

DETERMINING THE RATE CONSTANT OF KAOLINITE DEHYDROXYLATION

JIŘÍ HAVRDA, IVONA MAZAČOVÁ, VLADIMÍR HANYKÝĚ

*Institute of Chemical Technology, Department of the Technology of Silicates, Suchbátarova 5
166 28 Prague 6*

Received 29. 1. 1986

A method was worked out and conditions established for the determination of the reaction rate of kaolinite dehydroxylation. The temperature dependence of the rate constant was determined experimentally; dehydroxylation of kaolinite can be considered a 1st-order chemical reaction if the body thickness is 1 mm, the bodies have been preignited at 573 K and rapid changes in temperature are ensured both on heating up and cooling down the body.

INTRODUCTION

The firing of a ceramic body containing kaolinite in the temperature range upto melt formation involves dehydroxylation of kaolinite. On the basis of available findings [1 through 12], dehydroxylation of kaolinite can be characterized as a chemical reaction producing molecular water from the OH⁻ groups in the structure of kaolinite, and resulting in metakaolinite. The course of dehydroxylation and the subsequent transfer of water vapour through the reacted product determine the changes in weight of the body during firing, and dehydroxylation likewise affects the thermal balance of the process. Solution of a general model of body firing in the dehydroxylation region [14], which describes this process as a combination of diffusion with a chemical reaction and heat transfer with a source, requires the course of dehydroxylation to be known.

The present study therefore had the aim to work out a method for determining the rate constant of the reaction and its temperature dependence.

Use is made of the finding [4] that the chemical reaction was proved to control the process in the case when the layer thickness of the powdered specimen or body was less than 2.5 mm even at a very low water vapour pressure in the ambient atmosphere compared to equilibrium vapour pressure at the given temperature.

THEORETICAL

Diffusion of water vapour through the reacted product during the simultaneous course of dehydroxylation is described by a mass balance of a binary incompressible mixture involving a chemical reaction, on the assumptions introduced in formulating the model of body firing over the dehydroxylation region [13]:

$$\frac{\partial x_A}{\partial \tau} = \text{div} (D_{AB}(T, x_A) \text{grad } x_A) + r_A, \quad (1)$$

where x_A is the mass fraction of component A , i.e. water bound in the form of OH⁻ groups in the structure of kaolinite, τ is time, D_{AB} is the diffusion coefficient, T is temperature and r_A is the rate of formation of component A in a unit volume

of the mixture. In the solving of concentration fields, this term is a function of position and time in the most general case. On considering a homogeneous reaction usually taking place throughout the volume of the mixture, the volume rate of formation of component A will appear in term r_A . For example, for a n -th order reaction, term r_A can be expressed by the equation

$$r_A = -k_n(T) x_A^n, \quad (2)$$

where n is the dimensionless order of the reaction and k_n is the rate constant of the n -th order reaction, mostly distinctly dependent on temperature. In the case of a 1-st order reaction with the kinetic equation

$$r_A = -k(T) x_A, \quad (3)$$

the time dependence of concentration of component A has the form

$$x_A = x_{A_0} e^{-k(T)\tau}, \quad (4)$$

where x_{A_0} is the initial concentration of component A , while for the temperature dependence of the rate constant it holds that

$$k = k_0 \exp(-B_1/T), \quad (5)$$

where B_1 is the characteristic temperature and k_0 is a constant. Substitution of (3) into (1) yields the mass balance for a binary incompressible mixture involving a chemical reaction,

$$\frac{\partial x_A}{\partial \tau} = \text{div} (D_{AB}(T, x_A) \text{grad } x_A) - k(T) x_A. \quad (6)$$

This balance equation describes study of dehydroxylation for any tentative thickness or powdered sample or body, because study of dehydroxylation even on very thin layers of sample or kaolinite crystals always involves subsequent diffusion of vapour through the reacted product. However, the results of studies carried out so far indicate that at specimen thicknesses smaller than 2.5 mm and even at very low vapour pressure in the ambient atmosphere, the effect of diffusion of vapour through the reacted product can be neglected owing to the short diffusion path involved. In other words, body thicknesses smaller than 2.5 mm ensure conditions for a homogeneous chemical reaction. i.e. the reaction proceeds throughout the body volume.

In working out an experimental method it is convenient to introduce simplifications, in this case isothermal conditions. The method for determining the rate constant of the 1-st order reaction can then be based on determining the concentration of component A in terms of time according to equation (4) which under isothermal conditions acquires the form

$$x_A = x_{A_0} \exp(-k\tau). \quad (7)$$

On this assumption, experimental determination of the relationship $x_A = x_A(\tau)$, while knowing x_{A_0} , allows the value of the rate constant at a given temperature to be obtained from equation (7).

