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Controlled Rate Thermal Analysis of kaolinite dehydroxylation: effect of water vapour pressure on the mechanism

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Abstract

The present kinetic study is focused on one aspect of kaolinite dehydroxylation, namely the influence of water vapour pressure in the 10^{-3} to 5 hPa range and in the presence of crystalline defects. The experimental problem of keeping, throughout the dehydroxylation, the pressure gradients negligible around and within the sample is solved by means of Controlled Rate Evolved Gas Detection (CR-EGD). The dehydroxylation rate selected is as low as 0.014 h^{-1} (which corresponds to a duration of 70 h for the whole experiment). Moreover, more than 20 independent measurements of the apparent Arrhenius energy of activation are carried out all along the dehydroxylation, with help of the rate–jump method, and therefore, without any assumption about the rate law of the determining step. In these conditions, the apparent Arrhenius energy of activation measured during the dehydroxylation of a poorly crystallised kaolinite is shown to be constant in the range $0.02 < \alpha < 0.84$ (under 10^{-3} hPa) and in the range $0.18 < \alpha < 0.80$ (under 5 hPa), indicating that the rate law obeys the Arrhenius law in this range of extent of reaction. The corresponding activation energies obtained are (233 ± 15) kJ/mol under 10^{-3} hPa and only (188 ± 10) kJ/mol under 5 hPa. Although this decrease is in contradiction with previously published results, it can be interpreted by considering that, under 10^{-3} hPa, diffusion is the limiting step whereas, under 5 hPa, the part of water desorption probably becomes predominant.

Keywords: Dehydroxylation; Kinetic model; Kaolinite; CRTA; Arrhenius energy of activation

1. Introduction

The thermal transformation of kaolinite ($Si_4Al_4O_{10}(OH)_8$) to metakaolinite ($Si_4Al_4O_{14}$) and then mullite is commonly used in the fabrication of ceramic porcelain. The industrial importance of this process explains the numerous studies concerning this material. Early studies found, by means of conventional thermoanalytical techniques (DTA, TG with linear heating), that the dehydroxylation of kaolinite was highly dependent on experimental factors (specially sample mass and heating rate) which made it difficult to compare results from different authors [1–4]. This is not surprising if we bear in mind Criado et al. conclusions that it is only when the sample mass is less than 3 mg and the heating rate is lower than 0.5 K/min that such a kinetic study can be considered meaningful [5].

Another important experimental factor has been shown to be the pressure. The studies carried out

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under atmospheric pressure [6–9] conclude indeed to a reaction rate of first-order (F1) with respect to the degree of reaction, α. However, most studies carried out "under vacuum" conclude to a diffusion limiting rate for the dehydroxylation. Owing to the sheet-like nature of clays, one would expect this diffusion to be two-dimensional (D2) as proposed by Achar et al. [4]. Nevertheless, most authors found a three-dimensional process (D3) [10–13].

The earlier distinction between experiments carried out under atmospheric pressure and other carried out " under vacuum" is actually crude. As well pointed out by Flanagan et al. [14], the actual residual pressure over the sample, in spite of permanent evacuation, is highly sample mass and temperature-dependent: in the case of the dehydration of dehydrated nickel oxalate carried out at 110 °C, they observe a mass-dependency of the actual vacuum down to a mass as low as 3 mg.

In any case, if the water vapour pressure plays a major role on kaolinite dehydroxylation, it makes sense to try to carefully control it during the whole experiment and not only above, but also within the sample. This can be achieved by using Controlled Rate Thermal Analysis (CRTA) [15] of which we give some details in the Section 2. Hence, the interest of CRTA for the kinetic study of kaolinite dehydroxylation [16–18].

