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DEHYDROXYLATION OF KAOLINITE GROUP MINERALS

I. KINETICS OF DEHYDROXYLATION OF KAOLINITE AND HALLOYSITE

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The kinetics of dehydroxylation of kaolinite and halloysite have been tested by the methods of thermal analysis. They are determined by the particle sizes of these minerals and the order of stacking of the layers in their structures. The Arrhenius activation energy E and order of reaction n decrease with the increase in specific surface area of the minerals. An increase in the degree of disorder of the kaolinite lattice diminishes the value of E. It also influences the n value for fractions finer than 1 μm.

The kinetics of the processes of thermal dissociation of minerals have been the subject of numerous works. Most frequently, however, these investigations are limited to a formal description of the course of the process. On the other hand, there is a shortage of data about the influence of the chemical compositions of the substances, their structural imperfections and crystal habits on this process. All these, however, determine the course of the decomposition of minerals.

Dehydroxylation, that is the elimination of water from OH groups, in the structures of minerals and inorganic compounds, is one of the less well-known reactions of thermal dissociation. The dehydroxylation of kaolinite group minerals is the subject of this paper. Minerals of the kaolinite group (kaolinite, dickite, nacrite, halloysite) are polytype modifications of $Al_4Si_4O_{10}(OH)_8$. Their structures are built up of layers to one another. Each layer consists of sheets occupied by atoms of oxygen, aluminium and silicon, and OH groups. The sequence of sheets and their occupation runs as follows: $O_6-Si_4-O_4-(OH)_2-Al_4-(OH)_6$.

Minerals of the kaolinite group differ from one another as far as the mutual orientation of neighbouring layers is concerned. The manner of stacking of the layers governs the orientation of the OH groups of the external sheet of the layer and the length of the hydrogen-bonds that the OH groups make with oxygens of the neighbouring layer [1]. The manner of stacking of the layers also determines the number of layers in the elementary cell and its symmetry. Nacrite and dickite are monoclinic modifications ($2M_1$ and $2M_2$), kaolinite is triclinic ($1T_c$) and halloysite has a pseudo-monoclinic elementary cell.

Disorder is often observed in the stacking of the layers in the minerals of the kaolinite group. Most frequently it occurs in kaolinite as an irregular displacement of the layers in the b direction by about $1/3\ b_0$. The structure of halloysite is characterized by disorder involving displacement of the layers in both the a and b directions. The degree of this disorder of the kaolinite lattice can be expressed numerically by means of the ratios of the intensities of chosen lines in the X-ray diffraction patterns and the intensities of the bands of the OH groups in the infrared spectrum.

It has been assumed that kaolinite crystals have a mosaic structure. They are aggregates of blocks twisted one to another around the axis laying in the *ab* plane [2]. These blocks correspond to the areas coherently scattering X-rays. They are sometimes distinguishable with the electron transmission microscope.

Minerals of the kaolinite group form hexagonal plates with different perfections of habit. The habit of crystals and their size correspond to the degree of order as far as the stacking of the layers is concerned.

Dickite and nacrite give a double dehydroxylation peak at 670° in the DTA and DTG curves. Kaolinite gives a single symmetrical peak at 560°. This peak becomes more and more asymmetrical with the increase of the degree of structure disorder and the diminishing of the size of the plates. Its temperature decreases in the same direction. There are kaolinites giving dehydroxylation peaks similar to those of dickite. This is explained by the better than usual perfection of their crystals and their bigger sizes [3]. Halloysite gives an asymmetrical dehydroxylation peak at 540°. The differences in the shape of the dehydroxylation peak and its symmetry can be the result of differences in the structures of the kaolinite group minerals.

The specific character of minerals of kaolinite group makes them a good subject for investigations of the influence of structural factors and also crystal perfection and size on dehydroxylation, that is a topotactic process.

