively by the concentrations of the substances and products.

The kinetics of thermal decomposition of solids are influenced by many different factors, such as:

1. The geometry of the crystal lattice, the nature and direction of the chemical bonds, and the anisotropy of the properties of the crystals determined by them.
2. The grain size and morphology of the crystals.
3. Macro- and microdefects.
4. The pressure of the gaseous products of decomposition at the substrate–product boundary.
5. The dependence of the mechanism and the location of the reactions on the conditions under which they take place and the possibility of their change with the degree of decomposition of the original phase in the course of the process.

Consequently, investigations of the kinetics of thermal decomposition of solids by thermal analysis methods may be used to obtain information on the details of the internal structure of minerals. The kinetic parameters of the thermal decomposition of solids are structurally-sensitive values.

The thermal decomposition of layer silicates, and especially the dehydroxylation of kaolinites, are processes particularly dependent on structural factors. Their influence is well visible when dehydroxylation proceeds under non-isothermal conditions (DTA, TG and TD curves).

In this paper, the author surveys the more important results of recent investigations and proposes an explanation of the interrelations observed between the structure perfection and the size of the crystals and the course of decomposition of kaolinites, as revealed by thermal analysis methods.

Specificity of dehydroxylation of kaolinites

Kaolinites (kaolinite, dickite, nacrite, halloysite) are polytypes of the substance $Al_4Si_4O_{10}(OH)_8$. Their structures are built up of layers of several parallel sheets. The sequence of sheets in the layer is as follows:

$$O_6{-}Si_4{-}O_4(OH)_2{-}Al_4{-}(OH)_6 \ .$$

Kaolinite polytypes differ from one another in so far as the mutual orientation of neighbouring layers is concerned. The manner of stacking of the layers governs the orientation of the OH groups in the external sheet of the layer, and the strength of the hydrogen-bonds with the oxygens of the neighbouring layer.

In minerals of the kaolinite group, disorder in the stacking of the layers is often observed. It consists in irregular displacement of the layers in crystallographic direction b by about $1/3\ b_0$. The structure of halloysite is characterized by disordered displacement of the layers in both a and b directions. The degree of disorder of the structure of minerals of the kaolinite group can differ; it depends on the mode of their formation.

Minerals of the kaolinite group give different DTA and TG curves (Fig. 1). Dickite and nacrite exhibit a double dehydroxylation peak at 670° (Fig. 2). The magnitudes of the first and the second peaks can be different. Kaolinite gives a single symmetric peak at 560° (kaolinite Tc). This peak becomes more and more asymmetric with increase of the degree of structural disorder (kaolinite D) and with diminishing plate size. Its temperature decreases slightly in the same direction. There are also kaolinites which give a dehydroxylation peak similar to that of dickite. The temperature of the second peak is 650–700°, depending on the conditions of the experiments. This kaolinite of hydrothermal origin has been found by Hayes [1] and Volostnykh [2], and in clays by Stoch [3, 4].

The higher temperatures of dehydroxylation of dickite and some kaolinites than those of normal kaolinites, and the two-stage character, have been explained as a consequence of the greater size of their plate-like crystals [5, 6]. Dickites forming plates finer than 1–2 μm size give one endothermic peak at 600°. Grinding of dickites and kaolinites with higher than normal temperatures of dehydroxylation lowers the temperature of dehydroxylation, and their peaks becomes single, like that of kaolinite.

In the structure of kaolinite polytypes, only 2/3 of the cation sites of the Al–O–OH octahedra are occupied. The remaining 1/3 are vacant. The mutual distri-

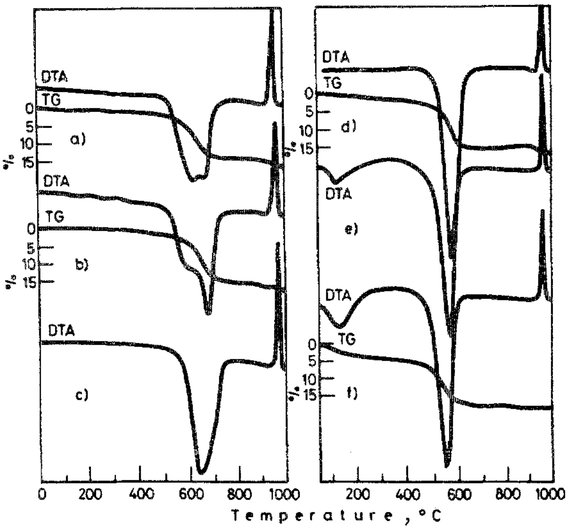

Fig. 1 DTA and TG curves of minerals of the kaolinite group: A, nacrite, Saxony; B, dickite, Nowa Ruda, Lower Silesia; C, kaolinite with a higher temperature of dehydroxylation, Abagajtuj, USSR; D, kaolinite Tc, Siersza, Upper Silesia; E, kaolinite D, Jaroszów, Lower Silesia; F, halloysite, Mierzęcice, Upper Silesia

