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KINETICS AND COMPENSATION EFFECT IN KAOLINITE DEHYDROXYLATION

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ABSTRACT

Activation parameters (E, A, $\Delta H^{\neq}$, and $\Delta S^{\neq}$) and the effect of various factors involved in kaolinite dehydroxylation reaction have been studied using isothermal TG measurements. Thermal decomposition of kaolinite is found to be diffusion controlled within $0 < \alpha < 0.65$–0.70. The rate of the water release in dehydroxylation has obeyed the expression for diffusion in a spherical particle and/or the rate equation of the second order reaction, depending upon the kaolinite nature. The values of activation energy (140–300 kJ/mol) increased with increasing of partial water pressure in the reaction environment and increasing of structural disorder (natural, or induced by grinding).

Activation parameters have shown a compensation behavior, following the equations:

$$\{E\} = 51.1 + 12.961 \log\{A\} \text{ and}$$
$$\{\Delta H^{\neq}\} = 222.0 + 0.680\{\Delta S^{\neq}\}$$

Isokinetic temperature $\beta = (679 \pm 2)$K derived from these relations is in good agreement with the temperature range of the isothermal measurements performed.

INTRODUCTION

In irreversible thermal decomposition of kaolinite the interaction of hydroxyl groups occur yielding water and dehydroxylated phase following the equation:

$$Si_4Al_4(OH)_8O_{10}\ (s) = Si_4Al_4O_{14}\ (s) + 4H_2O\ (g) + \Delta H \qquad (1)$$

where ΔH represents the enthalpy change of the endothermic process.

There has long been considerable interest in the search for the appropriate mechanism of the water formation and diffusion in dehydroxylation reaction. Differences have been reported among workers as to the nature of the proton bearing complex (ref. 1, 2) and the kind and path of its diffusion (ref. 3 - 5). However, the examination of the large samples (more than 100 mg) brought difficulties in the interpretation of the kinetic data due to large differences between the extent of dehydroxylation at the outside and the inside of the specimen (ref. 6 - 8). Previously, it has been assumed, that the rate of kaolinite dehydroxylation follows first order kinetics (ref. 1, 7, 8). Later was established (ref. 9, 10) that the reaction is controlled by diffusion process being well represented by equations for two or three-dimensional diffusion. Recently we have found (ref. 11, 12) that the prevailing part of kaolinites,

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within conversion range $0 < \alpha < 0.65$–0.70 decomposes isothermally according to the equation of the second order reactions:

$$\left[(1 - \alpha)^{-1} - 1\right] = kt \qquad (2)$$

and some specimens, only, dehydroxylate according to the three dimensional diffusion models:

$$\left[1 - (2\alpha/3)\right] - (1 - \alpha)^{2/3} = kt \qquad (3)$$

$$\left[1 - (1 - \alpha)^{1/3}\right]^2 = kt \qquad (4)$$

It has also been found (ref. 11 - 15) that activation parameters of kaolinite dehydroxylation reaction are sensitive to the crystallochemical, structural and morphological characteristics of kaolinite as well as to the reaction conditions.

In the study presented here compensation relations between activation parameters involved in kaolinite dehydroxylation have been investigated.

THEORETICAL CONSIDERATIONS

The values of kinetic parameters are not independent of each other and they take the form of the linear compensations laws described by Exner (ref. 16):

$$E = e + R\beta \ln\{A\} \qquad (5)$$

$$\Delta H^{\neq} = h_o + \beta \cdot \Delta S^{\neq} \qquad (6)$$

where e_o and h_o are constants and E, A, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ represent activation energy, frequency factor, enthalpy and entropy of activation recpectively. The expression is for the so called isokinetic temperature at which the rates of any group of related reactions which obey Eq. (5) or (6) are equal.

The values of E and A are calculated from the Arrhenius relation and $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been found by equation:

$$\ln (k\, h/\mathbf{k}\, T) = (-\Delta H^{\neq} / RT) + (\Delta S^{\neq} / R) \qquad (7)$$

where k is the rate constant at temperature T, $\mathbf{k}$ and h are Boltzmann´s and Planck´s constants respectively.

