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KINETICS OF DEHYDROXYLATION AND EVALUATION OF THE CRYSTALLINITY OF KAOLINITE

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ABSTRACT

This study presents results on the kinetics of kaolinite dehydroxylation. The accuracy of various methods of determining the values for the kinetic parameters and their sensitivity in detecting the mechanism of reaction is investigated. In particular, the differential order of reaction method of Baker, the general method of Achar et al., the integral method of Boy and Bohme, and the method of Coats and Redfern as modified by Fong and Chen are considered.

Kaolinites from well-known sources are used to study the influence of crystallinity on the values of kinetic parameters. The statistical significance of the various mathematical methods for the assessment of the data obtained from non-isothermal thermogravimetry is determined by comparison with experimental and theoretical data using a computer programme developed for this purpose. The study demonstrates that the kinetic parameters can be used to quantify the degree of crystallinity of kaolinite and also confirms other findings that the dehydroxylation of kaolinite is a second-order reaction.

INTRODUCTION

The study of the kinetics and mechanism of the dehydroxylation reaction of kaolinite has received much attention and has been studied by both isothermal and non-isothermal thermogravimetry under various experimental conditions. The reaction has been analysed by various mathematical techniques and numerous different values for the kinetic parameters associated with the reaction may be found in the literature. Recent improvements in instrumentation and mathematical appraisal of the reaction mechanism have meant that the kinetic parameters associated with it may be determined accurately from dynamic thermogravimetric analysis by comparisons to theoretical solid-state equations by computer methods.

The aim of the present study was to compare methods of assessing the mechanism of the kaolinite reaction and therefore obtain values for the

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kinetic parameters associated with the reaction, so that these values may be used to distinguish between kaolinites of differing crystallinity.

KINETICS OF KAOLINITE DEHYDROXYLATION

Appraisal of the historical development of the kaolinite dehydroxylation reaction tends to reflect the state of the mathematical appreciation of solid-state reaction kinetics and, in particular, the determination of the "mechanism" of the reaction or the path along which the decomposition reaction proceeds. This is usually represented as a function, $f(x)$, with respect to the fraction of material decomposed, x. The rate at which a decomposition reaction proceeds may be represented in terms of the rate of decomposition with time, dx/dt, by

$$\frac{dx}{dt} = k f(x)$$

where k is the rate constant which is related to temperature by the Arrhenius equation, i.e.

$$k = A \exp\left(-\frac{E}{RT}\right)$$

where E is the activation energy of reaction, A is a constant known as the pre-exponential factor, R is the gas constant and T is the absolute temperture. In order to determine the values of the kinetic parameters, E and A, it is necessary to determine the mechanism describing the reaction, i.e. whether the reaction proceeds by an order-of-reaction-type mechanism, diffusion-controlled mechanism, nucleation-type mechanism, etc., each of which may be described by a certain mathematical equation which may be introduced as a function of x, $f(x)$.

The initial investigators of the kaolinite dehydroxylation reaction (1955–1957) using both isothermal and dynamic methods considered the reaction to be first order, i.e. $f(x) = (1 - x)$ [1–6], until Tsuzuki and Nagasawa [7] considered other orders of reaction, i.e. $f(x) = (1 - x)^n$ where n is the order of reaction. Holt et al. [8] studied the dehydroxylation reaction at low water vapour pressures and investigated the effect of diffusion controlling the reaction and concluded that the reaction followed the parabolic law of diffusion. This work was followed by the dynamic study of Achar et al. [9] and the isothermal weight loss method of Brindley and Nakahira [10] who used the diffusion equation of Ginstlin and Brounstein. Brindley and Nakahira indicated how first-order kinetics may be confused with a diffusion-controlled process and how the two can be differentiated.

The various publications of Garn and Anthony [11–14] indicate that the reactions can be described by nucleation and growth equations. Garn [15,16] warned of the dangers of careless assumptions and experimentation, pointing out the fallacies in assuming, for example, that the nature of a quite complex reaction is known and only the kinetic parameters need to be determined from a given reaction mechanism.

During the late 1970's the development of new mathematical methods allowed the comparison of the various reaction mechanism equations available in the literature. Boy and Bohme [18] determined the statistical reliability of eleven reaction mechanism equations. They concluded that the reaction followed a second-order mechanism (yielding the lowest standard error of estimate and highest correlation coefficient for the linearising Arrhenius plot). This study presents the most consistent results with an activation energy of 215.64 kJ $mole^{-1}$ for an East German kaolinite.

