KINETICS OF KAOLINITE DEHYDRATION AND ITS DEPENDENCE ON MECHANOCHEMICAL ACTIVATION

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For the mechanochemical activation of two processes can be considered: the structural disordering of laminar crystals, and the formation of molecular dense aggregates from small particles. The activation energy of the dehydration is shown to decrease if the first process predominates, and vice versa. Therefore, to study and compare the kinetics of dehydration of different kaolinites the whole complex of properties the initial samples should be taken into account: the structure defectness, the particle size, particle-packing into aggregates, and the size and density of the aggregates.

The dehydration of kaolinite is one of the steps of technological processes such as the preparation of ceramics, refractories, zeolites and catalyst. It was of interest to study how mechanochemical activation, which has been widely used in recent years for processing low-active substances, influences the dehydration process.

As stated earlier [1], the formation of an X-ray amorphous product occurs on the mechanochemical activation of kaolinite, along with dehydroxylation, which results in a decrease of the coordination number of the Al atoms from 6 to 5 and 4. The molecular water formed remains completely in the activation product. Part of it is coordinatively bound to Al atoms $(Al-OH)_2$.

Experimental

Natural kaolinite with a high structural order (Hinkley's index [2] $C = 1.63$) and kaolinite synthesized according to [3] ($C = 0.97$) were taken for our investigations.

Mechanochemical activation was carried out on a centrifugal planetary mill in air for 60 min. Initial, activated and dehydrated samples were characterized by methods of X-phase analysis, high-resolution ^{27}Al NMR, electronmicroscopy and surface measurements.

10*

Thermogravimetric curves were recorded on a MOM derivatograph, with a sample weight of 100 mg, a shortened ceramic crucible $h = d = 12$ mm and a He stream of 80 cm^3 min^{-1}. Heating rates of 2.5, 5 and 10 deg/min of the dehydroxylation were employed.

Results and conclusions

The electronmicroscopic pictures show that the mechanochemical activation of natural kaolinite leads to the edge breaking of laminar crystals without any substantial decrease of the initial size (0.1–2 µm), and to shifting and turning of the layers. Small particles and fragments are packed in aggregates 2–3 µm in size. However, their fraction is negligible as compared to that of disordered defective "crystals". For synthetic kaolinite, the edge breaking of crystals and the formation of oval particles 0.1–0.5 µm in size is also observed, which corresponds to the size of the initial laminar particles. Along with such particles, 2–3 µm sized aggregates are formed, and these predominate in the sample. The specific surface area of the natural sample is practically the same before and after activation (11 and 9 m^2/g, respectively), but for the synthetic one it decreases essentially, from 60 to 13 m^2/g. The dehydration does not change the specific surface area for any sample.

In this work we studied the changes in dehydration-dehydroxylation kinetics as a result of mechanochemical activation of kaolinite. We analyzed the changes from a formal kinetic aspect, neither searching for an equation which most probably describes the dehydration, nor analyzing the limiting step. The reasons are as follows:

1. Polydispersed kaolinite powders were investigated without isolating a narrow fraction of particles. This results in the distortion of kinetic equations [4].

2. Use of an integral method of calculation (with the function linearization $\log g(\alpha)$ vs. $1/T$) gave no results. This method, based on approximate calculations, is not recommended for use when the experimental data range in the temperature interval > 100 K. The temperature interval for the thermal decomposition of kaolinite is essentially wider.

3. It is not possible to separate the evolution of the molecularly bound water loss and that of dehydroxylation water in the TG curves (Fig. 1), probably due to the large number of transition states from the Al–OH bonds in the initial kaolinite to the molecular water adsorbed on the surface of the activated particles.

To calculate the kinetic parameters, the well-known Ozawa method [5, 6] was used, which analyzes the dependence $\log \Phi_i$ vs. $1/T_i$ (Φ_i = linear heating rate, T_i = temperature to obtain a definite conversion degree).

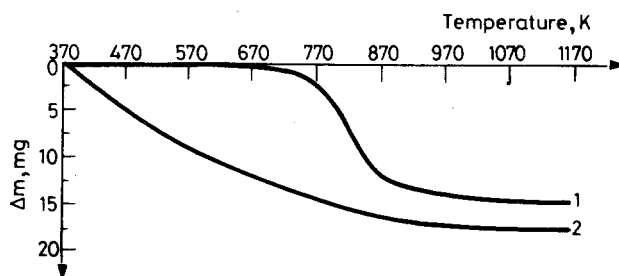Since the kinetic law for kaolinite dehydroxylation is reported to change at a

Fig. 1 TG curves of initial (1) and activated (2) natural kaolinite. Heating rate: 10 deg min^{-1}

conversion degree $\alpha > 60\%$ [7], we used conversion degrees $\alpha_1 = 20\%$, $\alpha_2 = 30\%$ and $\alpha_3 = 50\%$ for our calculations.

