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Kinetic study of talc dehydroxylation by controlled rate thermal analysis

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ABSTRACT

Controlled Rate Thermal Analysis (CRTA) has been used under both low water vapour pressure (10^{-3} mbar) and low transformation rate ($5.33\times10^{-6}s^{-1}$) to investigate the dehydroxylation kinetic of talc sample from Luzenac. The decomposition is first controlled by diffusion process in three dimensions (D4) up to $\alpha = 0.70$ then for $0.7 < \alpha < 1$, it becomes governed by first order mechanism (F1). The apparent activation energy determined experimentally was found constant at 417 ±20 $kJ.mol^{-1}$.

KEYWORDS

Controlled rate thermal analysis;
Talc;
Kinetic.

INTRODUCTION

Talc, a hydrated magnesium silicate, is a natural product, which has found a wide-spread application such as rubber, paper, pharmaceutical, cosmetic, ceramic refractory and ceramic porcelain industries. Generally, it is associated with minor amounts of chlorites, dolomites, calcites, magnesites and quartz[1].

From the structure point of view, talc $Mg_3Si_4O_{10}(OH)_2$, is a tri-octahedral clay mineral with no layer charge. It consists of two tetrahedral silicate SiO_4 sheets separated by an octahedral $MgO_4(OH)_2$ sheet. Each tetrahedron shares three corners with the adjacent tetrahedrons. Therefore, three oxygen atoms of each tetrahedron belong simultaneously to two silicon atoms while the fourth oxygen atom belongs to one tetrahedral only. The ratio of the silicon to oxygen atoms is 2:5, thus corresponding to the formula $[Si_4O_{10}]^{4-}$. The charge of the anion layers is counter-balanced by the appropriate numbers of magnesium cations (Figure 1).

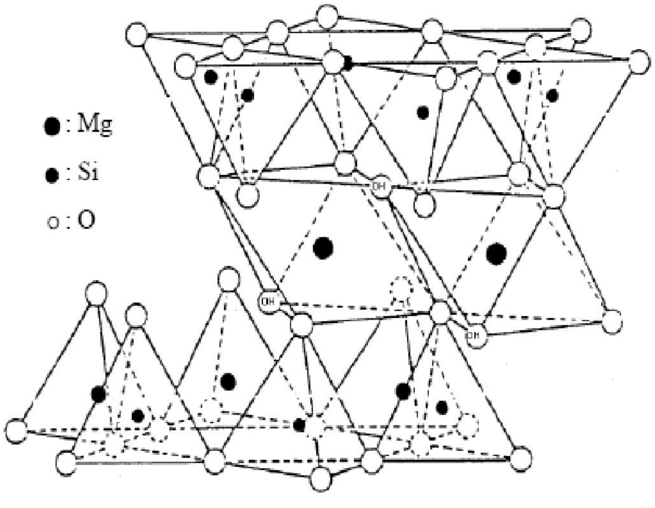

Figure 1 : talc structure

Talc crystallizes in the monoclinic system with space group C2/c or Cc. The values of the lattice constants in the direction of the crystallographic axes of the unit cell are a = 5,27Å; b = 9,12Å; c = 18,85Å; $\alpha = \gamma = 90°$ and $\beta = 100°$[2].

From thermal behaviour point of view the dehydroxylation of talc takes place near 1120K. The stoichiometric balance of its dehydroxylation can be written following the relation:

$$\underset{\text{Talc}}{Mg_3(Si_2O_5)_2(OH)_2} \rightarrow 3MgSiO_3(sd)+SiO_2(sd)+H_2O(g) \quad (1)$$

The three product of reaction are enstatite ($MgSiO_3$), amorphous silica (SiO_2) and water.

Numerous studies were carried out on the structure changes associated with heating talc to high temperature, using conventional thermoanalytical technique(DTA, TGA with linear heating and isotherm)[1-19] but few ones had interested on its kinetic dehydroxylation[6, 10, 14, 17, 19].

In order to deduce the mechanism of the talc dehydroxylation, Avgustinik and col.[6] examined the dehydroxylation of onotski talc (900 mesh) under isothermal conditions (673-1273K). Analysis of the results showed that dehydroxylation is best described by Jander's law D3 with activation energy of 176kJ. mol^{-1}.

Boskovic and col.[14] completed and confirmed the above study. It was found by TG analysis under isothermal conditions (673-1373K) and argon atmosphere that talc dehydroxylation is a diffusion controlled (D3 or D4). The activation energy associated is 209kJ. mol^{-1}.