The kinetics of kaolinite dehydroxylation have been investigated many times both under isothermal conditions and by the DTA and DTG methods. From TG under isothermal conditions Murray and White [4] denoted kaolinite dehydroxylation as a first-order reaction. Later investigations showed that its kinetics depend considerably on the pressure of water vapour. Kaolinite dehydroxylation takes place in accordance with a first-order reaction equation when the sample forms a very thin layer [5]. It was observed that at water vapour pressures below 4.5 mm Hg, kaolinite dehydroxylation continues as a process limited by diffusion, but at higher pressures in accordance with the equation of a first-order reaction [6]. Other investigations show diffusion to be limiting factor in this process independently of the water vapour pressure [7].

The kinetics of kaolinite dehydroxylation change after the degree of decomposition $\alpha = 0.7$ is exceeded. This has been explained by the increase of resistance to water diffusion through the layer of reaction products [8] or the two-stage removal of OH groups [9]. After the removal of OH groups from the external surface of the layer (the first-order reaction), the removal of internal OH groups (the second-order reaction) occurs.

Investigations [10–12] point to the dependency of the kinetics of kaolinite dehydroxylation on the degree of disorder of the kaolinite structure. Vaughan [13] supposes that the size of the kaolinite particles does not influence the dehydroxylation kinetics. There is a dependence, however, on the degree of structural disorder, that influences the activation energy and heat of this process. The activation energy of dehydroxylation of the minerals of the kaolinite group decreases in the following order: dickite – kaolinite – halloysite – disordered kaolinite.

Experimental

Tested minerals

Fractions of different grain size, separated by sedimentation from Polish residual kaolins (Kalno, Roztoka), sedimentary kaolins (Maria-III mine near Nowogrodziec) and kaolinite clays (Jaroszów, Baranów) have been considered as kaolinites with different degrees of crystallinity and grain sizes. The washed kaolins Sedlec (CSSR) and Alco (Spain) have also been investigated. The mineral compositions of the kaolins and fractions are presented in Table 1.

The halloysite samples came from Lubno near Siewierz (Upper Silesia) and Michalovce (Slovakia). The samples appeared to be monominerals.

Table 1

Mineral composition of kaolins and their fractions

Sample	Fraction, μm	Kaolinite, %weight	Micas quartz, %weight		Montmorillonite, %weight	X-ray cryst. index $\frac{I_{020}}{I_{110}}$	Spectral cryst. index $\frac{I_{3692}}{I_{3648}}$
kaoline Sedlec	4–1	84	15	1	–	0.76	1.659
kaoline Alco	<2	87	8	1	4	0.80	1.666
kaoline Roztoka (R-28)	2–0.5	93	0.2	–	6	0.91	1.566
clay Jaroszów	1–0.5	78	19	3	–	1.20	1.683
clay Baranów	1–0.5	87	8	1	4	1.20	1.743
kaoline Kalno-1 (K-1)	60–30	84	1	15	–	0.76	
	15–5	91	4	5	–	0.86	
	5–2	94	4	2	–	0.88	
	2–0.5	99	1	–	–	0.90	
	<0.5	99	1	–	–	0.94	
kaoline Kalno-2 (K-2)	30–15	91	3	6	–	0.94	
	15–5	94	2	4	–	0.94	
	5–2	91	5	4	–	0.87	
	2–0.5	98	1	1	–	1.00	
kaoline Maria-III (M-3)	15–5	61	9	30	–	0.74	
	5–2	79	7	14	–	0.69	
	2–0.5	90	5	5	–	0.62	1.625
	<0.5	88	9	3	–	0.68	

The mineral compositions of the samples taken for the investigations were controlled by X-ray diffraction DRON-1 diffractometer, CuK_α radiation. As an index of the degree of disorder of the kaolinite structure, the ratio of the intensities of the lines X-ray 020 and 110 has been taken. It assumes values of about 0.7 for kaolinite of well-ordered structure, and 1.2 and more for disordered kaolinite. This index better expresses deviations from the ideal order in the stacking of the layers in the kaolinite structure than the generally used Hinckley index [14]. The disorder of kaolinite has also been expressed by means of the ratio of the intensities of the 3.648 and 3.692 cm^{-1} bands in the infrared spectrum [15, 16]. The good mutual correlation of both indices has been observed.