bution of these vacances in adjacent layers can be obtained in two manners, denoted *B* and *C* by Bailey [7]. They correspond to two enantiomorphic varieties of kaolinite. The displacement of the positions of these vacances can be the cause of faults in the stacking of the layers. In the dickite structure the sequence of layers is of the type BCBCBCB, and not BBBBBBB or CCCCCCC as in kaolinite.

DTA investigations of various dickites revealed the existence of structures intermediate between dickite and kaolinite [8]. Similar conclusions resulted from an X-ray study on the disordering of kaolinites [9]. This was confirmed by the data for dickites of Jamaica, presented by Brindley and Porter [10].

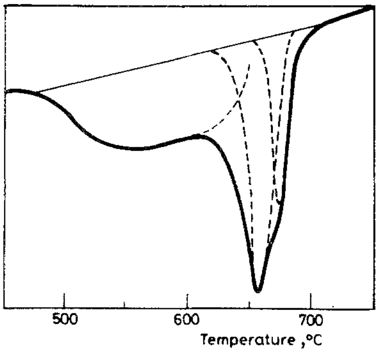

Fig. 2 Intimate structure of DTA dehydroxylation peak of dickite from Wisniówka near Kielce; heating rate 2 deg min−1, weight of sample 0.1 g

The faults in the arrangement of the layers result in the formation of kaolinite zones within dickite plates [8]. Sequences of layers such as BCBBBCBC appear [10]. This deviation from the ordered structure is manifested in the X-ray patterns by a decrease in intensity of some lines (Figs 3, 4). The degree of ordering of the dickite structure can be expressed by the ratio of the intensities of the lines 020 and 111 [11]. The ratio of the heights of the DTA peaks of the first and second stages of dickite dehydroxylation increases with the ratio of the intensities of these lines Figs 4 and 5).

The kinetics of kaolinite dehydroxylation have been the subject of many investigations. From TG under isothermal conditions, Murray and White [12] denoted kaolinite dehydroxylation as a first-order reaction. Later study indicated that at low water vapour pressures kaolinite dehydroxylation proceeds as a process limited by diffusion, but at higher pressures in accordance with the equation of a first-order reaction [13]. Other investigations show the diffusion to be the limiting factor in this process, inde-

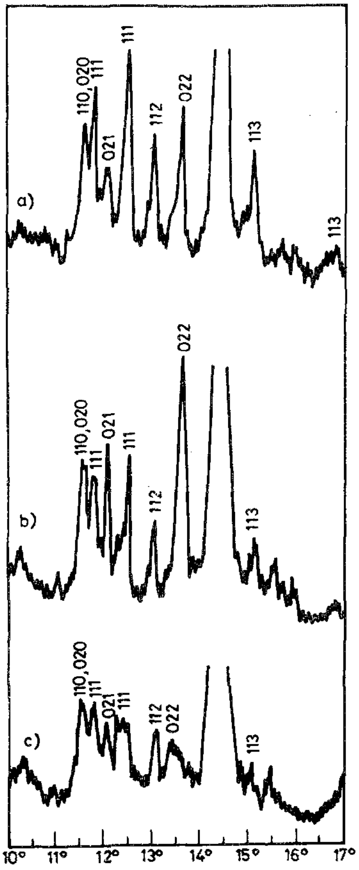

Fig. 3 X-ray patterns of dickites with a high (*a*) and a low (*b*, *c*) degree of structural order (CoK_{α})