Some authors[10, 17, 19] pointed out that the dehydroxylation of talc obeyed random nucleation kinetic model. Greenwood[10] has studied the kinetics of dehydroxylation of talc at water vapour pressure of 1kbar. He found that his experimental data can be adequately modelled by a first order rate law F1.

J.R.Ward[17] examined the dehydroxylation of talc in the temperature range of 1100-1160K by means of isothermal weight change determinations realised under Argon flow. He found that the reaction follows first order kinetics F1 with activation energy of 422kJ. mol^{-1}.

K. Bose and J. Ganguly[19] have studied the kinetic dehydroxylation of natural talc and synthetic one, at atmospheric pressure (1bar) as a function of grain size (1-15μm) and temperature (1050-1250K). He treated the experimental data in terms of second order reaction kinetics with activation energy of 372kJ. mol^{-1}; the rate of talc dehydroxylation increases while grain size decreases.

As we can see from these early studies realized by means of conventional thermoanalytical technique (TG with isothermal heating) dehydroxylation of talc was highly dependent on experimental factors (grain size, temperature dehydroxylation and nature of talc…) specially nature of atmosphere which made it difficult to compare results from different authors. An other important experimental factor that had not been takes in consideration in most previous studies is the water vapour pressure. As well pointed by Flanagan and al.[20], 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 3mg.

In any case, if the water vapour pressure had played a major role on kaolinite dehydroxylation[21] it makes sense to try to carefully control it during the whole experiment of talc dehydroxylation. This can be achieved by using Controlled rate thermal analysis (CRTA)[22].

The aim of the present work is to contribute to the study of the kinetic dehydroxylation of talc under low water vapour pressure (10^{-3}mbar). As pointed out by Galwey in his comprehensive survey of the thermal dehydration of crystalline solids[23], 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.

EXPERIMENTAL AND METHODS

Sample

The Talc sample used in this investigation was supplied by Talc de Luzenac (France). The physicochemical characterization and mineralogical composition of this sample were carried out by K. Belgacem et al.[24]. It contains 84% of talc and 16% of

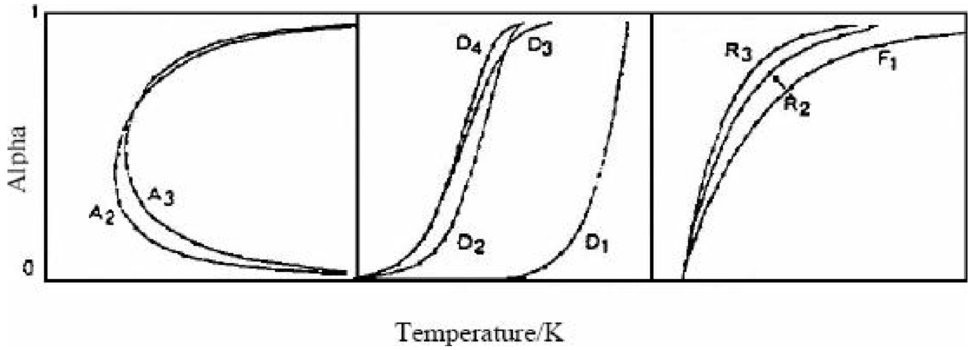

Figure 2 : theoretical α versus T kinetic curves as obtained with the assumption of a constant transformation rate

chlorite. The average of grain size is 10μm and its nitrogen surface area is 2,47m^2.g^{-1}.

Controlled transformation Rate thermal analysis (CRTA)

The Controlled Rate Thermal Analysis (CRTA) experiments were carried out on an apparatus built in house.

Dehydroxylation of sample was carried out using controlled rate thermal analysis technique which may be isobaric and isokinetic[22]. Under these conditions, variation of temperature as a function of time is obtained. The ability to reduce at will the rate of dehydroxylation allows one to sufficiently reduce the pressure and temperature gradients within the sample which are the principal source of experimental irreproducibility.

In heterogeneous kinetics, the change of the degree of advancement of reaction vs. time is usually described with help of mathematical functions f(α) like those listed by Sharp and al.[25] for a number of limiting cases.

For an elementary process, characterized by the function f(α), the rate law can be written:

$$\frac{d\alpha}{dt} = Af(\alpha)\exp\left[\frac{-E_A}{RT}\right] \qquad (2)$$

8/Where “α” is the degree of reaction, “A” is the pre-exponential factor, R is the gas constant, T is the temperature (K) and “Ea” is the Arrhenius activation energy for the elementary given process.