DETERMINATION OF THE REACTION MECHANISM AND KINETIC PARAMETERS

The present study investigated the accuracy of the various methods of determining both the values of the kinetic parameters and their sensitivity in detecting the mechanism of the kaolinite dehydroxylation. In order to do this, four methods of mathematical treatment were investigated: two differential methods; the order of reaction method of Baker [17] and the general method of Achar et al. [9] (modified to allow the examination of

TABLE 1

Kinetic functions used in the computer analysis

Function no.	Integrated form, g(x)	Differentiated form, f(x)	Name of mechanism
1	x^2	$\frac{1}{2}x$	1-d diffusion
2	$1-(1-x)^{1/2}$	$2(1-x)^{1/2}$	Contracting geometry, $n=\frac{1}{2}$
3	$1-(1-x)^{2/3}$	$\frac{3}{2}(1-x)^{1/3}$	Contracting geometry, $n=\frac{2}{3}$
4	$-[\ln(1-x)]^{2/3}$	$3[-\ln(1-x)^{2/3}](1-x)$	Avrami equation, $n=\frac{2}{3}$
5	$1[\ln(1-x)]^{1/2}$	$2[-\ln(1-x)^{1/2}](1-x)$	Avrami equation, $n=\frac{1}{2}$
6	$x+(1-x)\ln(1-x)$	$[-\ln(1-x)]^{-1}$	2-d diffusion
7	$1-\frac{2}{3}x-(1-x)^{2/3}$	$[-\ln(1-x)]^{-1}$	3-d diffusion
8	$(1-x)^{1/3}[(1-x)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-(1-x)^{1/3}](1-x)^{2/3}$	Jander equation
9	$(1-x)^2$	$(1-x)^{-1}-1$	Second order
10	$(1-x)^{1.5}$	$(1-x)^{-1/2}-1$	One and a half order
11	$\frac{3}{2}[(1-x)^{1/3}-1]^{-1}$	$1-\frac{2}{3}x-(1-x)^{2/3}$	Ginstling–Brounshtein
12	$(1-x)$	$-\ln(1-x)$	First order

various mechanisms by statistical analysis); and the integral methods of Boy and Bohme [18] and Fong and Chen's [19] modification of Coats and Redfern's treatment [20].

To assess each of the methods a program was written in FORTRAN IV which takes each of the methods in turn and determines the statistical accuracy of each Arrhenius plot for each reaction mechanism. In the case of the Baker method [17], this involved the comparison of various values of n (0–3.0 in 0.25 steps and $n = 0.666$). In the other three methods, a comparison was made of twelve commonly used theoretical reaction mechanism equations. These equations are presented in their integrated and differential forms in Table 1. To determine the best fitting mechanism for a particular set of data the correlation coefficient and standard error of estimates for each linearising plot is determined according to the methods of Fong and Chen [19] and Boy and Bohme [18], respectively.

In order to determine the accuracy of the program, the theoretical data of Bohme and co-workers [21] was used to compare results obtained using the different methods of analysis. They provide data for three reaction mechanisms; first order, 2-dimensional diffusion and the Avrami equation with $n = 2/3$, with an activation energy of 125 kJ $mole^{-1}$ and a pre-exponential factor of $5.5 \times 10^4\ s^{-1}$.

The results of the computer analysis for these theoretical equations for first-order reaction kinetics and the Avrami mechanism are presented in Tables 2 and 3. Considering the output from the Avrami equation, it can be seen from the results obtained using the method of Achar et al. [9], that the mechanism giving the highest regression coefficient, R, is mechanism number 12, which is the equation for a first-order reaction: however, the

TABLE 2

Output from computer program for the theoretical data for the first-order reaction equation

Mechanism number	E	A	R	SE
Achar method				
1	0.20585E 03	0.33111E 10	0.97719E 00	0.72236E 00
2	0.10533E 03	0.73993E 03	0.98805E 00	0.26527E 00
3	0.11205E 03	0.32869E 04	0.99526E 00	0.17683E 00
4	0.33802E 02	0.20309E−01	0.99995E 00	0.54859E−02
5	0.56723E 02	0.93787E 00	0.99999E 00	0.41205E−02
6	0.22269E 03	0.22709E 11	0.98958E 00	0.52327E 00
7	0.22269E 03	0.34063E 11	0.98958E 00	0.52327E 00
8	0.24321E 03	0.44726E 12	0.99797E 00	0.25045E 00
9	0.16580E 03	0.74835E 08	0.98091E 00	0.53065E 00
10	0.14564E 03	0.20237E 07	0.99369E 00	0.26534E 00
11	0.22979E 03	0.40392E 11	0.99344E 00	0.42714E 00
12	0.12548E 03	0.54725E 05	0.10000E 01	0.40146E−03