Apparatus

Thermal analysis was performed with the Universal Mettler Thermoanalyser TA-2. 100 mg of sample was taken and placed in platinum crucibles 5 mm in diameter. α-Al_2O_3 was the reference substance. The rate of heating 10°/min was applied. The air flow rate was 4 l/h. The T, TG, DTG and DTA curves were recorded.

Methods of investigation of dehydroxylation kinetics

The kinetics of dehydroxylation of the tested samples were determined on the basis of the TG and DTG curves. It has been assumed that they can be described by the Arrhenius equation concerning the kinetics of reactions in homogenous systems. The E factor of this equation (the activation energy) and also the n value (the order of reaction) have been determined by the Freeman – Carroll method [17]. For the tested samples the Freeman – Carroll equation is rectilinear within the limits of the degree of decomposition $\alpha = 0.1-0.8$. The straight lines were drawn by means of 18 – 20 points determined from the TG curves at intervals of 5 or 10°. E and n values have been calculated from them by the least squares method.

Piloyan and Novikova [18] use the equation $\ln\alpha - 2\ln T = A - E/RT$ and diagrams of $(\ln\alpha - 2\ln T)$ *vs.* $1/T$, where α is the degree of decomposition, T the absolute temperature, A the preexponential constant, and E the Arrhenius activation energy.

It is considered that the results of the investigations of reaction kinetics by thermal analysis may contain considerable errors due to the nonisothermal conditions of the measurement. However, they can be used for comparative purposes, among others to determine the influence of various factors on the process of thermal dissociation. All methods of kinetic investigation relating to the decomposition of solids provide data of a relative character. They are correct only for the conditions under which the measurement is performed.

Results and discussion

Kinetics of dehydroxylation of kaolinite and halloysite

It has been observed that the water loss kaolinite during dehydroxylation starting from the temperature of the beginning of the DTG peak (350–400°) up to 900° (the beginning of the rebuilding of the metakaolinite structure in the Si, Al-spinel) is smaller than its theoretical value (13.96 wt.%). Kaolinite with a well-ordered lattice and well-shaped crystals loses 13.60 wt.% H_2O in this temperature range. This amount of water gradually decreases with the increase in structural disorder, and for disordered kaolinite (X-ray crystallinity index of about 1.2) amounts to 12.65 wt.%. The size of the grains does not seriously influence the amount of water lost. This points to a smaller quantity of OH groups in disordered kaolinite. In addition, the slow dehydroxylation of such kaolinite most probably occurs at lower temperatures, but is unnoticeable in the TG and DTG curves.

Plots of the Freeman–Carroll equation for the dehydroxylation process of the tested samples yield straight lines of different slopes, depending on the grain size and degree of kaolinite disorder (Fig. 1). The parameter E and n obtained via these straight lines are shown in Table 2.

From the results it can be seen that the parameter E of the Arrhenius equation for kaolinite decreases with the increase of the specific surface area (Fig. 2) and the diminishing of the grain size of the kaolinite. For different grain fractions of the same sample there is a linear dependence between E and the specific surface area. The slope of the straight line depends on the crystal perfection and the degree of lattice disorder.

The value of the parameter n is near 1 or a little less, providing the kaolinite is finer than 2 μm. For coarser grains it assumes values of 1.4–2.0. When the kaolinite specific surface area is greater than 6 m^2/g (a mean grain diameter smaller than 1.4 μm), the grain size does not influence the n values. The influence of the degree of order of the stacking of the layers is then revealed. Comparison of the data for fractions smaller than 2 μm of kaolins Kalno and Maria-III demonstrates that an increase in lattice disorder causes a decrease in the n value.

The fineness of the kaolinite, expressed by its specific surface area, and the disorder in the stacking of the layers influence the decreases in E and n. The parameter E is sensitive mainly to the fineness. For grains finer than 1 μm, the parameter n assumes a value of about 1 and shows a dependence on the degree of disorder of the structure.