EXPERIMENTAL

All measurements of decomposition rate of 15-20 mg powdered samples were carried out isothermally using a DuPont 990 thermobalance (TGA 951) in the atmosphere controlled by flowing N_2 (1 $cm^3\,s^{-1}$) or N_2 saturated with H_2O (P_{H_2O} = 2.7 kPa). 15 kaolinites collected from Czechoslovakia, GDR, USA and Spain, reflecting variations in the structure, shape and size of the particles (ref.15) were used for the examination.

RESULTS AND DISSCUSSION

Kinetics of dehydroxylation

The retarded process of kaolinite dehydroxylation (isothermal alpha vs. time curves, see Fig. 1 and 2) obeyed the kinetic expresions (2) or (4), within

$0 < \alpha < 0.65-0.70$, depending upon the nature of kaolinite. Reduced-time plots for the model functions (2) $\sim$ (SO) and (4) $\sim$ (D_3) are shown in Fig. 3.

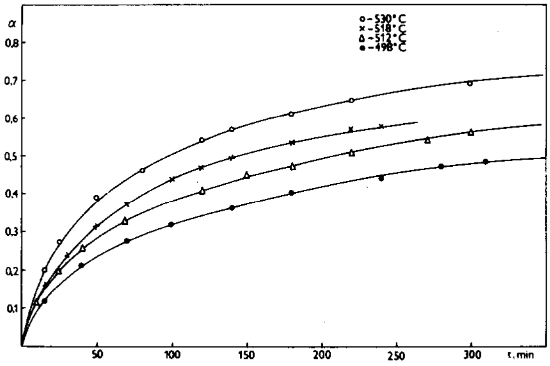

Fig. 1. Isothermal patterns of the thermal decomposition of the kaolinite from Keokuk (USA) in nitrogen flow, weight of the samples 17-20 mg. Mechanism "D_3" (three dimensional diffusion) according to the Eq. (4).

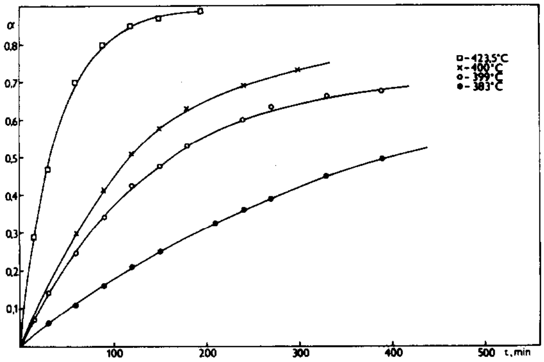

Fig. 2. Isothermal patterns of the thermal decomposition of the kaolinite from Lötheiner < 0.63 (GDR) in nitrogen flow, weight of the samples 17-20 mg. Mechanism "SO" (second order kinetics) following the Eq. (2).

Activation energy values (140-300 kJ/mol, see Fig. 5) were found to increase with the increasing structural disorder (defined by index HWB, ref. 11)as well as with the increase of p_{H_2O} in the reaction environment and with the decrease of the particle thickness of kaolinite (ref. 12). It is suggested that the interlayer bonding forces play an important role in the water diffusion as the rate determining step. In the case of kaolinite these correspond to the energy of

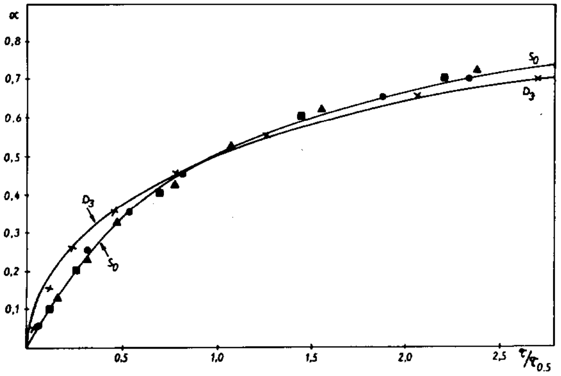

Fig. 3. Reduced-time plots for the model functions defined by Eqs. (2) and (4) including some experimental results.