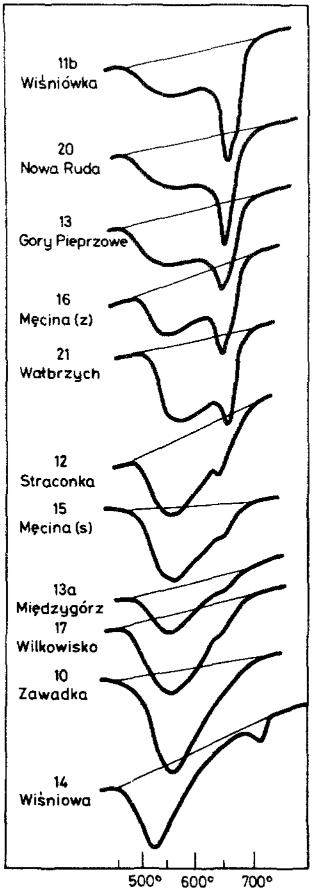

Fig. 4 DTA curves of dickites ordered according to decreasing perfection of the structure; heating rate 2 deg min $^{-1}$, weight of sample 0.1 g

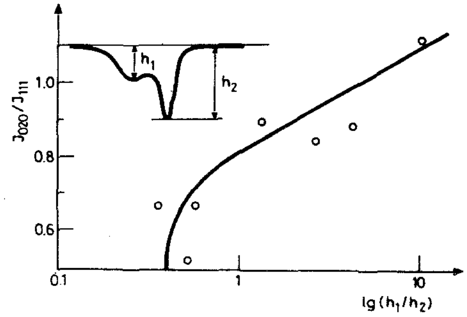

Fig. 5 Relation between X-ray index of structural order I_{020}/I_{111} and shape of DTA peak of dickite

pendently of the water vapour pressure [14]. The kinetics change after the degree of dehydroxylation $\alpha = 0.7$ is exceeded [15].

Carthew [16] points to the dependence of the kinetics of kaolinite dehyroxylation on the degree of ordering of the kaolinite structure and the size of the particles. The activation energy and the heat of dehydroxylation decrease with increase of the structural disorder.

It follows from our earlier DTA and TG studies [17] that the Arrhenius activation energy diminishes with decrease of the kaolinite grain size. There is a significant linear correlation between the specific surface area and the activation energy of a given kaolinite. The angular coefficient of the regression line varies with the degree of structural disorder. The value of the Arrhenius parameter n is 1 or a little less if the kaolinite plates are finer than 1.4 μm. For this fraction the value of n decreases with the degree of disorder in the stacking of the layers. When the kaolinite grains are coarser, the parameter n has an abnormally high value of about 2.0.

The curves illustrating the dependence of the rate of the dehydroxylation reaction on the degree of decomposition α show a maximum in the range $\alpha = 0.5-0.7$. Above this range the reaction slows. It takes place with higher α values if the kaolinite is finer-grained and its structure is more disordered.

The first stage of dehydroxylation of dickite has a similar activation energy to that for kaolinite finer than 0.5 μm (120 kJ per mol). For the second stage it is 150–172 kJ per mol and so is similar to that for coarse-grained kaolinite [18].

When dehydroxylation proceeds under equilibrium conditions, the influence of structural factors is not so visible. Isothermal studies under hydrothermal conditions have shown that the dehydroxylation temperature of kaolinite polytypes is 405°, any differences being within the error of measurement [19]. The pressure of water vapour influences the dehydroxylation temperature of kaolinite only slightly, changing it merely by several degrees [20].

Studies on the kinetics of dehydroxylation under isothermal conditions in air have shown that there are no differences between the various polytypes in this respect. The correlations between the decomposition kinetics and the structure of the mineral are diverse when compared with those resulting from DTA and non-isothermal thermogravimetry [21].

Interesting information on the dehyroxylation mechanism can be obtained by means of spectroscopic methods. Gastuche et al. [22] measured the second moment of the nuclear magnetic resonance lines of the protons in kaolinite at increasing α. They concluded that the average proton–proton distance remained constant until 60% dehydroxylation.

Using IR spectroscopy, Pampuch et al. [23] have shown that in kaolinite there are 3 types of OH groups. 2/3 of the OH groups situated in the external sheet of the layer participate in long hydrogen-bonds (0.313 nm). The others form shorter bonds (0.30 nm). The third type of OH groups are those located within the layer. The dehydroxylation of kaolinite begins with dissociation of the groups of the second type. The liberated protons form water molecules with external groups displaying longer bonds. About 12% of the retained OH groups remain in the metakaolinite structure [24].

Brindley and Nakahira [25] found that dehydroxylation proceeds simultaneously within the whole volume of the crystal, layer by layer.

Recent NMR studies [26] confirm this supposition. Dehydroxylation occurs layer by layer from $\alpha = 0$ to 70%. At $\alpha > 70\%$, the protons left in the kaolinite are distributed among two ensembles, P' and P''. P'' increases at the expense of P' as α increases. P' is linked to octahedrally coordinated aluminium. This gives an area of about one unit cell. Between them remain isolated protons which constitute ensemble P''.