The parameter E for halloysite dehydroxylation proved to be near the E values for dehydroxylation of the fine kaolinite fraction (Table 2). This supports the relations discussed above. Halloysite forms tubular crystals smaller than 1 μm. The n values for halloysite dehydroxylation amount to 0.8 and 0.9 and are similar to the values obtained for the fine-grained kaolinite. The temperature of the beginning of dehydroxylation increases with the increase of the ordering of the crystal

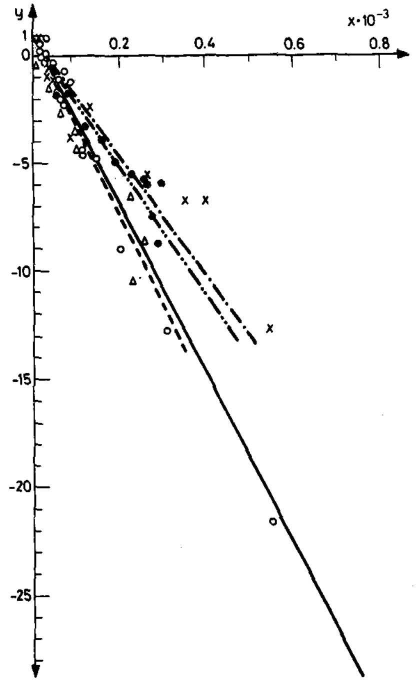

Fig. 1. Freeman-Carroll relation for determining of activation energy of dehydroxylation of kaolinite of different degree of crystallinity (symbols of samples see Tab. 1 and 2). $x = \dfrac{\Delta(1/T)}{\Delta \log W_r}$

$y = \dfrac{\Delta \log \dfrac{dw}{dt}}{\Delta \log W_r}$ ○○○ M-3, ××× Hal. Lubna, △△△ K-1, ●●● Jaroszow

lattice from halloysite to kaolinite with a high degree of crystallinity. Simultaneously, the DTA peak becomes more and more symmetrical as expressed by an increase in the index of shape s. It approaches 1 (Table 2). According to Kissinger [10], there is a dependency between s and n:

$$s = 0.63\, n^2.$$

An attempt has been made to find the correlation between the index of shape of the DTA peak of kaolinite and the parameter n for the tested samples. It was observed that for the kaolin fraction smaller than 2 μm this dependency can be expressed by the equation:

$$s = 0.30\, n^2.$$

On the other hand, a similar dependency for the coarser fractions of kaolins has not been observed. The size and habit of coarser grains of kaolinite influence

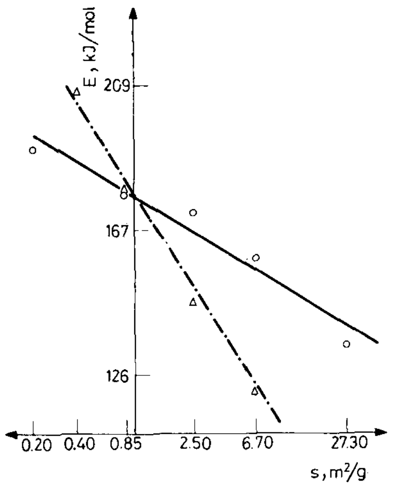

Fig. 2. Dependency of apparent activation energy of dehydroxylation of kaolins Kalno-1 and Kalno-2 on the specific surface area. ●●● Kalno-1; △△△ Kalno-2

Table 2

Influence of graining and crystallinity on kinetics parameters of dehydroxylation reactions of minerals of kaolinite group