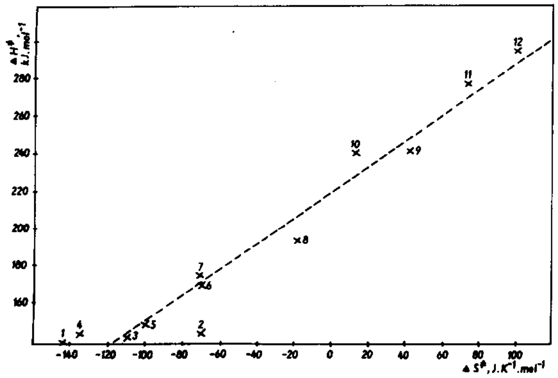

Fig. 4. Compensation plot showing $\Delta H^{\neq}$ vs. $\Delta S^{\neq}$ for dehydroxylation of kaolinites (Eq. 9).

hydrogen bonds between the OH groups in the octahedral layer and the oxygen atoms of the opposite tetrahedral sheet. The application of Eq. (4) for the linearization of the isothermal patterns confirmed the existing knowledge on diffusion as the controlling process in dehydroxylation reaction (ref. 9, 10).

Compensation behavior.

The apparent values of kinetic parameters (E, A, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) evaluated from the observed rate constants exhibit a pronounced compensation effect in Fig. 4 and 5. Kinetic compensation behavior has been subject of a number of studies summariezed by Galwey (ref. 18). The literature records some contraversies over the significance of this relation (ref. 19 - 21). The compensation relations found for kaolinite dehydroxylation follow the equations:

$$\{E\} = 51.1 + 12.961 \log \{A\} \quad (8)$$

$$\{\Delta H^{\neq}\} = 222.0 + 0.680 \{\Delta S^{\neq}\} \quad (9)$$

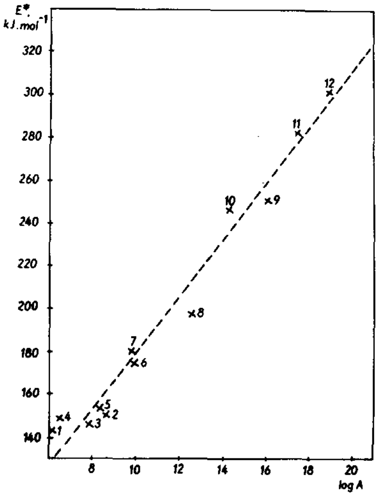

Fig. 5. Compensation plot showing E vs. log A for dehydroxylation of kaolinites (Eq. 8).

Isokinetic temperature β = (679±2) K calculated from these relations is in good agreement with the temperature range of the isothermal measurements performed.

CONCLUSIONS

It is suggested that dehydroxylation of kaolinite is a homogeneous process according to Taylor´s classification (ref. 22) starting on the surface with proton migration as proposed by Freund (ref. 23). The sensitivity of dehydroxylation kinetics to the structural characteristics indicates that diffusion of H_2O molecules formed also inside the crystal is important in determining the rate of the reaction.

The rate of water release in the decomposition of the powder kaolinite samples (within $0 < \alpha < 0.65-0.70$) follows three dimensional diffusion model and/or the rate equation of the second order reaction, depending upon nature of kaolinite.

The change in the reaction conditions (P_{H_2O}) does influence the reaction rate without changing the reaction mechanism and compensation behavior. The compensation behavior of kaolinite dehydroxylation was compared with another thermal decomposition studied by analogous experimental technique (ref. 24). It was assumed that the kinetic compensation effect, defined by parameters e_o, h_o and β (Eq. 5 and 6) reflects to a great extent the kinetic properties of the related reactions.

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