TABLE 2 (continued)

Mechanism number	*E*	*A*	*R*	*SE*
Baker method				
1	0.95250E 02	0.24336E 03	0.96812E 00	0.39792E 00
2	0.98609E 02	0.44418E 03	0.97620E 00	0.35371E 00
3	0.10533E 03	0.14799E 04	0.98805E 00	0.26527E 00
4	0.11205E 03	0.49303E 04	0.99526E 00	0.17683E 00
5	0.11541E 03	0.89992E 04	0.99748E 00	0.13262E 00
6	0.12548E 03	0.54725E 05	0.10000E 01	0.40146E−03
7	0.13556E 03	0.33278E 06	0.99817E 00	0.13269E 00
8	0.14564E 03	0.20237E 07	0.99369E 00	0.26534E 00
9	0.15572E 03	0.12306E 08	0.98770E 00	0.39799E 00
10	0.16580E 03	0.74835E 08	0.98091E 00	0.53065E 00
11	0.17588E 03	0.45508E 09	0.97379E 00	0.66330E 00
12	0.18595E 03	0.27673E 10	0.96661E 00	0.79595E 00
13	0.19603E 03	0.16828E 11	0.95956E 00	0.92861E 00
14	0.20611E 03	0.10233E 12	0.95273E 00	0.10613E 01
Boy – Bohme method				
1	0.22932E 03	0.20114E 12	0.99444E 00	0.39216E 00
2	0.11626E 03	0.48536E 04	0.99811E 00	0.11546E 00
3	0.11915E 03	0.55660E 04	0.99912E 00	0.80725E−01
4	0.33804E 02	0.16419E−01	0.99995E 00	0.55314E−02
5	0.56724E 02	0.84816E 00	0.99999E 00	0.41679E−02
6	0.23864E 03	0.55996E 12	0.99707E 00	0.29536E 00
7	0.24095E 03	0.19769E 12	0.99813E 00	0.23797E 00
8	0.25034E 03	0.10659E 13	0.99927E 00	0.15405E 00
9	0.14895E 03	0.43186E 07	0.99059E 00	0.33221E 00
10	0.13642E 03	0.21060E 06	0.99769E 00	0.15007E 00
11	0.24232E 03	0.24558E 12	0.99799E 00	0.24837E 00
12	0.12549E 03	0.54742E 05	0.10000E 01	0.47391E−03
Coats – Redfern method				
1	0.22932E 03	0.21245E 12	0.99444E 00	0.39216E 00
2	0.11626E 03	0.54232E 04	0.99811E 00	0.11546E 00
3	0.11915E 03	0.62016E 04	0.99912E 00	0.80725E−01
4	0.33804E 02	0.25704E−01	0.99995E 00	0.55314E−02
5	0.56724E 02	0.10809E 01	0.99999E 00	0.41679E−02
6	0.23864E 03	0.59016E 12	0.99707E 00	0.29536E 00
7	0.24095E 03	0.20825E 12	0.99813E 00	0.23797E 00
8	0.25034E 03	0.11206E 13	0.99927E 00	0.15405E 00
9	0.14895E 03	0.47043E 07	0.99059E 00	0.33221E 00
10	0.13642E 03	0.23130E 06	0.99769E 00	0.15007E 00
11	0.24232E 03	0.25862E 12	0.99799E 00	0.24837E 00
12	0.12549E 03	0.60643E 05	0.10000E 01	0.47391E−03

TABLE 3

Output from computer program for the theoretical data for the Avrami equation with $n = 2/3$