Sample	Fraction, μm	X-ray cryst. ind.	T_{max} °C	Index of the shape of peak, s	E, kcal/mol	n
kaoline Sedlec	1–4	0.70	550	1.2	176.3	1.4
kaoline Alco	<2	0.80	545	0.8	166.8	1.2
kaoline Roztoka (R-28)	2–0.5	0.90	540	0.7	150.0	0.9
clay Jaroszów	1–0.5	1.20	530	0.6	145.4	0.9
clay Baranów	1–0.5	1.20	530	0.9	110.3	0.9
halloysite Michalovce	<45	1.40	540	0.4	140.0 94.5	0.8
halloysite Łubno	<45	1.40	530	0.3	22.6	0.9
kaoline Kalno-1 (K-1)	60–30	0.70	545	1.3	189.7	1.6
	15–5	0.80	550	1.4	177.2	1.7
	5–2	0.90	550	1.0	171.8	1.4
	2–0.5	0.80	555	0.8	158.8	1.0
	<0.5	0.90	550	0.6	133.8	0.8
kaoline Kalno-2 (K-2)	30–15	0.90	555	1.1	206.9	2.0
	15–5	0.90	555	1.0	178.4	1.5
	5–2	0.90	555	0.9	146.7	0.8
	2–0.5	1.00	550	0.8	121.6	0.7
kaoline Maria-III (M-3)	15–5	0.70	560	—	196.0	1.8
	5–2	0.70	560	1.8	145.5	1.5
	2–0.5	0.60	560	1.0	165.1	1.4
	<0.5	0.70	550	0.6	109.9	0.9

the shape of the DTA peak and n. Consequently, the kinetics of dehydroxylation of plates with diameter above 1 μm or big aggregates of fine grains, are modified. In the case of grains finer than 1 μm, the grain size is not such an important factor, and the order of stacking of the layers is the main parameter influencing the n value of kaolinite.

The different coefficient in the equation obtained for kaolinite as compared with the Kissinger equation can be explained by the different measurement conditions. In the investigations presented in the paper, the DTA curves of mixtures of the tested kaolins and Al_2O_3 were used to determine the coefficient of shape of the DTA dehydroxylation peak. The dilution influences the increase in value of the index s.

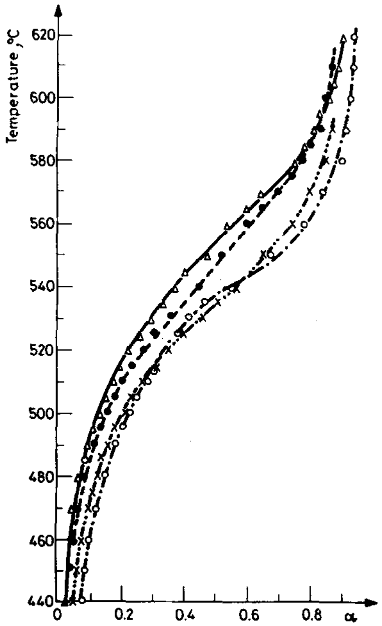

Fig. 3. Dependency of the degree of dehydroxylation of kaolinite of different crystallinity index on temperature (symbols of samples see Tables 1 and 2). ○○○ Hal. Michalovec; △△△ M-3; ××× Jaroszów; ●●● Sedlec

The symmetry of the DTA peak, expressed by the index s is used to determine the degree of stacking order of the layers. This is motivated only in the case of fine-grained kaolinites whose particles are smaller than 1 μm.

The curves of the degree of kaolinite decomposition α as a function of temperature were drawn (Figs 3 and 4). They are similar to the S-shaped curves of the degree of decomposition in relation to time for isothermal reactions.

The following stages can be distinguished in the curves: the initial stage, the stage involving rapid release of H_2O molecules, and the final stage of slow dehydroxylation. The initial stage, in which loss of water by the kaolinite occurs slowly for disordered kaolinite and halloysite and grain classes finer than 0.5 μm of the kaolinite with a high degree of crystallinity (kaolin Maria-III), is short. It is lengthened when coarse-grained kaolinite is dehydroxylated and the amount of water lost is greater.