The moment of change in the character of the dehydroxylation process in the range $50 < \alpha < 70\%$ corresponds fairly well to the maximum in the curves of the change of reaction rate (V) with the degree of decomposition α deduced from the TG curves [17].

EPR studies [27] also indicate that in the initial stage of dehydroxylation the proton structure of kaolinite does not change. On the other hand, a distortion of the coordination octahedra takes place, in which the OH groups participate, lowering the symmetry.

Dehydroxylation of kaolinites as intracrystal thermal dissociation

The processes of thermal dissociation of solids differ in the mode of formation of the solid products and the mutual relations of the crystals of the parent substances and products. This is a consequence of the deciding role of the structural factors in the course of these processes.

The best-known processes include the thermal dissociation of carbonates, sulphates, hydrates etc. It is generally accepted that the dissociation processes in these cases take place at the parent substance–product boundary. The products form a layer separated from the parent phase by a distinct boundary. The process is usually limited by the diffusion of gaseous products through the layer of solid products and may be described by the model of a contracting sphere or disc. The partial pressure of gaseous product at the boundary of the two phases determines the kinetics of the process and influences the measured value of the activation energy of the process (Zawadzki–Bretsznajder rule). It is strictly dependent on the partial pressure of gaseous component in the environment in which the sample is placed.

The dehydroxylation mechanism is significantly different. Taylor [28] reports that during this process the decomposition centres are distributed more or less evenly within a crystal and water is also evolved evenly in its entire volume. The decomposition either occurs by a homogeneous mechanism (e.g. $Ca(OH)_2$) or is preceded by the redistribution of metal cations or protons (as in brucite, $Mg(OH)_2$), i.e. it follows a homogeneous mechanism [23].

During the dehydroxylation, grains of the product grow within a crystal of the parent substance and remain in topotactic relation with it. Because of the distribution of the decomposition centres within the crystals of the parent substance, this mechanism can be called an intracrystalline one, since the new phase is formed within the whole volume without development of a separate layer of products.

The dehydroxylation of kaolinites is a peculiar type of intracrystalline thermal dissociation. The process occurs within the crystal of the substance, whereby the essential framework of its structure remains preserved.

In metakaolinite, a dehydrated form of kaolinite, the original structure is preserved in the plane of the axes *a* and *b*, but is lost in the third direction. The unit cell parameters a_0 and b_0 differ only slightly from those of kaolinite [25, 29]. There is also no change in the habit of kaolinite crystals.

Such a course of thermal dissociation is due to the exceptionally distinct anisotropy of the distribution of the strengths of the bonds in layered silicates. The anisotropy of the kaolinite structure is expressed by (1) strong ionic–atomic silica–oxygen and alumina–oxygen bonds within the layer, and (2) weaker hydrogen-bonds between layers.

The dehydroxylation of kaolinite can be subdivided into two stages:

(1) formation of water molecules from OH groups, and

(2) removal of water molecules.

The former depends on the distribution of OH groups in the structure, as well as on the direction and strength of the hydrogen-bonds. It begins with an increase in mobility of the protons and their dislocations. It is noticeable at 300° and can be manifested by an increased electric conductivity [23, 30, 31]. The participation of individual OH groups in the formation of water molecules and the course of this process were characterized in the above studies. However, there have as yet been no detailed studies of the second stage, i.e. the removal of water from dehydroxylating crystals. The stage of removal of water has a significant influence on the kinetics of the dehydroxylation process, as measured with thermal analysis methods.

For simplicity, we may assume that, due to the intracrystalline character of the dehydroxylation of kaolinites, the kinetics are determined by the partial pressure of water in definite areas of the crystal structure: the intracrystalline pressure. These areas may be defined as thermochemical domains, by analogy with the term "domain" used for minimal areas of crystal structure coherently diffracting X-ray radiation. Thermochemical domains are spaces free from structural discontinuities, bordered by dislocations, boundaries of mosaic blocks and others, along which gaseous products of the reaction can escape.

The thermal dissociation process starts when the intracrystalline pressure within the domains exceeds the value necessary to disrupt the weakest chemical bonds. The pressure within a domain during the thermal dissociation process is conditioned by the resistance to diffusion, which has to be overcome by water molecules before they can leave the solid.

Since the kaolinite structure contains water as OH groups amounting to 0.35 g/cm^3, at 430° its pressure will be as high as 450 atm.