Mechanism number	*E*	*A*	*R*	*SE*
Achar method				
1	0.58771E 03	0.18692E 34	0.93446E 00	0.15775E 01
2	0.31614E 03	0.51145E 17	0.95928E 00	0.65577E 00
3	0.34493E 03	0.56311E 19	0.98125E 00	0.47725E 00
4	0.12455E 03	0.46038E 05	0.95091E 00	0.28555E 00
5	0.19404E 03	0.43298E 10	0.97885E 00	0.28568E 00
6	0.64670E 03	0.53575E 37	0.96479E 00	0.12420E 01
7	0.64670E 03	0.80362E 37	0.96479E 00	0.12420E 01
8	0.73656E 03	0.25741E 43	0.99300E 00	0.61732E 00
9	0.57521E 03	0.18258E 35	0.95159E 00	0.13089E 01
10	0.48886E 03	0.32427E 29	0.97919E 00	0.71382E 00
11	0.67905E 03	0.38085E 39	0.97867E 00	0.10041E 01
12	0.40250E 03	0.57593E 23	0.99495E 00	0.28609E 00
Baker method				
1	0.27296E 03	0.13632E 15	0.89728E 00	0.94609E 00
2	0.28735E 03	0.12386E 16	0.92240E 00	0.84766E 00
3	0.31614E 03	0.10229E 18	0.95928E 00	0.65577E 00
4	0.34493E 03	0.84465E 19	0.98125E 00	0.47725E 00
5	0.35932E 03	0.76754E 20	0.98782E 00	0.39869E 00
6	0.40250E 03	0.57593E 23	0.99495E 00	0.28609E 00
7	0.44568E 03	0.43216E 26	0.99007E 00	0.44577E 00
8	0.48886E 03	0.32427E 29	0.97919E 00	0.71382E 00
9	0.53203E 03	0.24332E 32	0.96574E 00	0.10071E 01
10	0.57521E 03	0.18258E 35	0.95159E 00	0.13089E 01
11	0.61839E 03	0.13700E 38	0.93769E 00	0.16143E 01
12	0.66157E 03	0.10280E 41	0.92450E 00	0.19216E 01
13	0.70475E 03	0.77137E 43	0.91220E 00	0.22301E 01
14	0.74793E 03	0.57881E 46	0.90084E 00	0.25393E 01
Boy–Bohme method				
1	0.70236E 03	0.76333E 41	0.99037E 00	0.69169E 00
2	0.36807E 03	0.14734E 21	0.99620E 00	0.22662E 00
3	0.37824E 03	0.48079E 21	0.99806E 00	0.16633E 00
4	0.12548E 03	0.54672E 05	0.10000E 01	0.58535E−04
5	0.19496E 03	0.53252E 10	0.10000E 01	0.98513E−03
6	0.72931E 03	0.25080E 43	0.99392E 00	0.56927E 00
7	0.72909E 03	0.61613E 42	0.99602E 00	0.45947E 00
8	0.76997E 03	0.30281E 45	0.99814E 00	0.33101E 00
9	0.51715E 03	0.34636E 31	0.97026E 00	0.90885E 00
10	0.45443E 03	0.10243E 27	0.99236E 00	0.39812E 00
11	0.74054E 03	0.32258E 43	0.99557E 00	0.49276E 00
12	0.40342E 03	0.73286E 23	0.10000E 01	0.39577E−02

TABLE 3 (continued)

Mechanism number	*E*	*A*	*R*	*SE*
Coats – Redfern method				
1	0.70236E 03	0.77833E 41	0.99037E 00	0.69169E 00
2	0.36807E 03	0.15297E 21	0.99620E 00	0.22662E 00
3	0.37824E 03	0.49864E 21	0.99806E 00	0.16633E 00
4	0.12548E 03	0.61287E 05	0.10000E 01	0.58535E−04
5	0.19496E 03	0.57226E 10	0.10000E 01	0.98513E−03
6	0.72931E 03	0.25555E 43	0.99392E 00	0.56927E 00
7	0.72909E 03	0.62779E 42	0.99602E 00	0.45947E 00
8	0.76997E 03	0.30823E 45	0.99814E 00	0.33101E 00
9	0.51715E 03	0.35567E 31	0.97026E 00	0.90885E 00
10	0.45443E 03	0.10557E 27	0.99236E 00	0.39812E 00
11	0.74054E 03	0.32859E 43	0.99557E 00	0.49276E 00
12	0.40342E 03	0.75831E 23	0.10000E 01	0.39577E−02

mechanism giving the lowest standard error of estimate, *SE*, is in fact the Avrami equation. This agrees with the findings of Heide et al. [22] who suggest that no information about the "most probable" mechanism can be obtained by comparing the experimental values with the model equations alone and in a later publication Bohme et al. [21] suggest the use of the standard error of estimate as a more sensitive indication of the most probable mechanism.