A first CRTA study was carried out by Akhouayri [16], with a poorly crystallised kaolinite, under a single residual pressure as low as 2×10^{-5} hPa. It is worth pointing out that to really get and keep such a low pressure above the sample in spite of its dehydroxylation, two diffusion pumps were used which are each connected to the sample chamber through 50 mm bore tubings. A three-dimensional diffusion (D3) limiting process was found to occur when the degree of reaction was in the range 0.15–0.65. An important conclusion was also that the kinetic results obtained by CRTA, in these conditions, were independent of the sample mass in the range 5–500 mg. Moreover, an increase in grain size (in the range 1–5 μm) resulted in a decrease in apparent activation energy. This approach was extended to a broader temperature range (−30 to 1000 °C) by Ortega et al. [17]. From the shape of the CRTA curve, they distinguished three temperature domains corresponding to the water desorption of kaolinite, the dehydroxylation of the superficial hydroxyl groups and the disorganisation of kaolinite, respectively.

The second CRTA study on kaolinite dehydroxylation, carried out by Dion et al. [18], showed that under a residual pressure of 3×10^{-2} hPa, both D3 and F1 processes may compete for a well crystallised kaolinite with 8 μm grain size. They highlighted the role of defects of kaolinite on its dehydroxylation kinetics: under a residual pressure of 3×10^{-2} hPa and for identical conditions of rate of reaction, a F1 process was found to predominate for well-crystallised samples with few defects, whereas a diffusion controlled (D3) process was found to be favoured in poorly crystallised kaolinite with numerous defects. Furthermore, transmission electronic microscopy [19] of partially dehydroxylated samples seemed to show that the reaction principally starts at the defect sites. However, for well-crystallised samples, dehydroxylation was also seen to start from the sheet edges. Under low water vapour pressure, the presence of defects would, thus, seem to increase the importance of a diffusion controlled process.

The aim of the present work is to fill a few gaps in the earlier studies "under vacuum", specially to operate in a larger range of low pressures (10^{-3} to 5 hPa) in order to specify and, if possible, understand the influence of water vapour pressure on the rate of kaolinite dehydroxylation. As pointed out by Galwey in his comprehensive survey of the thermal dehydration of crystalline solids [20], only measurements with a very careful control of the experimental conditions (and specially, of course, of the water pressure) can be expected to bring a new and concrete knowledge in this field. This is what we have aimed to achieve with the help of CRTA. Moreover, we also tried to detect any change of kinetic model during each isobaric experiment: as will be seen, this is achieved by use of the "rate–jump" method [21] for the determination of apparent Arrhenius activation energies all along the process of kaolinite dehydroxylation.

2. Experimental and methodology

2.1. Sample

The kaolinite under investigation was commercially obtained from Sigma (lot 80H0525) from a deposit in Georgia (USA). The particle size distribution was found between 1 and 6 μm with a peak around 4 μm.

The BET specific surface area of this kaolinite was determined from the nitrogen adsorption isotherm at 77 K, in the relative pressure range from 0.05 to 0.35, with the conventional cross-sectional molecular area of 0.162 nm^2. The resulting specific surface area was 19.5 m^2/g.

A quantitative analysis of defects was determined by the Hinckley index (HI) of crystallinity [22] calculated by means of the following equation:

$$\mathrm{HI} = \frac{h_1 + h_2}{h(1\,\bar{1}\,0)}$$

where h_1 and h_2 are the relative intensities of the $(1\,\bar{1}\,0)$ and $(1\,1\,\bar{1})$ reflections with respect to the local background noise of the (02.11) band, where $h(1\,\bar{1}\,0)$ is the real intensity of the $(1\,\bar{1}\,0)$ reflection. The resulting HI for the studied kaolinite is 0.54.

The average thickness of the crystalline coherent domain (along $\vec{c}$ axis) of the studied kaolinite was also determined by means of the following equation:

$$\Delta(2\theta) = \frac{k\lambda}{h_c \cos\theta}$$

where θ is the diffraction angle of the 0 0 2 reflection ($\cos\theta = 0.97653$), λ the wave length of the used X-ray (1.54056 Å), h_c the coherent domain expressed in Å, k the constant related to the diffractometer (=0.90), and $\Delta(2\theta)$ is the width of the 0 0 2 reflection measured at mid-height and expressed in degree.