Since the above experiment is carried out in “isokinetic” conditions, we can state:

$$\frac{d\alpha}{dt} = \text{constant} = C$$

When using CRTA, a first idea of the kinetic law involved is easily obtained by comparing the experimental curves α vs T with the set of isokinetic theoretical curves built by Criado and al.[26] and which easily split into three groups, on the basis of their general shape (Figure 2).

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 R2 and R3 correspond to an interfacial reaction. Processes D2, D3 and D4 correspond to the case when the transformation rate is limited by diffusion through the layer of solid product and process A2 and A3 corresponds to nucleation and nuclei growth.

Activation energy (Ea)

The experimental activation energy Ea of a reaction can be obtained directly during a single rate jump experiment using a set-up described elsewhere[27]] where the reaction rate is changed between two values with periodical use of a second diaphragm (assessed by means of an automated vacuum valve) allowing to operate at two alternate pumping rates.

Thus for a single value of α during a reaction, without any presumption of the reaction mechanism and whilst keeping all other parameters identical (sample mass, residual pressure) an expression of the activation energy, at a given value of α, can be obtained:

$$Ea = \frac{R \times T_1 \times T_2}{T_2 - T_1} \ln\left[\frac{C_2}{C_1}\right] \qquad (3)$$

Where T1 and T2 are the temperatures corresponding to the rates C1 and C2.

In our study, the activation energy was measured using two CRTA curves obtained under the same residual water vapor pressure and at two different rates. Here again, temperatures can be evaluated for the same value of α and an activation energy deduced using the equation 3.

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 talc is assumed to be expressed by the product of the f(α) function by a term only depending on temperature and pressure, which we shall call the "apparent rate coefficient", ka(T,p).

2) The dependence of ka(T,p) on temperature is assumed to follow the Arrhenius law:

$$\mathbf{ka(T,p) = Aa(p)exp[-\frac{Ea}{RT}]} \qquad (4)$$

3) The apparent pre-exponential factor $A_a(p)$ and the apparent Arrhenius energy of activation E_a are assumed not to depend on temperature.

RESULTS AND DISCUSSION

Figure 3 reports the experimental CRTA curves obtained after thermolysis of 114mg of sample between 25°C and 1000°C under residual water vapour pressure 10^{-3} mbar. This thermogram exhibits two decomposition steps.

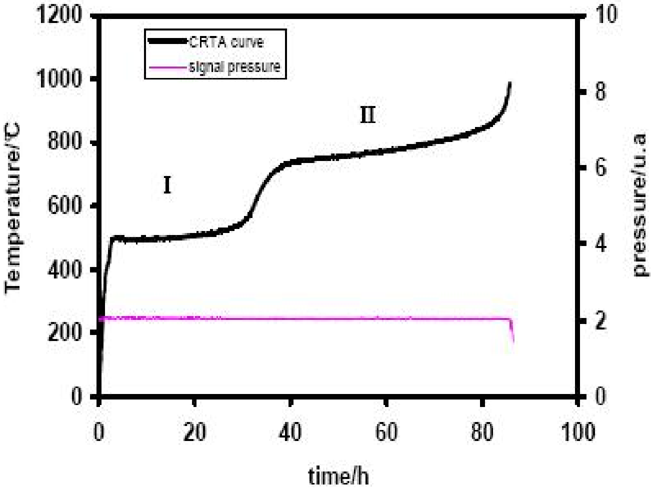

Figure 3 : experimental CRTA curve of talc sample obtained under water vapour pressure 10^{-3} mbar

The first decomposition step (I), having the minor length, was attributed to the removal of the hydroxyl group from brucite layer of chlorite and the second step (II) was attributed to the loss of water from talc structure and mica[24]. The total thermolysis occurs within 83h which corresponds to a constant rate of $3.35\times10^{-6}s^{-1}$.

Activation energy

The experimental activation energy calculated during the thermal decomposition of the studied sample was determined from two CRTA curves carried out at residual water vapour pressure of 10^{-3} mbar and constant rates equal to C1 $=3.35\times10^{-6}s^{-1}$ and C2 $= 1.38\times10^{-5}s^{-1}$ which correspond to a rate ratio of 4,11 (Figure 4).

In Figure 5 are reported the different values of the experimental Ea as a function of the degree of reaction α. The apparent activation energies measured can be considered as constant with main value equal to 417 ± 20 kJ. mol^{-1}.