Execution of isothermal experiments at various temperatures, i.e. over the temperature range from the initial dehydroxylation temperature upwards, will yield the values of rate constants at several temperatures and thus will express the temperature dependence of the rate constant.

The experimental arrangement of the method must then comply with the maximum body thickness of 2.5 mm and a low water vapour pressure in the ambient atmosphere. In addition to this, it is necessary to ensure a rapid change in temperature throughout the body volume from its initial value to the required temperature of dehydroxylation, and also rapid cooling after time τ down to a temperature lower than that of dehydroxylation onset, i.e. a temperature at which the reaction will stop abruptly throughout the body volume.

EXPERIMENTAL

Dehydroxylation was studied on thin plates of Podbořany kaolin $1 \times 11 \times 50$ mm in size over the temperature range of 773 to 873 K. The specimens 1 mm in thickness were prepared by grinding bodies drawn by a vacuum auger. After drying at 378 K, the specimens were ignited at 573 K to remove the last residues of technological water from the body preparation and of interstructural molecular water from the illitic-montmorillonitic component of the Podbořany kaolin [14].

The initial concentration $x_{A0} = 0.106$ kg/kg was determined by igniting these initial specimens at 1173 K to a constant weight. The remaining thin plates were gradually placed in a furnace preheated at the required various temperatures, and after the chosen exposure cooled rapidly by removal from the furnace. Following subsequent heating at 1173 K to constant weight, the value of the residual concentration of water in the specimen, x_A , was determined.

The chosen sample thickness of 1 mm, the experimental arrangement of the method and the working procedure employed all ensured compliance with the conditions demanded from the method. The experimental results are listed in Table I.

Table I
Concentration of residual water x_A in the specimen
in terms of temperature for various times of holding

$\frac{T}{K}$	τ/hrs					
	1	3	4.5	6	9	20
	$x_A(\tau)$ kg/kg					
773		0.081		0.067	0.046	0.028
798		0.075		0.039		
823		0.042	0.021	0.019		
853		0.025	0.021	0.014		
873	0.018					

DISCUSSION AND CONCLUSION

The experimentally established dependence of concentration on time for the individual temperatures was found to correspond well to equation (7). The chosen specimen thickness of 1 mm thus meets the requirement for neglecting the diffusion of vapour through the decomposition product and allows data describing dehydroxylation as a chemical reaction to be obtained. A linearized form of this equation

was used to calculate the rate constant of dehydroxylation for each temperature. The calculated rate constant values are listed in Table II and can be said to be comparable to the values given in studies [3, 4, 12].

Table II
The values of rate constants of dehydroxylation
at various temperatures

$\frac{T}{K}$	773	798	823	853	873
$\frac{k \times 10^5}{s^{-1}}$	1.8	4.7	8.6	9.3	49

The temperature dependence of the dehydroxylation rate constant obtained was approximated by equation (5) and the following values of the constants were determined:

$$k_0 = 36\,034\,956\,s^{-1} \quad B_1 = 21\,903\,K, \quad (8)$$

valid for the temperature interval $T \in \langle 773\,K; 873\,K \rangle$.

The findings obtained from the experiments with dehydroxylation of Podbořany kaolinite can be summarized into the following points:

(i) The method and the conditions of the experimental procedure employed allow the rate constant of dehydroxylation of kaolinite to be determined.

(ii) Under the given conditions, dehydroxylation of kaolinite can be regarded as a 1-st order chemical reaction.

(iii) Over the temperature interval in question, the temperature dependence of the rate constants described by equation (5) and the values of the constants (8).

References

- [1] Čičel B., Novák I., Horváth I.: *Mineralogy and Crystallochemistry of Clays* (in Czech) Veda, Bratislava 1981.
- [2] Kingery W. D.: *Introduction to Ceramics*, John Wiley and Sons, New York 1960.
- [3] Murray P., White J.: *Brit. Ceram. Soc.*, 54, 187 (1955).
- [4] Brindley G. W., Nakahira M.: *J. Amer. Ceram. Soc.*, 40, 10, 346—350 (1957).
- [5] Holt J. B., Cutler I. B., Wadsworth M. E.: *J. Amer. Cer. Soc.* 45, 3, 133 (1962).
- [6] Toussaint F., Fripiat J. J., Gastuche M. C.: *J. Phys. Chem.* 67, 26 (1963).
- [7] Sharp J. H., Brindley G. W., Achar Narahari B. N.: *J. Amer. Ceram. Soc.*, 49, 7, 279 (1966).
- [8] Brindley G. W., Sharp J. H., Patterson J. H., Achar Narahari B. N.: *Amer. Mineralogist*, 52, 201 (1967).
- [9] Hancock J. D., Sharp J. H.: *J. Amer. Ceram. Soc.*, 55, 2, 74 (1972).
- [10] Anthony G. D., Garn P. D.: *J. Amer. Ceram. Soc.*, 57, 3, 132 (1974).
- [11] Selvaratnam M., Garn P. D.: *J. Amer. Cer. Soc.*, 59, 7, 376 (1976).
- [12] Howard Johnson B., Kessler F.: *J. Amer. Ceram. Soc.*, 52, 199 (1969).
- [13] Havrda J., Mazačová Y., Oujří F., Hanykýt V.: *Silikáty* 31, 1, 17 (1987).
- [14] Babůrek J.: *Ber. Deut. Keram. Ges.*, 49, 12, 411 (1972).