The coherent domain for the kaolinite studied was found equal to 215 Å. As the X-ray diffraction pattern of the studied kaolinite shows a sheet width equal to 7.13 Å, the coherent domain contains about 30 sheets.

2.2. Controlled Rate Thermal Analysis (CRTA)

CRTA is part of the broader method of Sample Controlled Thermal Analysis (SCTA), where a feedback from the sample is used to control its heating. In CRTA, this feed-back continuously controls the heating in such a way that the reaction rate follows a predetermined program. The simplest program (and also the easiest to use for a kinetic study) is one where the rate of reaction is kept constant; this is what will be done here. A major interest of this choice is to be able to set this rate at such a low value to ensure that the pressure and temperature gradients within the sample can be considered to be negligible (this statement follows from the conclusions of [16], which we reported in Section 1). Now, there is a special experimental set-up that allows to control, not only the reaction rate, but also the residual pressure above the sample, which is what we need for the present study.

In this technique, which can be precisely called "CR-EGD", the permanent control of the two parameters (reaction rate and residual pressure) is obtained by means of a single control loop. This is achieved by an experimental design where the residual pressure above the sample is also directly related to the rate of reaction: this residual pressure is also, indeed, the pressure upstream a diaphragm through which the system is permanently evacuated. A constant pressure drop through the diaphragm means a constant gas flow which all originates from the sample, which is therefore, dehydroxylating at constant rate. The constant pressure drop is obtained, following the CRTA principle, by feeding the sample heating controller with the pressure signal. The heating, therefore, takes place in such a way that the pressure above the sample (and upstream the evacuation diaphragm) remains constant. A detailed description of the set-up can be found in [23].

Since the earlier experiment is carried out in "isokinetic" conditions, we can state:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \text{constant} = C$$

with

$$\alpha = \frac{\Delta m}{\Delta m_\infty}$$

where Δm is the sample mass loss at time "t" and Δm_∞ the final mass loss at time "t_F"; the rate of reaction, C, is simply measured by the time needed for the reaction to be completed. Because of the constant rate of evacuation, the above mass losses are directly proportional to the time elapsed, hence, a simple expression of the degree of reaction (or of advancement) α:

$$\alpha = \frac{t - t_I}{t_F - t_I}$$

where t_I is the time of the starting time of the CRTA experiment.

The recording of the sample temperature versus time is then comparable to a TG recording delivering the mass loss versus temperature.

In heterogeneous kinetics, the change of the degree of advancement (or reaction) versus time is usually described with help of mathematical functions $f(\alpha)$ like those listed by Sharp et al. [24] for a number of limiting cases.

For such limiting cases, where a single process imposes its rate to the reaction, one can write:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)$$

One usually assumes the rate coefficient "k" to vary with temperature according to the Arrhenius law. In our experimental conditions, where the rate of reaction and residual pressure are both kept constant, the rate law can be written:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left[-\frac{E_A}{RT}\right]$$

or still:

$$\ln[f(\alpha)] = \ln\left(\frac{C}{A}\right) + \frac{E_A}{R}\frac{1}{T}$$

The latter equation, which gives $\ln[f(\alpha)]$ versus $1/T$ is therefore, suited for describing the degree of reaction versus temperature provided the experiment is carried out isokinetically and provided the reaction studied is characterised by one function $f(\alpha)$, one Arrhenius activation energy E_A and one pre-exponential factor "A".

Process "F1" corresponds to the case when the transformation rate of each single particle, is limited by a random nucleation (or germination), itself followed by a very rapid growth of the nuclei (or germs).

Processes D2–D4 correspond to the case when the transformation rate is limited by diffusion through the layer of solid product.

Criado et al. [25] made use of the following equation:

$$T = \frac{E_A}{R\{\ln f(\alpha) - \ln(C/A)\}}$$

for theoretical isokinetic reactions occurring with a single process. They then showed that the resulting curves had most characteristic shapes, depending on the limiting phenomenon.