Values of the pre-exponential Arrhenius factor were calculated by using the method of Gorbachev et al. [8, 9] from the equation:

$$\log(AR/E) = \log(\Phi/T^2) + E/RT$$

The derivation of this equation [8] is based on a hypothetical description of the process by a $d\alpha/dt = k(1-\alpha)^n$ function.

The calculated kinetic parameters are listed in Table 1. It should be noted that the values obtained for the natural kaolinite sample are close to those given in the literature ($E = 37$ kcal/mol, $\log A = 9$ [7]).

According to the TG curves (Fig. 1), the activated kaolinite samples are less stable and their decomposition becomes evident at considerably lower temperatures than those of the initial samples. Furthermore there are essential differences in their kinetic stabilities.

After mechanical treatment of the natural kaolinite, the activation energy of the dehydration decreased. This caused an increase in the decomposition rate constant (Fig. 2).

On treatment of the synthetic kaolinite sample, the activation energy of the dehydration increased, as did the decomposition rate constant throughout the

Table 1 Kinetic parameters of kaolinite dehydration

Kaolinite sample	E, kcal/mol*	$\log A*$
Natural	33	8.6
Natural, activated	18	4.9
Synthesized	10	0.6
Synthesized, activated	42	14.8

l The values of E and $\log A$ aee value averages, obtained at $\alpha_1 = 20\%$, $\alpha_2 = 30\%$ and $\alpha_3 = 50\%$.
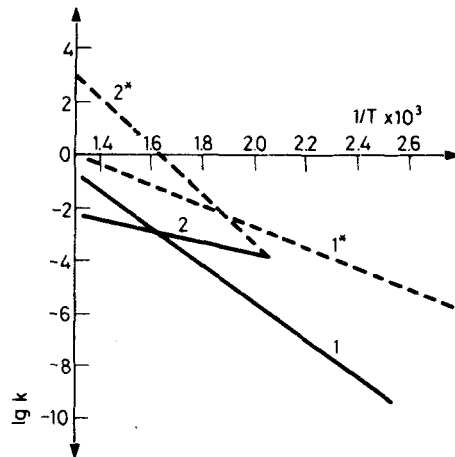
Fig. 2 Kinetic stability of natural (1) and synthesized (2) kaolinites and their activated samples (1* and 2* respectively)

whole temperature interval (Fig. 2). This increase in the decomposition rate constant depends mainly on the strong increase in the pre-exponential factor (i.e. entropy factor).

We can explain the difference in the behaviour of the activation energy of the dehydration after mechanochemical activation of the two types of kaolinites as follows:

On activation some of the Al–OH bonds are attenuated and ruptured and molecularly-bound water is formed. It is obvious that water is removed more easily from the interlayer space of defective particles than from the initial crystals. This is true in the case of well-ordered crystals of natural kaolinite, in the activated sample of which such particles predominate. On the activation of small crystals of the synthetic kaolinite, disordering occurs as well. This process, however, is superimposed on the formation of molecularly dense aggregates from the small particles. Water removal from such aggregates in hindered, which appears to exert a very strong influence on the dehydration process.

Thus, it is shown that, when studying and comparing the kinetics of kaolinite dehydration, one should consider the complexes of properties of the initial samples: the structure defectness, the particle size, particle-packing in aggregates and the size and density of the aggregates.

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Zusammenfassung — Bei der mechanochemischen Aktivierung von Kaolinit sind zwei Prozesse zu betrachten: Die strukturelle Unordnung laminarer Kristalle und die Bildung molekular dichter Aggregate aus kleineren Teilchen. Es wird gezeigt, dass die Aktivierungsenergie der Entwässerung abnimmt, wenn der erste Prozess vorherrscht, und zunimmt, wenn der zweite Prozess überwiegt. Deshalb muss bei vergleichenden Untersuchungen zur Entwässerung verschiedener Kaolinite der Gesamtkomplex der Eigenschaften der Ausgangsproben berücksichtigt werden, also die strukturelle Perfektion, Teilchengrösse, Vereinigung von Teilchen zu Aggregaten sowie Grösse und Dichte der Aggregate.

Резюме — В эволюции каолинита при механохимической активации можно выделить два процесса: разупорядочение структуры слоистых кристаллов и формирование из мелких частиц молекулярно плотных агрегатов. Показано, что в случае, когда преобладает первый процесс, наблюдаемая энергия активации процесса дегидратации уменьшается. Во втором случае — увеличивается. Сделан вывод, что при изучении и сравнении кинетики дегидратации каолинитов следует учитывать совокупность свойств исходных образцов: дефектность структуры, размер частиц, упаковку частиц в агрегаты, размер и плотность агрегатов.