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DEHYDROXYLATION OF KAOLINITE GROUP MINERALS

II. KINETICS OF DICKITE DEHYDROXYLATION

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The kinetics of dickite dehydroxylation have been investigated by the method of thermal analysis. It has been found that this is a two-stage process. The higher temperature of dickitedehydroxylation than that of kaolinite is the result of the different arrangement of the layers in its structure. A disturbance in the order of the stacking of the layers in the dickite structure causes a lowering of the temperature of dehydroxylation and a reduction of the activation energy of this process. This causes in turn the appearance of an additional peak or bend at 580° in the DTA and DTG curves.

Dickite is different from kaolinites and halloysite because of the higher temperature of its dehydroxylation. The endothermic peak in the dickite DTA and DTG curves appears at 670°. It is preceded by a wide endothermic bend an about 600°. Its height is less than the height of the main peak at 670°.

The higher temperature of dehydroxylation of dickite than that of kaolinite, and its two-stage character, have been explained in different ways. The higher temperature of the main DTA peak (670°) may be due to the greater sizes and perfection of the plates [1, 2]. Grinding of dickite lowers the dehydroxylation temperature and the endothermic peak of dickite becomes like that of kaolinite. The first wide peak at about 600° in the DTA curves of dickite results from the loss of OH groups from the surface of the plates [3]. However, it has been observed [4] that the quantities of structural water released in the first and second stages of dehydroxylation can be different.

The magnitudes of the first and the second DTA and DTG peaks can also be different. Dickites giving an intensive broad peak at 600° have been found. On the other hand, they have a weak peak at 670°. Stoch [4] states that the first stage of dickite dehydroxylation is caused by the disorder of its structure. The disorder is equivalent to the existence of domains or zones in the structure of dickite whose mutual orientation of neighbouring layers is the same as in kaolinite. They undergo dehydroxylation at lower temperature, thereby providing the first peak. The disorder of the dickite structure has been proved by the X-ray method [5, 6]. It causes a decrease in the intensity of some lines, especially the (111) lines. The line intensity ratio $\frac{I_{020}}{I_{111}}$ may be taken as an index of the structural disorder of dickite. The ratio of the heights of the DTA peaks of the first and the second stages of the dehydroxylation increases in proportion to the increase in value of the ratio $\frac{I_{020}}{I_{111}}$ [5]. This conception has been supported by Brindley and Porter's investigations of Jamaican dickite [6].

Near the dehydroxylation temperature, some well-ordered dickites give a 14 Å line in the X-ray pattern. This is explained by the formation of an intermediate structure of chlorite type due to the earlier dehydroxylation of the layers [7].

Experimental

Monomineral samples of dickite have been subjected to investigation. The sample came from Wisniówka near Kielce (dickite forming very thin layers in Cambrian quartzites) and Nowa Ruda (dickite occurring as a filling of fissures in Carboniferous kaolinite shales).

The apparatus used and the methods of determination of the kinetic parameters of dickite dehydroxylation have been described earlier [8].

Results and discussion

Kinetics of dickite dehydroxylation

The examined dickite samples give two endothermic peaks at 580° and 680° in the DTA and DTG curves. The peaks suggest a two-stage decomposition of this mineral (Fig. 1). The curves of the dehydroxylation rate as a function of the

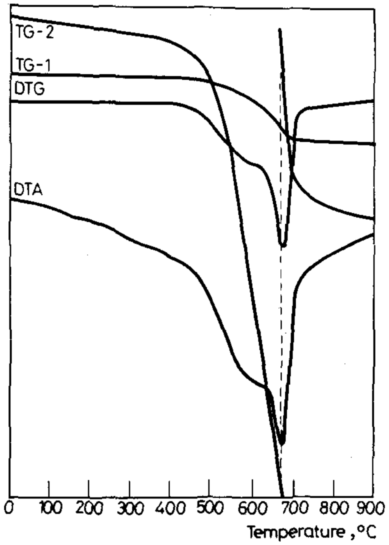

Fig. 1. Thermal analysis curves of Nowa Ruda dickite

decomposition degree α (Fig. 2) confirm the two-stage character of this process. The shapes of these curves reveal that the first stage of dehydroxylation of the tested dickite samples continues up to $\alpha = 0.3-0.4$, that is until about 1/3 of the OH groups have been released from the structure. The remaining 2/3 disappear during the second, main stage of dehydroxylation. The curves of the dependences of the degree of reaction α on the temperature are presented in Fig. 3. They are different from the curves for kaolinite. Special attention should be paid to the final stage of dehydroxylation, that is $\alpha > 0.5$, when the release of water is not slowed down, as happens during kaolinite dehydroxylation, but undergoes an acceleration. As far as dickite is concerned, this last stage is preceded by a distinct plateau in the curve.

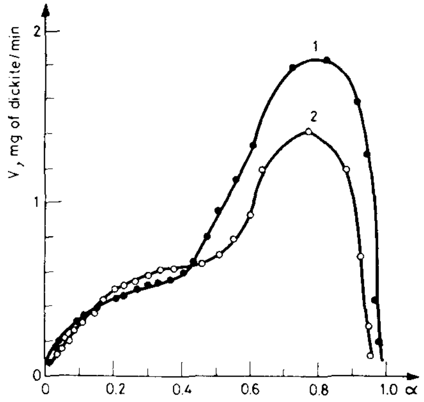

Fig. 2. Dependency of the rate of dickite dehydroxylation on the degree of its decomposition ●●● dickite Wisniówka; ○○○ dickite Nowa Ruda

Freeman – Carroll plots for the reactions of dickite dehydroxylation consist of two straight lines, corresponding to two processes with different E values (Fig. 4, Table 1).