A set of experiments was carried out under 10^{-3} and 5 hPa of water vapour pressure. For these experiments, a 40 mg sample was heated from 25 to 1000 °C at a constant reaction rate of $0.014\ \mathrm{h}^{-1}$ (which corresponds to a completion of the dehydroxylation in around 70 h).

2.3. Rate–jump method

Our aim is to directly measure the variation of the rate of reaction with temperature without any assumption about the rate law. For that purpose, we applied the "rate–jump" method. This required, in the CR-EGD set-up described earlier [26], the periodical use of a second diaphragm (assessed by means of an automated vacuum valve) allowing to operate at two alternate pumping rates (in the ratio of 1:3).

A 200 mg sample was decomposed during 2 h, under a constant residual pressure of water vapour (10^{-3} or 5 hPa) and at a constant reaction rate C_1. At the end of this step, for a degree of reaction α, the sample temperature is T_1. Then, thanks to the opening of the second diaphragm, the reaction rate is suddenly raised to value C_2 (three times higher than C_1) which is maintained, again, over 2 h. To reach this second rate of reaction, the sample is automatically brought (by means of the CRTA control loop) to value T_2. It seems correct to consider that, in such an experiment, the increase in the reaction rate from C_1 to C_2 is only due to the temperature increase from T_1 to T_2, since the sample mass, degree of reaction, residual pressure and limiting process are all kept unchanged.

In spite of this simplification which directly results from the experimental conditions, a few assumptions are to be made to carry out the data processing. Here, they are:

1. The rate of dehydroxylation of kaolinite is assumed to be expressed by the product of the $f(\alpha)$ function by a term only depending on temperature and pressure, which we shall call the "apparent rate coefficient", $k_{app}(T, p)$.
2. The dependence of $k_{app}(T, p)$ on temperature is assumed to follow the Arrhenius law:
$$k_{app}(T,p) = A_{app}(p)\exp\left[-\frac{E_{app}}{RT}\right].$$
3. The apparent pre-exponential factor $A_{app}(p)$ and the apparent Arrhenius energy of activation E_{app} are assumed not to depend on temperature.

Under these conditions, one can write:

$$\frac{d[\ln(k_{app})]}{dT} = \frac{E_{app}}{RT^2}$$

Now, in our experimental conditions, where the change in reaction rate C is only due to the temperature change, we can write:

$$\frac{C_2(T_2)}{C_1(T_1)} = \frac{k_{app,2}(T_2)}{k_{app,1}(T_1)}$$

Hence, the following evaluation of the apparent Arrhenius activation energy:

$$E_{app} = \frac{RT_1T_2}{T_2 - T_1} \ln\left[\frac{C_2}{C_1}\right]$$

In our experiments, the water vapour flows produced by the sample at the two rates are 0.14 and 0.42 mg/h, respectively (i.e. $C_2/C_1 = 3$, as said earlier).

3. Results

The CRTA curves obtained for the dehydroxylation of our kaolinite sample are shown in Fig. 1. These experiments were triplicated, but did not show any visible difference from one trace to the other. These isokinetic experiments (carried out under water vapour pressures of 10^{-3} and 5 hPa) are reported here in the form of the degree of reaction, α, as a function of temperature. Here, we have considered that, under 10^{-3} hPa, $\alpha = 0$ at 250 °C (523 K) which is the temperature at which the constant pressure regime, required for CRTA, is reached. At around 800 °C (1073 K), a rapid drop in the pressure signal is observed. The percentage of mass loss at this point is found to be $100\,\Delta m/m_0 = 13.93\%$; the theoretical percentage of mass loss corresponding to the complete dehydroxylation is 13.98%. Therefore, this point corresponds to the end of the dehydroxylation regime and α is taken equal to 1. Under 5 hPa, the CRTA regime starts at 260 °C (533 K) and ends at 820 °C (1093 K). At this temperature, the BET surface area has decreased and the kaolinite structure is completely lost, as previously observed via XRD and MAS NMR [19].

