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THE KINETICS OF DEHYDROXYLATION AND MULLITIZATION OF ZETTLITZ KAOLIN IN THE PRESENCE OF CALCIUM(II) AS AN INGREDIENT

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ABSTRACT

The method of differential thermal analysis and Kissinger's approach were used in this study to investigate the kinetics of dehydroxylation and mullitization. The relatively high resistance to the breaking of structural bonds and the diffusion to water molecules through the lamellar gas layer of water vapour limits the activation energy to 178 kJ mol^{-1}, as determined in the experimental work.

It is assumed that the relatively moderate activation energy value of mullitization, 487 kJ mol^{-1}, obtained during the exothermic reaction is the result of a moderately defective structure and of the influence of calcium(II) which decreases the activation energy.

INTRODUCTION

A number of non-isothermal methods have been developed [1–4] which can be applied to investigations of the kinetics of the thermal decomposition of kaolinite. In the present work, a differential thermal analysis (DTA) method was used and the obtained results were then analysed by Kissinger's method [1]. Kissinger established an equation that enables the calculation of the activation energy

$$\ln(\theta/T_m^2) = C - E/RT_m \tag{1}$$

where E, R, T_m, θ and C are the activation energy, gas constant, peak temperature, heating rate and integrating constant, respectively.

Non-isothermal heating of kaolin samples in a DTA apparatus up to 1000 °C produces several characteristic peaks. Two of these are endothermic and reflect the loss of adsorbed water and dehydroxylation. Another is the exothermic peak indicating the formation of a new crystal phase, most often that of mullite.

A number of authors have tried to determine the nature of the crystal phase formed during the exothermic reaction [5–15], the most interesting results being those concerned with the influence caused by the presence of different ions.

A disagreement concerning the possible products of the exothermic reaction between different authors arose from the complexity of the processes that may take place. The degree of this disagreement can be judged from the list of products proposed: mullite and spinel phase; mullite and SiO_2; γ-Al_2O_3 and SiO_2; AlSi spinel, SiO_2 and mullite.

Another group of authors studied the influence of cation and anion additions on the processes during the exothermic reaction, as well as at higher temperatures. They concluded that the size of the ions and their mobility can influence the formation of mullite, or γ-Al_2O_3 and SiO_2.

The kinetics of dehydroxylation and mullitization of Zettlitz kaolin in the presence of a high percentage of Ca^{2+} cations as a natural ingredient, was the subject of the present investigation.

EXPERIMENTAL

The starting material of the experiments was Zettlitz kaolin containing about 95% of kaolinite. A relatively high percentage (1.21%) of CaO can influence the kinetics of the process (Table 1). Figure 1 shows the diffractograph of Zettlitz kaolin.

DTA curves were obtained on a MOM Derivatograph, Model C. The samples were prepared under identical conditions.

RESULTS AND DISCUSSION

The DTA curves were recorded at the different heating rates of 1.25, 2.5, 5 and 10 °C min^{-1} (Fig. 2).

TABLE 1

Chemical composition of Zettlitz kaolin (wt.%)

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Loss on ignition
46.93	37.52	0.19	0.45	1.04	0.14	0.32	0.13	13.25
54.10	43.25	0.23	0.52	1.21	0.17	0.37	0.15	–