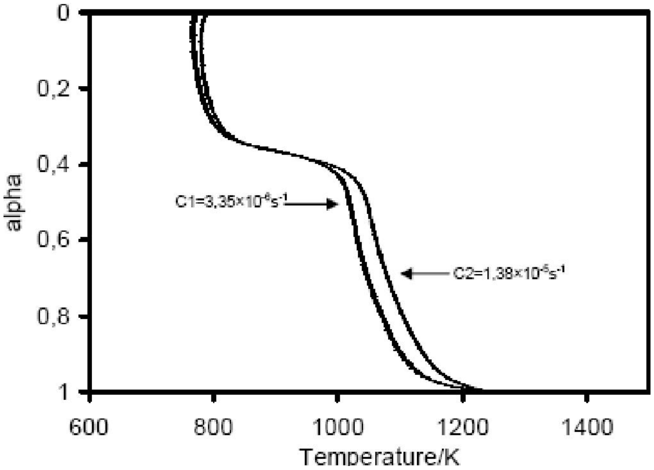

Figure 4 : Two CRTA curves obtained under two different rates (C1 and C2) and same water vapor pressure (10^{-3}mbar)

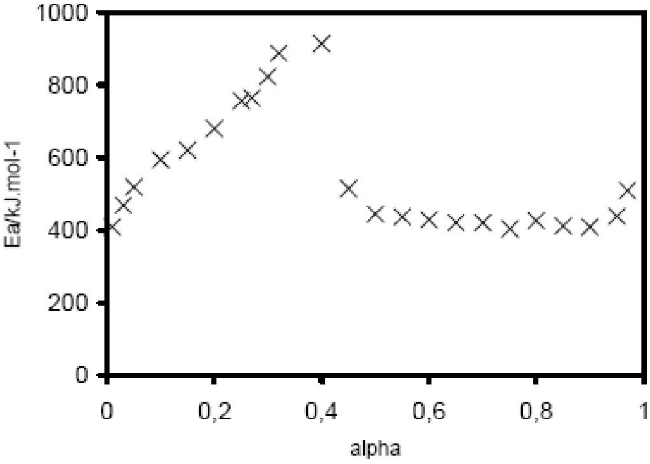

Figure 5 : Variation of the measured activation energy with the degree of reaction along the two steps

It is possible to observe two different domains of variation of the activation energy with degree of reaction clearly separated at α = 0.4, i.e. for T = 923K.

However, for T < 923K, Ea increases with degree of reaction until reaching the value 911kJ. mol^{-1} then increases again to a constant value mainly equal 417kJ. mol^{-1}. Thus we will consider that this temperature (T=923K) corresponds to the beginning of the talc dehydroxylation.

Kinetic analysis of the dehydroxylation process of talc

The isokinetic experiment in the form of the degree of reaction, α, as a function of temperature corresponding to the talc dehydroxylation process is reported in Figure 6.

The degree of reaction α, which varies linearly with time (isokinetic curve), was calculated such that the limits 0 and 1 correspond respectively to T = 923K and where the residual water vapor pressure started to drop (T = 1266K). Thus the dehydroxylation of talc occurs, under these conditions, in the temperature range between 923K and 1266K with a constant rate equal to $5.33\times10^{-6}s^{-1}$.

The sigmoid shape of the CRTA curve represented in Figure 6 resembles those of the theoretical of the isokinetic curves obtained for diffusion controlled mechanism. An anomaly can be noticed here is that the point of inflection of the CRTA curve corresponds to a degree of transformation $\alpha = 0.29$ which differs from the range where this inflection point is normally found between 0.47 and 0.60 for simple diffusion controlled processes[26].

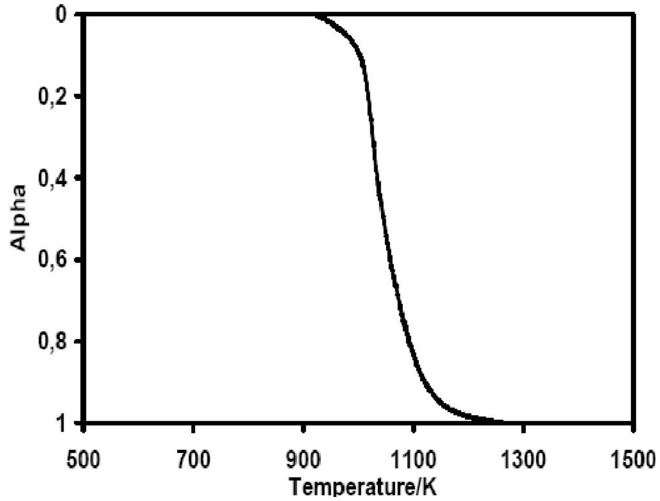

Figure 6 : α vs T experimental CRTA curve corresponding to talc dehydroxylation obtained under $P_{H2O} = 10^{-3}$mbar and C = $5.33\times10^{-6}s^{-1}$.