As an example, the curve obtained using the rate–jump method under 5 hPa is shown in Fig. 2. Each temperature jump or drop is the response to a sharp

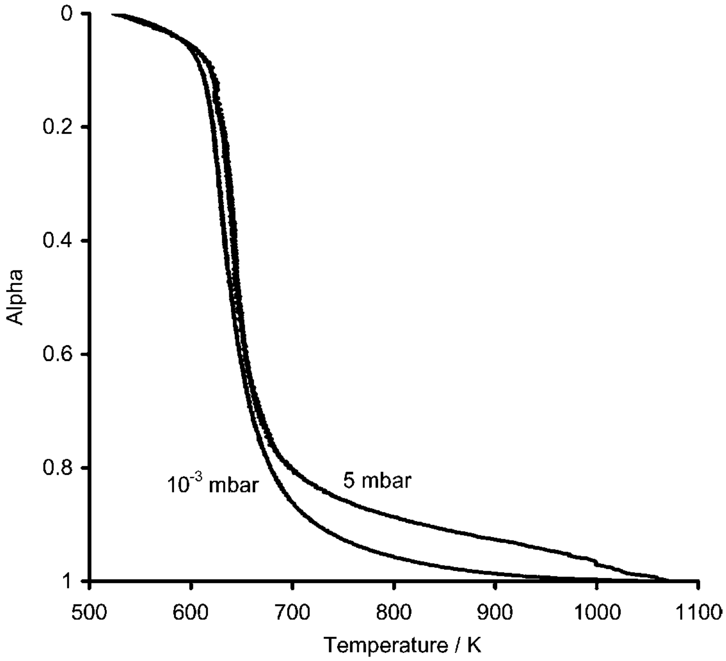

Fig. 1. CRTA curves obtained for kaolinite dehydroxylation under two water vapour pressures of 10^{-3} and 5 hPa for the same rate of reaction ($0.014\ h^{-1}$).

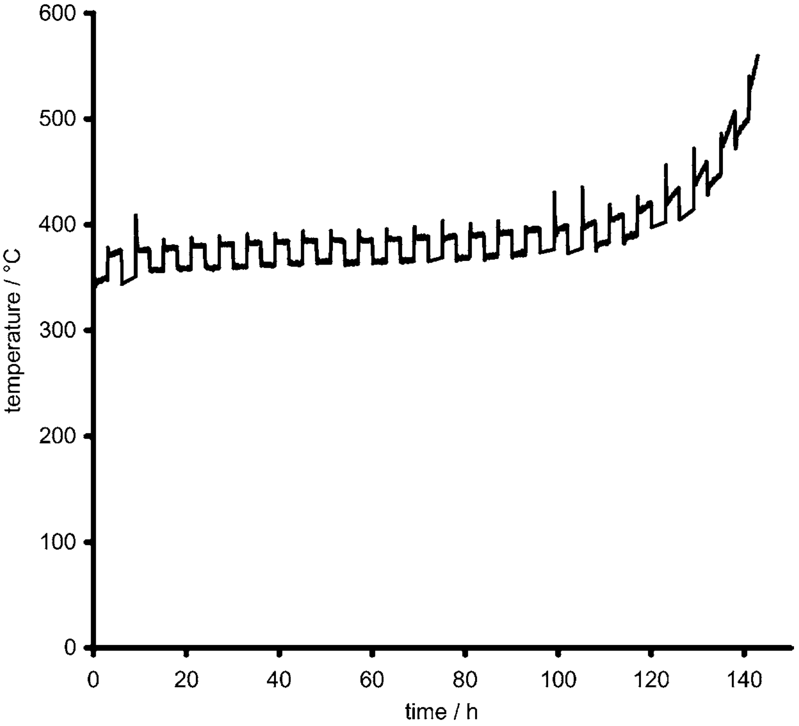

Fig. 2. Experimental curve obtained during the rate–jump method for kaolinite dehydroxylation carried out under water vapour pressure of 5 hPa. The abrupt changes in the temperature curve correspond to the variation in the rate (0.14 and 0.42 mg/h).

change in rate (between 0.14 and 0.42 mg/h) and it allows to derive an apparent activation energy by considering two temperatures T_1 and T_2 corresponding to the same degree of reaction.