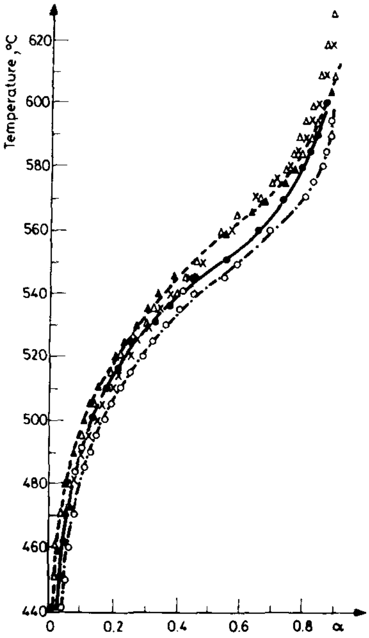

Fig. 4. Dependency of the degree of dehydroxylation of different fractions of kaoline Kalno-1 on temperature. ○○○ < 0.5 μm; ●●● 2–0.5 μm; ▲▲▲2–5 μm; △△△ 5–15 μm; ××× 30–60 μm

Similar, the final stage of dehydroxylation of halloysite, disordered kaolinite and fine fractions of well-crystallized kaolinites is short. This is well visible in the diagrams of $\ln \alpha - 2 \ln T$ *vs.* $1/T$, in which section B relates to this stage (Figs 5 and 6). The dependences of the rate of reaction v on the degree of decomposition α are presented in Figs 7 and 8. The rate of loss of water is expressed as a weight percentage of the kaolinite decomposed per minute. The Figures reveal that kaolinite with a high degree of crystallinity, e.g. kaolin Sedlec, reaches the maximum rate of dehydroxylation if the degree of its decomposition α equals 0.52. With the further progress of the reaction, the rate of loss of water decreases slowly. In the case of disordered kaolinite (Jaroszów clay), the rate of reaction v is greatest when the degree of its decomposition α amounts to 0.66, and after-

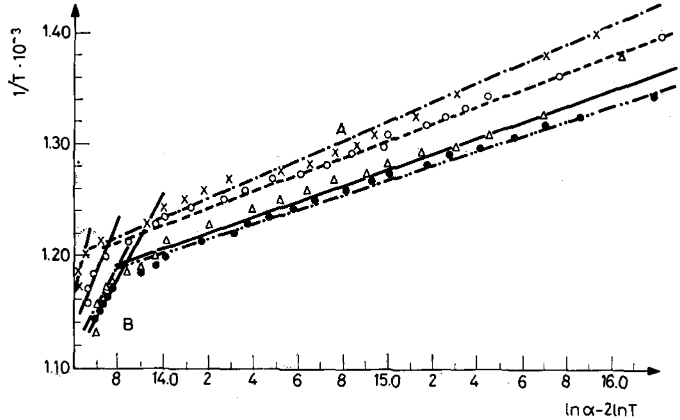

Fig. 5. Piloyan-Novikova relation for determining of activation energy of dehydroxylation of kaolinite of different degree of crystallinity (symbols of samples see Tables 1 and 2). ●●● M-3; ○○○ Jaroszów; △△△ Sedlec; ××× al. Lubno

wards it decreases rapidly. For halloysite the maximum rate of dehydroxylation is reached when $\alpha = 0.68$. The degree of decomposition α at the point of maximum rate is 0.69 for the grains smaller than 0.5 μm of kaolin Kalno, and 0.62 for kaolin Maria. Both of these contain kaolinite with a high degree of lattice disorder. The value of α decreases with the increase in grain size of the kaolinite, and for fractions 5–15 μm of these kaolins it amounts to 0.55 and 0.44, respectively. The degree of decomposition α at the point of the maximum reaction rate depends on the grain size and the degree of lattice disorder. This degree is the greater, the smaller the size of the kaolinite grains and the greater the lattice disorder for kaolinites with similar grain size.