The kinetic analysis of the obtained CRTA curve was carried out assuming that the dehydroxylation occurs according to a single elementary process, characterised by a function f(α), by following ln[f(α)] as a function of 1/T. TABLE 1 lists the rate laws of these processes and gives the linear correlation coefficient r and the activation energy deduced.

TABLE 1 : Linear regression coefficients r and Arrhenius parameters obtained for kinetic laws applied to the CRTA curve of talc.

Kinetic law	Ea / kJ.mol^{-1}	Aa / s^{-1}	r
A2	90	0.4732	0.5693
A3	60	0.0103	0.3143
F1	183	26738	0.9225
R2	92	0.3775	0.9225
R3	122	15.624	0.9225
D1	125	4.3834	0.8003
D2	191	6626.55	0.9273
D4	225	87015.42	0.9642

It can be see that all elementary process cited in the literature (D2, D4 and F1) give a satisfying value of r.

Considering the value of r, it follows that D4 is the most probable elementary mechanism but the deduced activation energy (225kJ. mol^{-1}) is too low with respect to Ea measured experimentally (417kJ. mol^{-1}).

This observation indicates that the dehydroxylation process does not occur according to a single elementary process. It is thus possible to retain the hypothesis of a complex mechanism with the participation of a diffusion process, most probably in three dimensions D4, for which the value of Ea measured is 417kJ. mol^{-1}.

To check the complex mechanism, a more elaborate method using Origin 7.5 program was attempted. It consists in fitting the experimental CRTA curve by the theoretical curves corresponding to D4, D2, F1, R2 and R3 elementary processes. From the value of Ea obtained experimentally, the program iterates until a minimal difference between experimental and calculated curves is obtained.

As can be seen in Figure 7, the best fit was achieved with a combination of D4 and F1. From this result, the dehydroxylation of talc can be split into two parts. The first part of the transformation would seem to be dominated by a three dimensional diffusion mechanism (D4) up to $\alpha = 0.70$. The second part ($0.7 < \alpha < 1$)

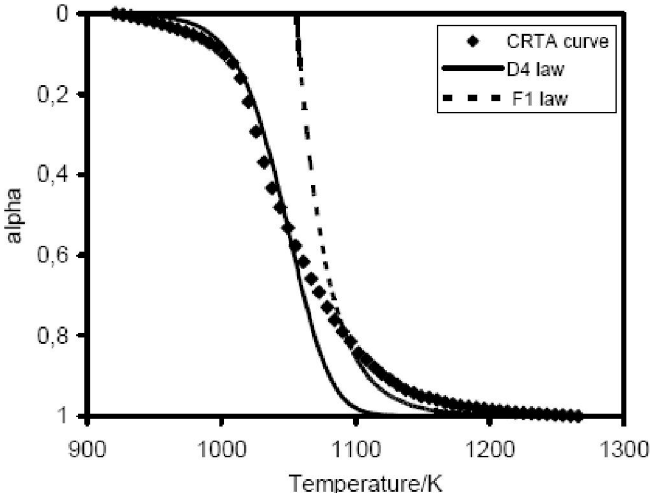

Figure 7 : Comparison of the experimental CRTA curve of talc dehydroxylation with that computed from the kinetic analysis assuming D4 and F1 processes.

would seem to be controlled by first order process F1.

Although the diffusion process which occurs in three dimensions seems opposed to the two-dimensional structure of talc this may be partially justified if one consider the diffusion between the crystallites and within crystallite defect.

CONCLUSION

The apparent activation energy measured experimentally by means of two CRTA curves at residual water vapour pressure 10^{-3}mbar was found constant at 417 ± 20 kJ. mol^{-1}. This is in agreement with that measured by J.R. Ward[17], under argon atmosphere and isothermal conditions (422kJ. mol^{-1}).

Both the results obtained experimentally and from the fitting suggest that the dehydroxylation occurs according to two elementary processes (diffusion and first order) which are found in majority of works[6, 10, 14, 17]. The diffusion was best described by three dimensional process (D4) up to $\alpha = 0.70$ and for $\alpha >$ 0.70 the thermal transformation of talc becomes controlled by a random nucleation (F1).

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