We have listed in Tables 1 and 2, the apparent Arrhenius activation energies measured all along the experiments carried out at 10^{-3} and 5 hPa, respectively.

During each experiment, the apparent activation energies obtained can be considered as constant over a relative large domain: in the range $0.02 < \alpha < 0.84$ for the experiment under 10^{-3} hPa and in the range $0.18 < \alpha < 0.80$ for the experiment under 5 hPa.

The mean values, in these ranges, are then 233 ± 15 kJ/mol under 10^{-3} hPa; 188 ± 10 kJ/mol under 5 hPa.

3.1. Data processing

The procedure which will be followed here is one with progressive refinement, up to the point where the rate law (and the corresponding process) is clearly discriminated.

The rate–jump experiments show that the apparent Arrhenius activation energies are constant only for temperatures up to 422 °C (under 10^{-3} hPa) and 434 °C (under 5 hPa), i.e. for a up to 0.84 and 0.80. It is, thus, possible to consider that a process characterised by the measured activation energy ends at these points. For this apparently unique process, it is thus, possible to consider $\alpha' = 1$ at 422 and 434 °C, respectively. Under these conditions, it is possible to plot $f(\alpha')$ versus $1/T$ in the case of the nine functions listed by Sharp. These results are given in Tables 3 and 4 for the experiments carried out under 10^{-3} and 5 hPa, respectively.

It can be seen that under 10^{-3} hPa, only the diffusion processes (D2–D4) provide an acceptably good linear regression coefficient, whereas under 5 hPa, the acceptable processes are those labelled F1, R2 and R3. For each function, the Arrhenius activation energy and the exponential factor are calculated

Table 1
Apparent Arrhenius activation energies measured during the CRTA of kaolinite dehydroxylation carried out under 10^{-3} hPa

α	E_{app}/kJ mol^{-1}
0.022	232
0.055	243
0.058	234
0.063	230
0.077	222
0.085	225
0.086	222
0.099	223
0.105	223
0.123	232
0.135	230
0.142	230
0.195	231
0.225	239
0.269	227
0.338	232
0.404	240
0.470	229
0.548	237
0.666	235
0.731	245
0.795	247
0.841	248

from the slope and intercept of the obtained straight lines.

A further step to narrow our choice consists in comparing these computed Arrhenius activation energies with those experimentally assessed by the rate–jump method. This now allows to clearly highlight, because of the best fit of the activation energies (together with a good linear regression coefficient), the process D3 for the dehydroxylation under 10^{-3} hPa and the process F1 for the dehydroxylation under 5 hPa.

Table 2
Apparent Arrhenius activation energies measured during the CRTA of kaolinite dehydroxylation carried out under 5 hPa

α	E_{app}/kJ mol^{-1}
0.181	190
0.195	189
0.211	189
0.228	190
0.237	187
0.284	191
0.291	190
0.332	190
0.381	190
0.419	188
0.584	179
0.642	179
0.803	190

Table 3
Linear regression coefficients, *r* and Arrhenius parameters obtained for nine kinetic laws applied to the CRTA curve obtained under 10^{-3} hPa ($0.02 \leq \alpha \leq 0.84$, $C = 0.014\ \mathrm{h}^{-1}$)

Kinetic law	E_{app}/kJ mol^{-1}	A_{app} s^{-1}	r^2
A2	34.23	7.01×10^{-3}	0.1439
A3	4.62	1.9×10^{-5}	0.0027
F1	123.05	2.05×10^{5}	0.7560
R2	61.52	1.10	0.7560
R3	82.03	63.19	0.7560
D1	130.83	2.42×10^{5}	0.8554
D2	**177.57**	$\mathbf{1.25 \times 10^{9}}$	**0.9553**
D3	**240.82**	$\mathbf{7.22 \times 10^{13}}$	**0.9817**
D4	**199.80**	$\mathbf{2.24 \times 10^{10}}$	**0.9742**