The existence of domains free of structure discontinuities is supported by electron photographs of kaolinite plates decorated with gold particles. The higher the degree of structural order, the larger is the size of the domains.

During the dehydroxylation of kaolinite, the weakest diffusion resistances can be expected along the interlayer spaces. They will diminish with the degree of decomposition α and reduction in the amount of OH groups. These are natural channels for the removal of water molecules. Reduction of the intracrystalline pressure is also realized through the vacancies and discontinuities of the layers.

The removal of water molecules from kaolinite is presented schematically in Fig. 6.

The particular role of the interlayer space in the removal of water molecules is supported by the fact that during heating the first periodicity to be disturbed is that in the c direction, i.e. perpendicular to the basal (001) planes of the layers. The layers are subjected to bending as supported in points by the remaining P' patches.

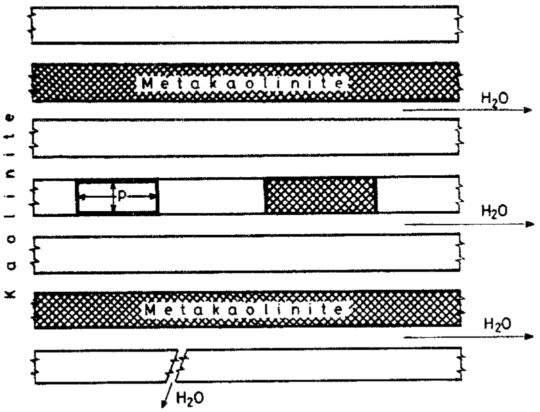

Fig. 6 Removal of water molecules from the structure of kaolinite during dehydroxylation

Since the intracrystalline pressure is very high, the changes in partial pressure of water vapour in the environment influence the decomposition temperature only slightly, as mentioned above.

In contrast to the reaction of decomposition of carbonates, the pressure of the gaseous products of thermal dissociation influence the kinetics of dehydroxylation of kaolinite only slightly. On the other hand, it is conditioned by the value of the intracrystalline pressure at a given moment. This in turn depends on the size and degree of perfection of the crystals. The low decrease of this pressure is favoured by a high degree of crystallinity of the mineral, and consequently by the large volume of fragments free from discontinuities, facilitating the removal of water molecules.

During the heating of kaolinite in the range 430—600°, its density diminishes considerably, from 2.55 to 2.35 g/cm^3 [29], while it increases slightly at higher temperatures. The structure loosens due to the loss of OH groups and changes in the interlayer spaces.

During dehydroxylation, the interlayer distance decreases from 0.713 nm to 0.685 or 0.675 nm. Heating above 600° results in total collapse of the structure, and the average distance diminishes to ca 0.554 nm [29]. Consequently, higher interlayer distances during the first dehydroxylation stage render possible the removal of water through the interlayer space. After the collapse of the structure above 600°, the remaining water molecules are removed slowly, as shown by the low slope of the right side of the DTG and DTA peaks for perfect, coarse-crystalline kaolinites.

The dehydroxylation of kaolinite is connected with the gradual contraction of the sample, as follows from the TD and DTD curves (Fig. 7). Sometimes, however, dehydroxylation is accompanied by a rapid increase in volume of the sample. Such a phenomenon appears at the beginning of the second stage of dickite dehydroxylation (Fig. 8). Consequently, it was proposed to use it to distinguish dickite from kaolinite [32]. An explosive increase in volume accompanies the dehydroxylation of kaolinite with a higher than usual dehyroxylation temperature.

This phenomenon can be explained by assuming that in both cases there are kaolinite varieties having perfect crystals, more than 1 μm in size with a well ordered structure. Consequently, the removal of water molecules from the interior of crystals during dehydroxylation is particularly difficult. When the intracrystalline pressure exceeds the critical value, violent separation of the layers and the liberation of water occur. This is manifested by the rapid increase in volume of the sample.

The swelling of vermiculite accompanying its dehydration is based on the same principle. It is observed when its plates are sufficiently large.

When kaolinite plates are less than 1 μm in size or display numerous discontinuities dividing them into small domains, the removal of water vapour is easy and the above phenomenon does not take place. The same refers to fine-grained dickite, which gives only one peak in the DTA curve.