The method of Baker [17] by its very mathematical nature can only determine the order-of-reaction-type equations and cannot distinguish the Avrami equation. The integral methods of Coats and Redfern [20] and Bohme et al. [21], as expected from their mathematical derivation, produce the same straight line plot with the same activation energies and the same values for the statistical parameters. The integral plot produces a more linear function than the differential plot of Achar et al. with much lower standard errors of estimate. It can be seen that three kinetic equations give perfect correlation coefficients for the Avrami data and cannot be distinguished by this parameter alone. However, the lowest value for the standard error of estimate does in fact reveal that the Avrami equation with $n = 2/3$ (equation number 4) is the best fitting mechanism. The only difference between the two integral methods is in the estimation of the pre-exponential factor, *A*. It can be seen from the results that the method of Boy and Bohme produces the more accurate estimate of the pre-exponential factor.

Thus, in the present study, the method of Boy and Bohme was used to determine the mechanism of the kaolinite dehydroxylation reaction and the associated kinetic parameters.

TABLE 4

Computer output for the decomposition reaction of a kaolinite from a laterized profile from Brazil [a]

Mechanism number	*E*	*A*	*R*	*SE*
Achar method				
1	0.62345E 02	0.66450E 00	0.52980E 00	0.19523E 01
2	0.18206E 02	0.21693E−02	0.33733E 00	0.99381E 00
3	0.34326E 02	0.22990E−01	0.60762E 00	0.87764E 00
4	−0.17098E 02	0.28486E−04	−0.53099E 00	0.53374E 00
5	0.38181E 01	0.90807E−03	0.13532E 00	0.54681E 00
6	0.95342E 02	0.99466E 02	0.72842E 00	0.17541E 01
7	0.95342E 02	0.99466E 02	0.72842E 00	0.17541E 01
8	0.12758E 03	0.37681E 05	0.85500E 00	0.15138E 01
9	0.16329E 03	0.28127E 09	0.99072E 00	0.33829E 00
10	0.11493E 03	0.70017E 05	0.98387E 00	0.40867E 00
11	0.11337E 03	0.72676E 03	0.80890E 00	0.16119E 01
12	0.66657E 02	0.17429E 02	0.89267E 00	0.65742E 00
Baker method				
1	−0.60314E 01	0.68452E−04	−0.99199E−01	0.11723E 01
2	0.20852E 01	0.27291E−03	0.36644E−01	0.11124E 01
3	0.18206E 02	0.43386E−02	0.33733E 00	0.99381E 00
4	0.34326E 02	0.68970E−01	0.60762E 00	0.87764E 00
5	0.42385E 02	0.27499E 00	0.71067E 00	0.82076E 00
6	0.66567E 02	0.17429E 02	0.89267E 00	0.65742E 00
7	0.90748E 02	0.11047E 04	0.96066E 00	0.51315E 00
8	0.11493E 03	0.70017E 05	0.98387E 00	0.40867E 00
9	0.13910E 03	0.44378E 07	0.99046E 00	0.37851E 00
10	0.16329E 03	0.28127E 09	0.99072E 00	0.33829E 00
11	0.18747E 03	0.17828E 11	0.98854E 00	0.55991E 00
12	0.21165E 03	0.11299E 13	0.98552E 00	0.71237E 00
13	0.23583E 03	0.71618E 14	0.98229E 00	0.87977E 00
14	0.26000E 03	0.45392E 16	0.97915E 00	0.10550E 01
Boy – Bohme method				
1	0.17195E 03	0.35296E 08	0.92913E 00	0.13384E 01
2	0.92507E 02	0.29848E 03	0.94364E 00	0.63466E 00
3	0.98255E 02	0.57005E 03	0.95326E 00	0.60921E 00
4	0.28780E 02	0.28190E−01	0.94951E 00	0.48602E 00
5	0.49696E 02	0.10344E 01	0.96276E 00	0.27298E 00
6	0.18646E 03	0.24070E 09	0.94134E 00	0.13076E 01
7	0.19304E 03	0.17680E 09	0.94794E 00	0.12685E 01
8	0.98255E 02	0.11400E 04	0.95326E 00	0.60922E 00
9	0.17615E 03	0.18970E 10	0.99474E 00	0.35471E 00
10	0.14087E 03	0.18259E 07	0.99056E 00	0.38139E 00
11	0.19365E 03	0.19321E 09	0.94759E 00	0.12772E 01
12	0.11244E 03	0.22461E 05	0.97178E 00	0.53391E 00