Table 1

Kinetic parameters of the reaction of dickite dehydroxylation

Dickite	Fraction, μm	X-ray cryst. ind.	T_{max}, °C	E, kJ mol of kaolinite	E, kJ mol H_2O
Wiśniówka	<45	0.8	580 680	120.8 151.3	30.6 101.9
Nowa Ruda	<45	0.8	580 680	127.9 172.6	40.9 111.1

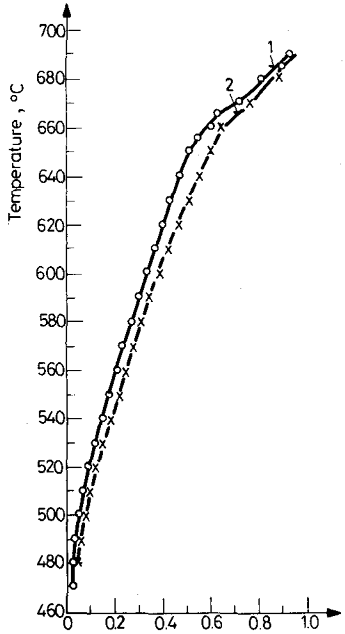

Fig. 3. Dependency of the degree of dickite dehydroxylation on temperature. ○○○ dickite Wisniówka; ××× dickite Nowa Ruda

This also points to the different kinetics of the two stages of dehydroxylation. The E value for the second stage is about 20% higher than for the first. It should be noted, however, that the value of the parameter E for the first stage of dickite dehydroxylation is lower than the E value of typical kaolinites. The value of the parameter E for the second stage of dickite dehydroxylation reaches that obtained for kaolinite.

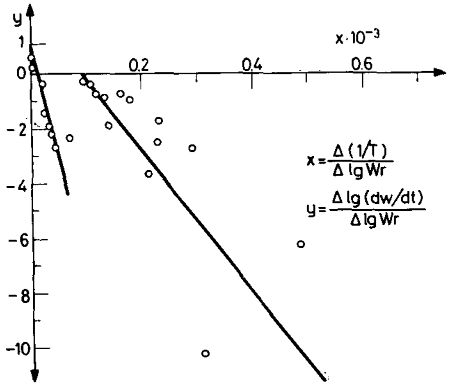

Fig. 4. Freeman-Carroll relation for the evaluation of the activation energy of Wisniówka dickite

These results can easily be explained if it is assumed that the first stage of dickite dehydroxylation covers the domains of mutual orientation of layers different from the one for dickite. Considering their small sizes and their lattice defects, dehydroxylation of domains of this kind ought to have a smaller E value than dehydroxylation of the domains in which the arrangement of layers is perfect.

Conclusions

Dickite has a considerably higher dehydroxylation temperature than kaolinite. The rate of this process reaches its maximum at 670° (the DTA and DTG peaks). The degree of decomposition is then $\alpha = 0.7$. This is a result of the different arrangement of the layers in the dickite structure than in kaolinite, which is known to influence both the direction of the external OH groups involved in hydrogen-bonding joining the layers and also their strength. A high degree of dickite crystallinity also influences the higher temperature of dehydroxylation.

Faults in stacking of the layers in the dickite structure cause the existence of domains with a mutual orientation of layers similar to that in kaolinite. The dehydroxylation of these domains can account for the first stage of dickite dehydroxylation. This stage has a low E value, similarly as for kaolinite consisting of grains finer than 0.5 μm and with a disordered structure. The E value for the main stage of dickite dehydroxylation is similar to that for coarse-crystalline kaolinite with a well-ordered structure.

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Résumé — La cinétique de la déshydroxylation de la dickite a été étudiée par les méthodes de l'analyse thermique. On a établi que celle-ci obéit à un processus en deux étapes. La température de la déshydroxylation de la dickite est plus élevée que celle de la kaolinite en raison d'un arrangement différent des couches dans la structure. L'altération de l'ordre d'empilement des couches dans la structure de la dickite provoque la diminution de la température de déshydroxylation ainsi que la réduction de l'énergie d'activation de ce processus. Elle entraîne aussi l'apparition d'un pic supplémentaire ou d'un épaulement à la température de 580°, sur les courbes d'ATD et TGD.

ZUSAMMENFASSUNG — Die Dehydroxylierungskinetik von Dickit wurde durch die Methoden der Thermoanalyse untersucht. Es wurde festgestellt, daß es sich um einen Zweistufenvorgang handelt. Die höhere Temperatur der Dehydroxylierung von Dickit im Vergleich zu Kaolinit resultiert aus der unterschiedlichen Anordnung der Schichten in seiner Struktur. Die Störung der Ordnung in der Stapelung der Schichten in der Struktur von Dickit setzt die Dehydroxylierungstemperatur herab und hat die Abnahme der Aktivierungsenergie dieses Vorganges zur Folge. Sie verursacht gleichsam das Auftreten eines zusätzlichen Peaks oder einer Krümmung in den DTA- und DTG-Kurven bei der Temperatur von 580°.

Резюме — Методами термического анализа исследована кинетика дегидроксилирования дикита. Установлено, что этот процесс является двухстадийным. Более высокая температура дегидроксилирования дикита по сравнению с каолинитом, является результатом различного расположения слоев в их структурах. Нарушение последовательности слоев в структуре дикита, вызывает понижение температуры дегидроксилирования и энергии активации этого процесса. Это также приводит к появлению дополнительного пика или перегиба на кривых ДТА и ДТГ при температуре 580°.