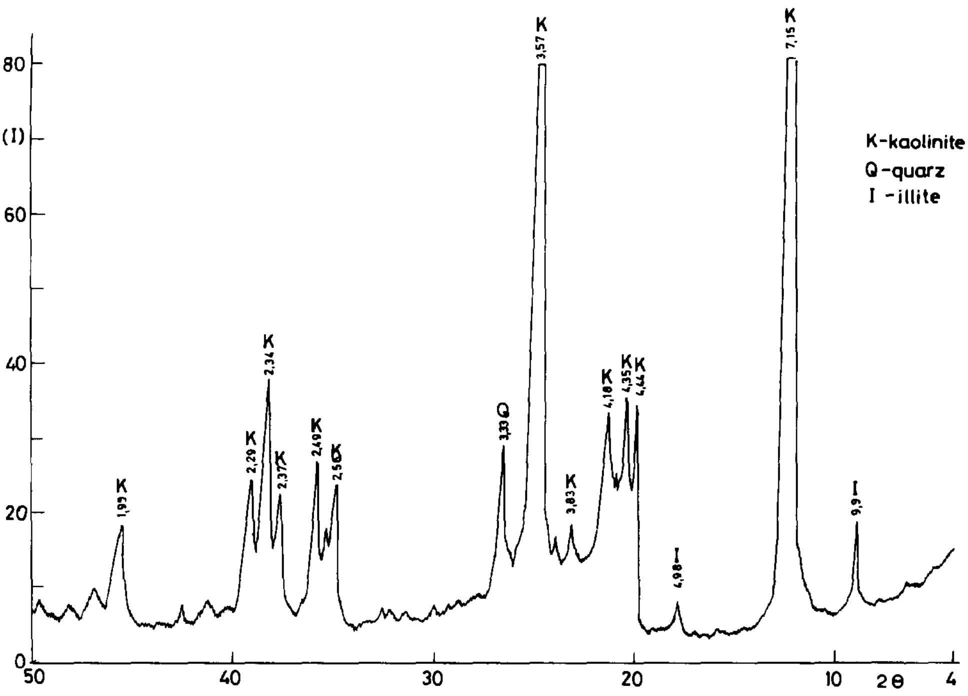

Fig. 1. Diffractograph of Zettlitz kaolin.

Table 2 gives the temperatures of the endothermic, T_1, and exothermic, T_2, peaks, the positions of which change depending on the heating rate, θ.

Plotting the graphs according to eqn. (1) for (a) the dehydroxylation and (b) the mullitization processes gave linear traces, see Fig. 3. Applying a least-squares method, the slopes and intercepts were defined. Finally, the activation energy of dehydroxylation was calculated as 178 kJ mol^{-1}, and that of mullite formation was 487 kJ mol^{-1}.

In evaluating an activation energy, it is possible to discuss more precisely the limiting stage and the resistances to the chemical reaction. During dehydroxylation, the hydrogen bonds, as well as the bonds within an

TABLE 2

Kinetic parameters

Heating rate, θ (°C min^{-1})	T_1 (K)	$-\ln \theta/T_1^2$	T_2 (K)	$-\ln \theta/T_2^2$
1.25	791	−13.12	1205	−13.960
2.5	818	−12.49	1228	−13.345
5	840	−11.85	1240	−12.652
10	853	−11.20	1253	−11.975

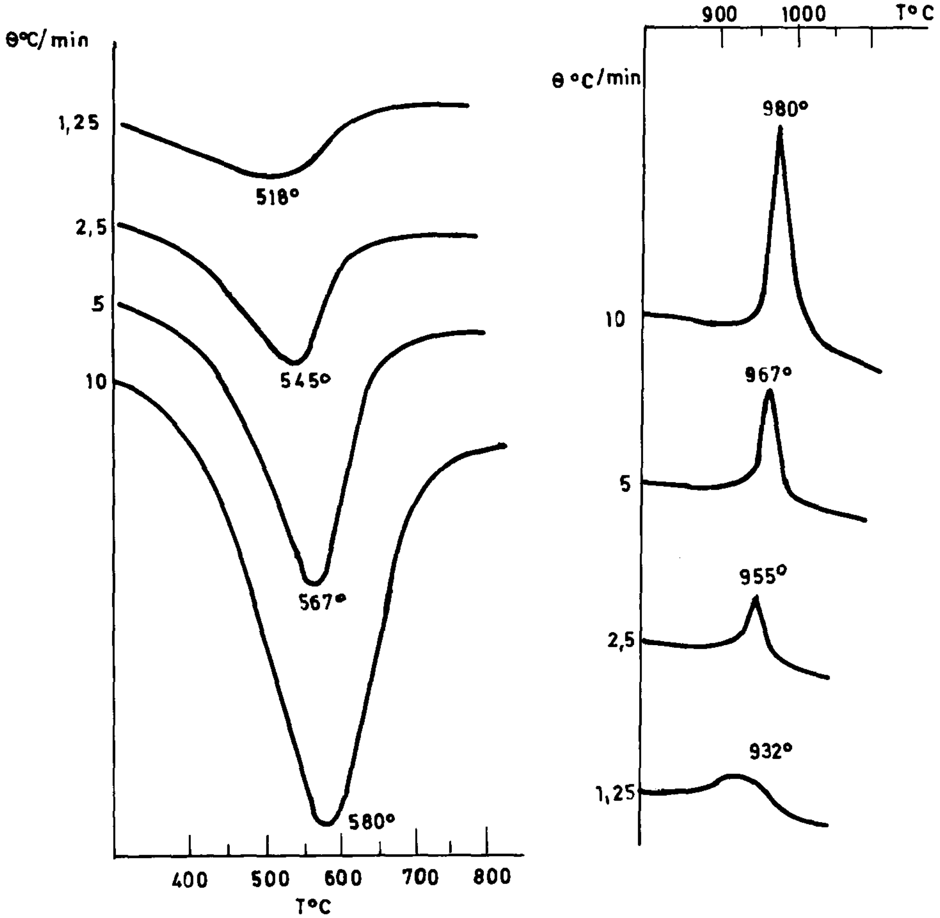

Fig. 2. DTA of kaolin at different heating rates.