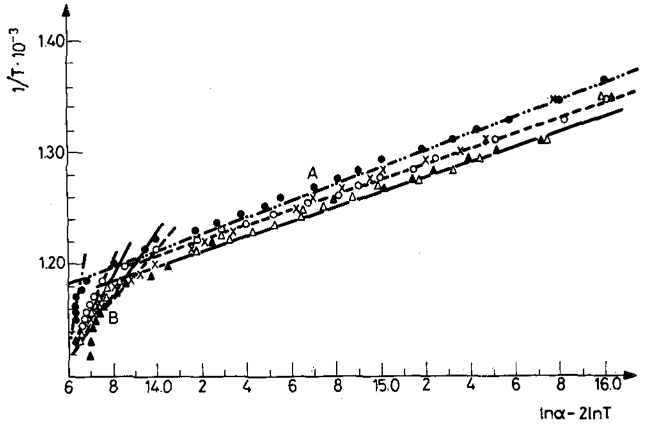

Fig. 6. Piloyan-Novikova relation for determining of activation energy of dehydroxylation of different fractions of kaoline Kalno-1. ●●● < 0.5 μm; ○○○ 2–0.5 μm; △△△ 2–5 μm; ××× 30–60 μm; ▲▲▲ 5–15 μm

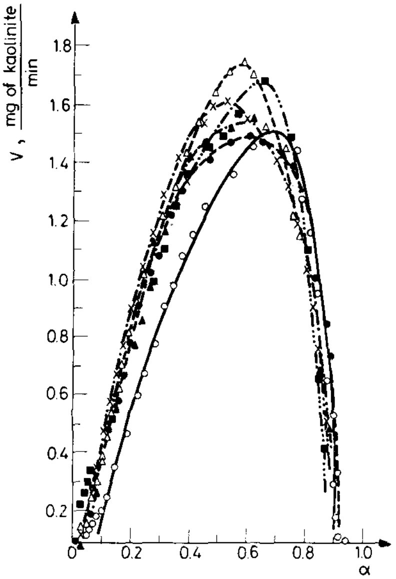

Fig. 7. Dependency of rate of dehydroxylation of kaolinite of different degree of crystallinity (symbols of samples see Tables 1 and 2) on the degree of decomposition α. ●●● M-3; ▲▲▲ ALCO; ■■■ Jaroszów; △△△ R 28; ××× Sedlec; ○○○ Hal. Michalovce

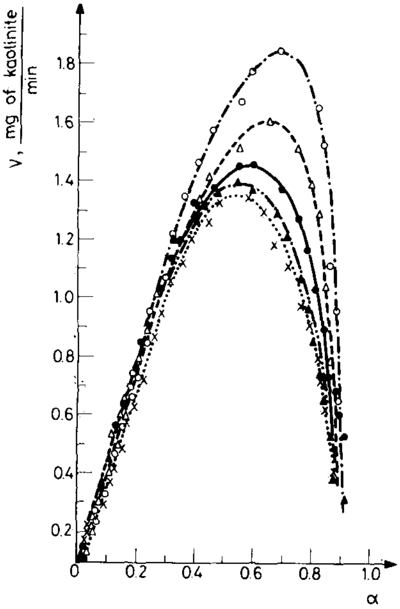

Fig. 8. Dependency of rate of dehydroxylation of different fractions of kaoline Kalno-1 on the degree of decomposition α. ○○○ < 0.5 μm; △△△ 2–0.5 μm; ●●● 2–5 μm; ▲▲▲ 5–15 μm; ××× 30–60 μm

Conclusions

The kinetics of kaolinite and halloysite dehydroxylation are determined by two factors, namely, the sizes of the grains of the mineral and the degree of disorder the stacking of the layers in the structure. These influences overlap. The kinetics of dehydroxylation can be expressed by the Arrhenius equation. The parameter E (activation energy) of this equation changes its value with the grainsize of the kaolinite. It decreases in proportion to the increase in the specific surface area of the mineral. The value of the parameter n (order of reaction) equals 0.7–0.9, that is the value approaches 1 only for grains finer than 1 μm. For coarser grains it increases with their diameter, assuming values of 1.4–2.0. The shape of curves presenting the dependence of the degree of decomposition of the kaolinite α on the temperature (the temperature increases proportionally to the time at the rate 10°/min) changes with the grain size. A reduction in the grain size shortens the initial and end stages of dehydroxylation when the rate of the process is slow. The temperature necessary to complete the process is also reduced. An increase in grain size causes an extension of the dehydroxylation process in time. With the increase in grain size, the maximum rate of the process is achieved at a smaller degree of decomposition α. After this value is exceeded, the process gradually slows down.