STANOVENÍ RYCHLOSTNÍ KONSTANTY DEHYDROXYLACE
KAOLINITU

Jiří Havrda, Yvona Mazačová, Vladimír Hanykýř

Vysoká škola chemicko-technologická, Katedra technologie silikátů, 166 28 Praha

Pro stanovení rychlostní konstanty dehydroxylace kaolinitu je vypracována metoda založená na měření časové závislosti koncentrace zbytkové vody při izotermním výpalu deskových těles s tloušťkou 1 mm. Experimentálně je stanovena teplotní závislost rychlostní konstanty ve tvaru $k = 36\,034\,956 \exp(-21\,903\text{ K}/T) \text{ s}^{-1}$ platná v teplotním intervalu $T \in \langle 773\text{ K}; 873\text{ K} \rangle$. Bylo zjištěno, že dehydroxylaci kaolinitu lze považovat za chemickou reakci 1. řádu za podmínek: (a) tloušťka tělesa 1 mm, (b) tělesa předem vyžhána při teplotě 573 K, (c) skoková změna teploty při ohřevu i chlazení tělesa a (d) nízká tenze vodních par v okolním prostředí. Za těchto podmínek lze zanedbat difúzi par produktem rozkladu a získat data popisující dehydroxylaci jako chemickou reakci.

ОПРЕДЕЛЕНИЕ СКОРОСТНОЙ КОНСТАНТЫ
ДЕГИДРОКСИЛИРОВАНИЯ КАОЛИНИТА

Иржи Гаврда, Ивона Мазачова, Владимир Ганыкирш

*кафедра технологии силикатов Химико-технологического института
166 28 Прага*

Для определения константы скорости дегидроксилирования каолинита разработали метод, основывающийся на измерении временной зависимости концентрации остаточной воды при изотермическом обжиге пластинчатых тел толщиной 1 мм. Экспериментальным путем установили температурную зависимость константы скорости в виде $k = 36\,034\,956 \exp(-21\,903\text{ K}/T) \text{ с}^{-1}$, имеющей силу в температурном интервале $T \in \langle 773\text{ K}; 873\text{ K} \rangle$. Было установлено, что дегидроксилирование каолинита можно считать химической реакцией первого порядка при условиях: (a) толщина тела 1 мм, (б) тела заранее обжигали при температуре 573 K, (c) скачкообразное изменение температуры при нагреве и охлаждении тела, (д) низкое давление водяного пара в окружающей среде. При таких условиях можно пренебрегать диффузией паров продуктом разложения и можно получать данные, описывающие дегидроксилирование в виде химического взаимодействия.

RTG. TOPOGRAFIA — METÓDA SLEDOVANIA ŠTRUKTÚRNYCH DEFKTOV — bola vyvinutá v roku 1967. Je to doplnková metóda k transmisnej elektrónovej mikroskopii. Dovoľuje zrakom sledovať a fotografovať štruktúrne defekty, ako sú dislokácie, alebo rovinné defekty v kryštáloch. Fyzikálny základ metódy je difrakcia, preto metóda je vhodná len pre vzorky s malým počtom porúch na hrúbke niekoľko milimetrov.

Využitie tejto metódy je späté s prípravou monokryštálov vysokej kvality. V sedemdesiatych rokoch táto metóda umožnila prípravu kvalitných kryštálov kremeňa, neskôr sa metóda použila na vylepšenie laserov s heterogénnymi spojmi, čo bolo podmienené poznaním chovania sa dislokácií vrstiev $\text{Al}_x\text{Ga}_{1-x}\text{As}$ pomocou rtg. topografie. Rozvoj počítačovej techniky umožnilo obrazy defektov rekonštruovať a simulovať štruktúrne defekty.

I. Vojtaššák