octahedral–tetrahedral layer, are broken, and the resistances to the diffusion of water molecules through the laminated gas layer are overcome. All these resistances to diffusion limit the total rate of the dehydroxylation process. The value of the activation energy is a measure of these resistances. According to the literature, the activation energy values of the dehydroxylation process for kaolinites of different origin vary in the range of 140–190 kJ mol^{-1}. The value of the activation energy determined in the present work, 178 kJ mol^{-1}, indicates relatively high diffusion resistances.

With temperature increase, the metastable phases of meta-kaolinite and AlSi spinel are formed. The resistances to the chemical reaction of mullitization are the rate-determining factors of the reaction. According to literature data, activation energy values fall into the range 210–840 kJ mol^{-1} [14]. The distribution of the results can be explained by differences in the nature of the raw material and the influence of the impurities present. The relatively moderate activation energy of 487 kJ mol^{-1} determined in the present work

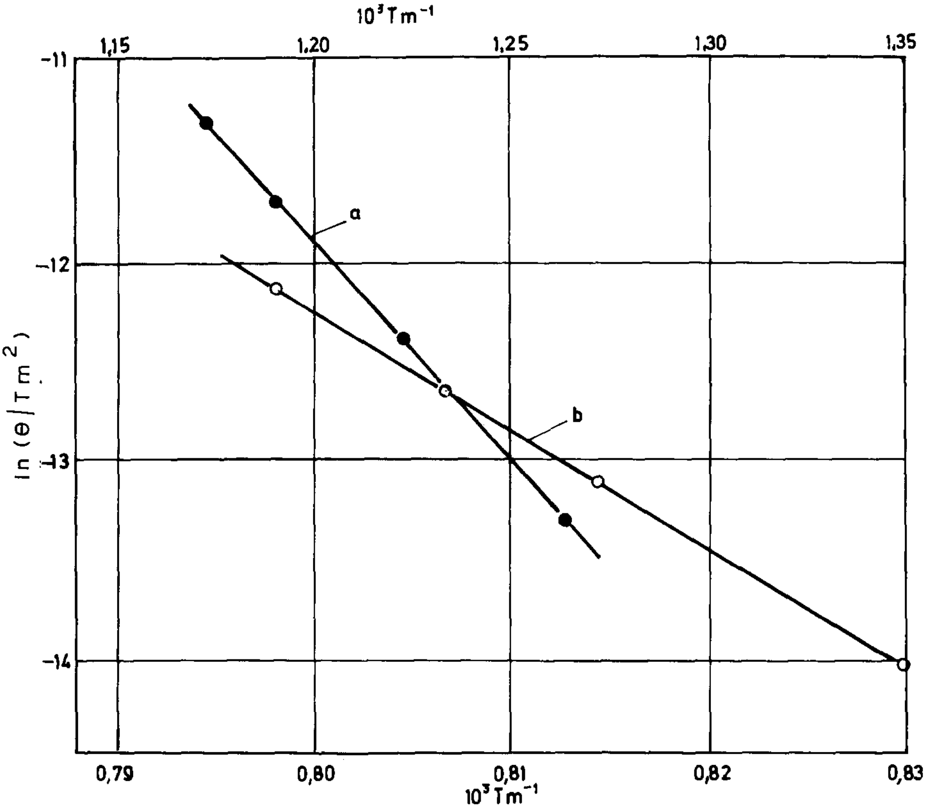

Fig. 3. ln $\theta/T_m^2 = f(1/T_m)$ dependency of (a) dehydroxylation and (b) mullite formation.

indicates a moderately distorted kaolinite structure, and suggests that the calcium(II) present probably influences the decomposition of meta-kaolinite into mullite.