As a check, a last step consists in plotting a computed curve *f*(α) versus *T*, where the temperature is calculated from the relationship:

$$T = \frac{E_{\mathrm{app}}}{R\{\ln f(\alpha') - \ln(C/A_{\mathrm{app}})\}}$$

where E_{app} is the experimentally measured activation energy and where the mean value of A_{app} is calculated at $\alpha' = 0.45$, by means of the selected *f*(α) function. The computed curves are compared with the experimental ones: we can see in Figs. 3 and 4 that the agreement is satisfactory.

Table 4
Linear regression coefficients, *r* and Arrhenius parameters obtained for nine kinetic laws applied to the CRTA curve obtained under 5 hPa ($0.18 \leq \alpha \leq 0.80$, $C = 0.014\ \mathrm{h}^{-1}$)

Kinetic law	E_{app}/kJ mol^{-1}	A_{app} s^{-1}	r^2
A2	86.93	93.2	0.5063
A3	53.48	1.5	0.1994
F1	**187.32**	$\mathbf{1.3 \times 10^{10}}$	**0.9554**
R2	**93.66**	$\mathbf{2.9 \times 10^{2}}$	**0.9554**
R3	**124.88**	$\mathbf{1.0 \times 10^{5}}$	**0.9554**
D1	132.33	1.5×10^{5}	0.4809
D2	200.91	3.4×10^{10}	0.6709
D3	297.80	6.4×10^{17}	0.8219
D4	235.34	4.9×10^{12}	0.7409

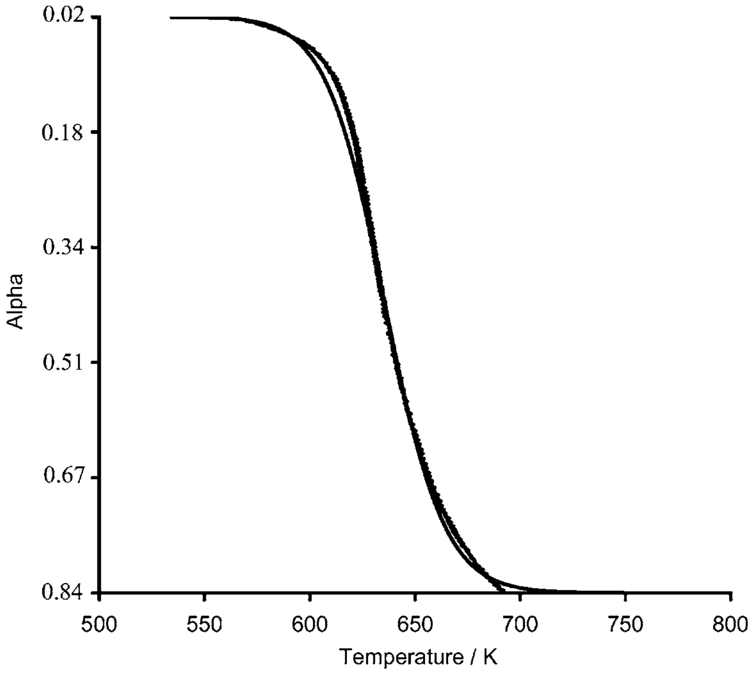

Fig. 3. Comparison of the experimental CRTA curve of kaolinite dehydroxylation obtained under a residual water vapour pressure of 10^{-3} hPa, with that constructed from the kinetic analysis, assuming a D3 limiting process.