The influence of disorder in the stacking layers becomes noticeable when dehydroxylation of samplesof similar grain size (especially when the diameter of the grains is smaller than 1 μm) is taken into consideration. The direction in the change of the dehydroxylation kinetics caused by a disturbance of the stacking of the layers is similar to that caused by a reduction of the grain size. Disorder of the crystal lattice shortens the initial and end stages of the process when its rate is low. The maximum rate of the process occurs when the degree of decomposition is about 0.7, and shortly afterwards it is completed.

The kinetics of the reaction of thermal dissociation are known to depend on the partial pressure of the gaseous products of decomposition. According to the Bretsznajder–Zawadzki principle, the partial pressure of the gaseous products of decomposition influences the value of the Arrhenius activation energy [19]. Structural errors, especially discontinuities such as domain boundaries and mosaic blocks, make release of the water vapour easy. It is the easier, the smaller the grain size of the mineral. The surface of the grains and the structure defects are the sites where the dissociation can begin most easily and where the formation of the nuclei of new solid phase is likewise easy.

It has not been established so far whether the thermal decomposition of kaolinite occurs either on the phase boundary or in the total volume of the crystal. However, in both cases, lattice defects, and especially the boundaries of mosaic blocks and domains, will facilitate release of the water molecules, thereby accelerating the process. An increase in the specific surface area of the investigated minerals will have a similar influence. In this way, the established dependences can be explained.

From the investigations carried out it emerges that the E value determined from the TG curves provides information about the specific surface area, i.e about the particle size of the tested sample. With a computer technique this value can be easily obtained.

The index of the shape of the dehydroxylation peak is used to express the degree of crystallinity of kaolinite. Carthew [20] has worked out an appropriate method which denotes the grain size of kaolinite, that is sometimes connected with the degree of structural disorder (fine-grained kaolinites). The possibility of drawing conclusions on the degree of dispersion of the sample from the DTA, DTG and TG curves considerably broadens the range of information that can be provided by the thermal analysis.

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RÉSUMÉ — On a étudié par les méthodes de l'analyse thermique, la cinétique de déshydroxylation de la kaolinite et de l'halloysite. Les déterminations ont été effectuées à partir de la taille des particules de ces minéraux et de l'ordre d'empilement des couches dans leur structure. L'énergie d'activation E d'après Arrhénius et l'ordre de réaction diminuent avec l'augmentation de la surface spécifique des minéraux. L'augmentation du degré de désordre du réseau de la kaolinite diminue la valeur de E. Elle influence de même la valeur n des fractions inférieures à 1 μm.

ZUSAMMENFASSUNG — Die Kinetik der Dehydroxylierung von Kaolinit und Halloysit wurde durch Methoden der Thermoanalyse geprüft. Die Bestimmungen erfolgten über die Teilchengrösse dieser Mineralien und die Reihenfolge der Anhäufung der Schichten in ihrer Struktur.

Die Aktivierungsenergie E nach Arrhenius und die Reaktionsordnung nehmen mit zunehmender spezifischer Oberfläche der Minerale ab. Die Zunahme des Grades der Unordnung des Kaolinitgitters setzt den Wert von E herab. Sie beeinflusst auch den Wert n der Fraktionen feiner als 1 μm.

Резюме — Методами термического анализа исследована кинетика дегидроксилирования каолинита и галлуязита. Определены размеры частиц этих минералов и порядок последовательности слоев в их структуре. Энергия активации Аррениуса E и порядок реакции n уменьшаются с увеличением площади удельной поверхности минералов. Увеличение степени беспорядка решетки каолинита уменьшает значение E. Это также оказывает влияние на величину n для зерен размером меньше чем 1 μм.