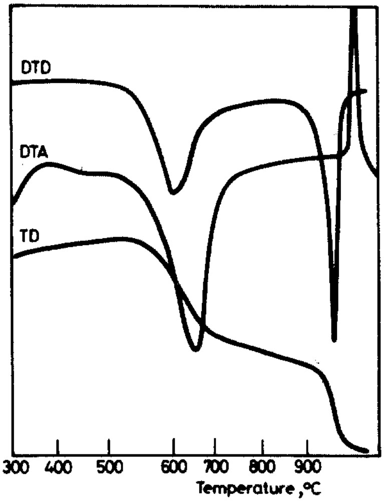

Fig. 7 TD, DTD and DTA curves of kaolinite from Żarów, Lower Silesia; weight of sample 5 g

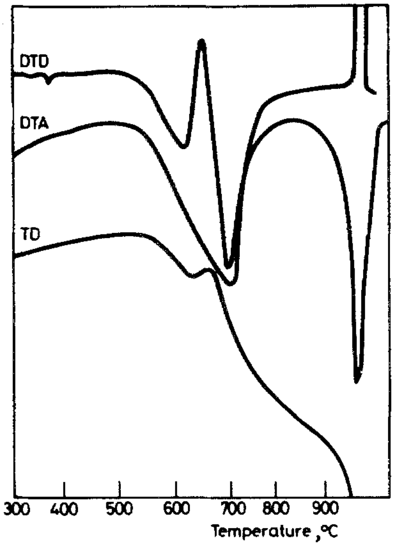

Fig. 8 TD, DTD and DTA curves of dickite from Nowa Ruda, Lower Silesia; weight of sample 5 g

Kaolinite interlayers in the dickite structure decompose at lower temperature (Fig. 4). The appearance of 1.4 nm X-ray lines during the dehydroxylation of dickite [33] can be explained as resulting from preserved pairs of dickite layers. The phenomena described above confirm the theory on the role of the pressure of water vapour within the plates of mineral in its dehydroxylation process.

The highest rate of removal of water corresponds to the temperature of the peak in the DTG curve, and the maximum in the curve of the rate of decomposition relative to the degree of decomposition α. The dehydroxylation degree at this point is merely ca. 0.5 when the kaolinite is coarsely-crystalline [17]. The remaining the water is removed relatively slowly, as manifested by the wide symmetric peak in DTG and DTA curves. This water is closed within the already collapsed metakaolinite structure, in the form of P'' patches.

When kaolinite is fine-crystalline or the degree of its structural order is low, the value of α is more than 0.7. In this case a higher amount of water can be evolved before collapse of the structure. The size of the domains free of dislocations becomes smaller with decreasing degree of the structural order of the kaolinite, and the smaller its plates. Consequently, the removal of water vapour from them is easier and the amount within domains falls quickly.

This explains the results of previous studies (loc. cit.) which have shown (1) the lower temperature of the beginning of dehydroxylation, (2) the lower energy necessary to overcome the diffusion resistance, manifested by the lower value of parameter E for this process, (3) the lower heat of this process, and (4) the more rapid recombination of residual OH groups and their removal, and hence the higher the decomposition degree at the point of the maximum rate of the process and the asymmetric DTG and DTA peaks.

When the size of the kaolinite plates or domains decrease below 1 μm and tends to 0 value, the intracrystalline pressure of water vapour also diminishes. This is manifested by the *n* value approaching 1 and by the decrease of *E*. Consequently, the kinetics of this process can be still better characterized by using the Arrhenius equation. It may therefore be concluded that the process in question approaches still closer to reaction in a homogeneous system.

The above considerations are an attempt to use various data on the dehydroxylation of minerals of the kaolinite group to present a coherent conception explaining the details of the mechanism of this fairly specific process.

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Zusammenfassung — Beziehungen zwischen dem Ordnungsgrad der Struktur, der Kristallgröße und dem durch DTA und DTG verfolgten Verlauf der Dehydroxylierung von Kaolinit-Polytypen werden diskutiert. Die Dehydroxylierung von Kaolinit ist ein besonderer Typ einer homogenen, intrakristallinen thermischen Dissoziation. Die Kinetik dieses Prozesses ist von der Geschwindigkeit der Entfernung des Wasserdampfes aus der Struktur der Probe, also vom Wasserdampfpartialdruck in der Probe abhängig.

Резюме — Обсуждена связь между совершенством структуры различных политипов каолина, размером кристаллов и процессом их дегидроксилирования, проведенного методами ДТА и ДТГ. Процесс дегидроксилирования каолинов является особым типом гомогенной, внутрикристаллической термической диссоциация. Кинетика реакций этого процесса зависит от скорости удаления паров воды из структуры и от давления паров воды в структурных доменах.