Chakraborty and Ghosh [7,8] showed that during the dehydroxylation of kaolinite, SiO_2 is not a reaction product, thus suggesting that dehydroxylation results not in the formation of Al_2O_3 and SiO_2, but in the formation of metastable meta-kaolinite phase. They claim that at 980 °C meta-kaolinite decomposes to AlSi spinel, amorphous SiO_2 and a very small amount of mullite. With further heating, at about 1250 °C, the AlSi spinel formed finally decomposes to mullite by exothermic reaction. On the other hand, according to the works of Mackenzie [10] and Bulens et al. [11], it can be seen that the presence of different anions and cations can greatly influence the course of the kaolinite–mullite transformation.

If calcium(II) is present in kaolinite, AlSi spinel may not be formed; instead mullite is formed directly. If magnesium(II) is predominant, the decomposition of meta-kaolinite results in AlSi spinel, which is further decomposed to γ-Al_2O_3 and SiO_2. It is assumed that magnesium(II), being smaller then calcium(II), is more movable, and at about 900 °C it blocks the

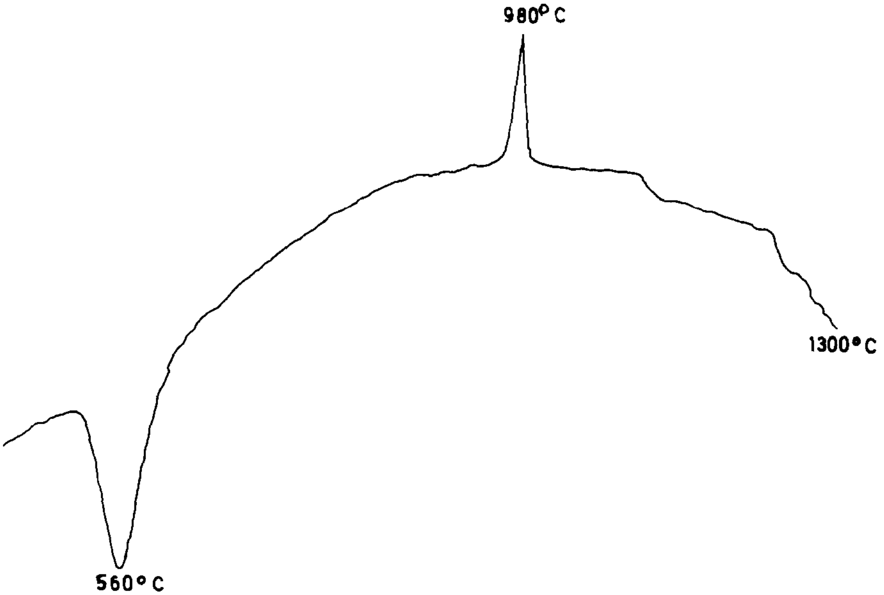

Fig. 4. DTA of Zettlitz kaolin up to 1300 ° C on Linseis apparatus, at a heating rate of 10 ° C min^{-1}.

formation of AlSi spinel phase so that the transformation process is directed toward γ-Al_2O_3 and SiO_2. On the other hand, calcium(II) moves more slowly, penetrating deeper into meta-kaolinite, and encouraging the transformation of AlSi spinel to mullite.

When analysing the DTA curves of kaolin obtained at temperatures of up to 1300 ° C (Fig. 4), no exothermal effect is apparent in the range 1150–1250 ° C, which implies that the mullite was formed earlier, within the range 900–1050 ° C. Thus, it is assumed that the calcium(II), present naturally in the kaolin influenced the process of meta-kaolinite decomposition into mullite, via AlSi spinel, and that an exothermal effect at about 980 ° C is the result of this reaction.

CONCLUSIONS

The activation energy of kaolinite dehydroxylation, 178 kJ mol^{-1}, determined for Zettlitz kaolin, indicates the relatively high resistances that are present during the breaking of the kaolinite structural bonds, as well as the diffusion resistance to water molecules throughout the gaseous laminar layer of water vapour.

It was estimated from the diffractograph that Zettlitz kaolin has a moderately defective structure and that the determined activation energy of kaolinite mullitization, 487 kJ mol^{-1}, does not represent the real state of its structure. It is assumed that the 1.21% CaO present in the kaolin as a natural ingredient, causes an additional decrease in the activation energy. The physico-chemical characteristics of calcium(II) influence the course of the transformation of meta-kaolinite via AlSi spinel to mullite, in such a way as to decrease the activation energy of the mullitization of the system.

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