TABLE 4 (continued)

Mechanism number	E	A	R	SE
Coats – Redfern method				
1	0.17195E 03	0.38315E 08	0.92913E 00	0.13384E 01
2	0.92507E 02	0.34970E 03	0.94364E 00	0.63466E 00
3	0.98255E 02	0.66123E 03	0.95326E 00	0.60921E 00
4	0.28680E 02	0.53266E−01	0.94951E 00	0.48602E 00
5	0.49696E 03	0.14222E 01	0.96276E 00	0.27298E 00
6	0.18646E 03	0.25956E 09	0.94134E 00	0.13076E 01
7	0.19304E 03	0.19014E 09	0.94794E 00	0.12685E 01
8	0.98255E 02	0.13223E 04	0.95326E 00	0.60922E 00
9	0.17615E 03	0.20551E 10	0.99474E 00	0.35471E 00
10	0.14087E 03	0.20202E 07	0.99056E 00	0.38139E 00
11	0.19365E 03	0.20775E 09	0.94759E 00	0.12772E 01
12	0.11244E 03	0.25539E 05	0.97178E 00	0.53391E 00

[a] Bacanga 2 clay (amorphous free).

ANALYSIS OF KAOLINITE DEPOSITS

The dehydroxylation reaction of kaolinites from a variety of locations was studied using Stanton Redcroft mass flow (with O.S. 12 temperature measuring device) and Stanton Redcroft TG 750 thermo balances at a constant heating rate of 5°C min^{-1}. The reaction mechanism and activation energy values were determined by the method of Boy and Bohme [18]: entropy change values for the reaction were determined from the pre-exponential factor using the equation presented by Zsako [23].

Redfern [24] defines activation energy in the solid state as the average excess energy a molecule must possess to react. Keatch and Dollimore [25] state that this energy can be obtained from the vibration of an atom or molecule in the lattice which could, at a certain temperature, provide sufficient energy at a particular point for the reaction to start with some sites being energetically favoured, e.g. dislocations, lattice defects, etc. Thus for the kaolinite dehydroxylation, a high value of activation energy will indicate that a well-ordered structure is decomposing, whereas, a low value will indicate the presence of lattice defects, etc., i.e. a poorly ordered structure and therefore a lower degree of crystallinity.

Results of the computer analysis for kaolinites from the different locations indicate that the reaction proceeds by a second-order mechanism, in agreement with Boy and Bohme [18]. Table 4 shows an example of the computer output for a kaolinite from a laterized profile (Brazil) using the Boy and Bohme method: this gives the reaction mechanism number 9, i.e. second-

TABLE 5

Kinetic parameters of the dehydroxylation reaction and crystallinity indices of the kaolinites studied

Sample	Activation energy (kJ mole)$^{-1}$	Entropy change (kJ mole)$^{-1}$	Crystallinity indices		
			X-Ray [26]	Infrared	
				Neal and Worall [27]	Parker [28]
China clay 1 (Cornwall)	198.7	19.9	0.24	0.89	2.67
China clay 2 (Cornwall)	214.6	11.9	0.22	0.83	2.59
API 4	189.8	22.6	0.22	0.76	2.11
API 7	175.7	45.1	0.31	0.68	1.91
PUGU K (Kenya)	178.6	33.4	0.24	0.59	2.03
Kaolinite from a laterized profile (Brazil)	176.1	115.9	0.33	0.62	2.29

order, and an activation energy of 176.1 kJ mole^{-1}.

Values for the kinetic parameters of the dehydroxylation reaction for the various kaolinites are presented in Table 5, which also includes the values of "crystallinity indices" determined from X-ray-diffraction according to the method of Kunnel et al. [26] and from infrared spectroscopy by the methods of Neal and Worral [27] and Parker [28]. The values in Table 5 show that there is a relation between the crystallinity indices and the kinetic parameters, i.e. a well-crystallized kaolinite like China Clay-2 has a high activation energy and correspondingly low entropy change. The X-ray index [26] is small since the method measures broadening of the 001 reflection, while the infrared index of Neal and Worral [27] approaches the value of 1 and the index of Parker [28] gives a relatively high value which is an indication of a well-ordered structure.

In the light of these results, it is suggested that the kinetic parameters derived from non-isothermal thermogravimetry for the dehydroxylation reaction can be used to assess the degree of crystallinity of kaolinites.

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