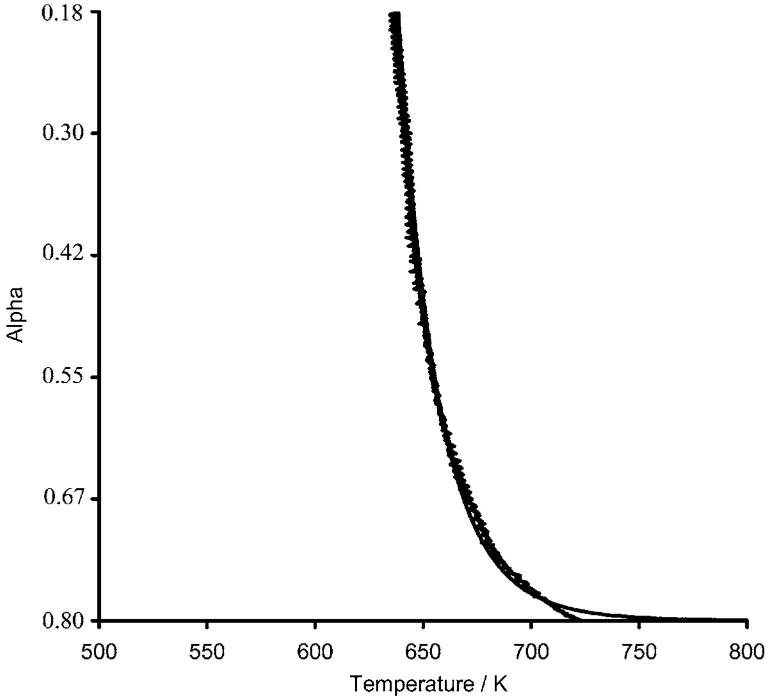

Fig. 4. Comparison of the experimental CRTA curve of kaolinite dehydroxylation obtained under water vapour pressure of 5 hPa, with that constructed from the kinetic analysis, assuming an F1 limiting process.

4. Discussion and conclusions

Our results obtained on kaolinite dehydroxylation can be summarised and explained as follows:

(1) In our CRTA experiments, the dehydroxylation carried out under 5 hPa takes place, in the whole range $0 < \alpha < 1$, at a higher temperature than the dehydroxylation carried out under 10^{-3} hPa, in spite of an identical rate of reaction (i.e. of an identical duration of the whole experiment carried out under a constant reaction rate). This means that, at identical temperature, the reaction rate is lowered by the increase in water vapour pressure.

(2) Under 10^{-3} hPa, the dehydroxylation of our poorly crystallised kaolinite seems to be limited by a three-dimensional diffusion process D3 (whereas for a well-crystallised kaolinite, an F1 process is partially observed [18]). Although the mathematical equation of D3 is questioned [27], our result is in agreement with most studies carried out under vacuum.

(3) Under 5 hPa, the dehydroxylation of our kaolinite now follows an F1 process (i.e. a random nucleation followed by instantaneous growth) which is the one observed by authors operating under an atmospheric pressure of air or under a non-controlled pressure of water vapour. In other words, it is in the small pressure range from 10^{-3} to 5 hPa that the change of process takes place.

(4) Unexpectedly, the apparent Arrhenius activation energy decreases as the water vapour pressure increases. This decrease is in contradiction with previously published results [28]. The physical meaning of activation energy may indeed be questioned for the thermolysis of a solid [29]. Nevertheless, a simple explanation can be found for our result if one takes into account the highly probable chemisorption of water on the surface of the metakaolinite. Since, it is only in the low pressure range that chemisorption is usually influenced by pressure, this would explain the change of process in such the narrow pressure range from 10^{-3} to 5 hPa. Under the lowest pressure, only a small fraction of the metakaolinite surface is covered with chemisorbed water and most water produced by kaolinite dehydroxylation is directly evacuated without passing through a chemisorbed state. Conversely, under the highest pressure, the whole metakaolinite surface is covered with chemisorbed water; water desorption becomes limiting and can then influence the observed rate of dehydroxylation. The resulting process is not anymore only diffusion-governed and the apparent Arrhenius energy of activation is at least partly dependent on the desorption energy of the chemisorbed water.

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