

THERMAL AND KINETIC PARAMETERS OF PHYLLOSILICATE DEHYDRATION

R. LOZANO *, J. ROMAN and F. DE JESUS

*Departamento de Química Inorgánica y Bioinorgánica, Facultad de Farmacia,
Universidad Complutense, 28040 Madrid (Spain)*

A.L. LAFUENTE and C.G. HUECAS

*Departamento de Edafología, Facultad de Farmacia, Universidad Complutense,
28040 Madrid (Spain)*

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ABSTRACT

This paper describes the application of differential scanning calorimetry (DSC), thermogravimetry and differential thermogravimetry to the analysis of the thermal dehydration of a natural phyllosilicate (Sierra del Segura, Spain).

The thermal and kinetic parameters of the thermal dehydration, under nitrogen atmosphere, have also been determined by differential scanning calorimetry (DSC). From the DSC curve, activation energies and pre-exponential Arrhenius factors for the endothermic processes of the loss of water, have been calculated using a new method, and the mechanism of these reactions has been determined.

The samples have been identified by IR spectroscopy and X-ray powder diffraction.

INTRODUCTION

The use of differential thermal analysis (DTA) in mineralogical studies is well established [1]. DTA is, however, largely non-quantitative, a limitation overcome by DSC which also produces improved thermal resolution.

Thermal methods are usually employed as a complementary technique to characterise the composition of mineralogical samples. The most common methods applied to the study of soil samples are X-ray diffraction and IR spectrophotometry and, occasionally, electron microscopy.

In this paper, we apply a non-isothermal method, previously reported in refs. 2–6, to determine the kinetics parameters of the dehydration of a natural clay by means of DSC.

The presence of CaC_2O_4 in the sample has been observed; this can be due to a previous treatment of the soil to obtain a sample free of carbonates.

* Author to whom correspondence should be addressed.

EXPERIMENTAL

Analysis of products

Soil samples were collected in Sierra del Segura (Spain) and were purified by controlled sedimentation for 8 h, using an NH_3 solution as dispersing agent.

The fraction smaller than 2 μm was then separated and treated with a 6% H_2O_2 solution and 0.5 N acetic acid solution, to remove organic material and carbonates present in the sample.

The IR spectra were measured on a Perkin-Elmer recording spectrophotometer model 283 using KBr pellets.

X-ray diffraction analysis was carried out on a Philips PW 1130 diffractometer fitted with a graphite monochromator, using $\text{Cu } K\alpha$ radiation. The samples were saturated with Mg^{2+} solvated with ethyleneglycol and heated at 550 °C for 3 h. All diffractograms were from oriented samples on glass slides.

Thermogravimetric analysis

Thermogravimetric analysis was performed on a Mettler TG-50 thermobalance. The constants were as follows: heating rate, 5 °C min^{-1} ; sample mass, 10 mg.

The analysis was made in a dynamic nitrogen atmosphere between 25 and 950 °C. An alumina pan was used.

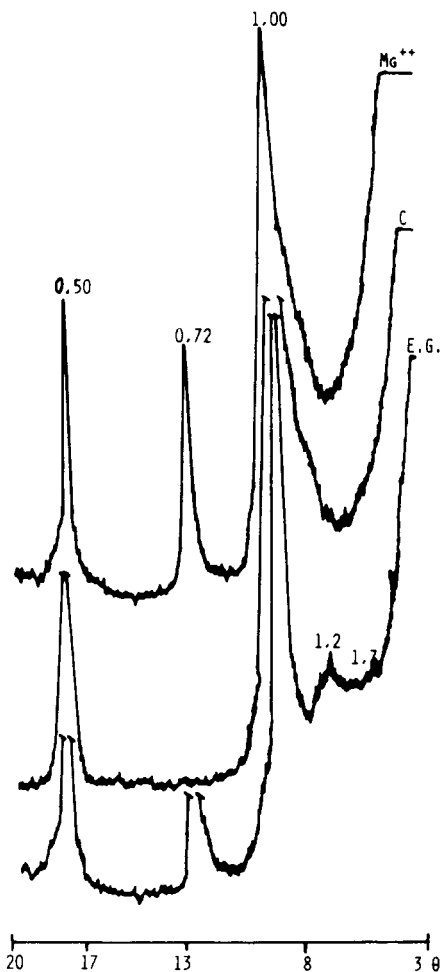
Differential scanning calorimetry

Differential scanning calorimetry was performed using a Mettler TA 3000 system with a Mettler DSC-20 differential scanning calorimeter.

The scanning rate used was 5 °C min^{-1} and samples of about 5 mg were employed so as to render the temperature non-uniformity within the sample insignificant. An aluminium pan was used under a dynamic nitrogen atmosphere. The instrument calibration was checked periodically with standard samples of indium (purity, 99.99%). Several runs were carried out.

RESULTS AND DISCUSSION

The IR spectra show a band at 3618 cm^{-1} which corresponds to the stretching tension of the OH groups in the smectite. Two wide bands at 3400 and 1635 cm^{-1} are due to the stretching tension of interlayer water and hygroscopic water, respectively, of smectite.



Mg²⁺: sample saturated with magnesium

C : sample calcinated at 550 °C

E.G.: sample solvated with ethyleneglycol

Fig. 1. X-ray diffractogram.

The presence of illite is indicated by a low intense band at 685 cm^{-1} , characteristic of these phyllosilicates [7,8].

In the X-ray spectra of the $\leq 2\ \mu\text{m}$ fraction (Fig. 1), the presence of illite, kaolinite, quartz and traces of smectite can be distinguished, the illite being the major phyllosilicate present in the sample, indicated by three sharp, intense, basal reflections at 1.0, 0.5 and 0.33 nm. Reflections at 0.73 and 0.357 nm correspond to kaolinite diffractions. The spacings at 1.2 and 1.7

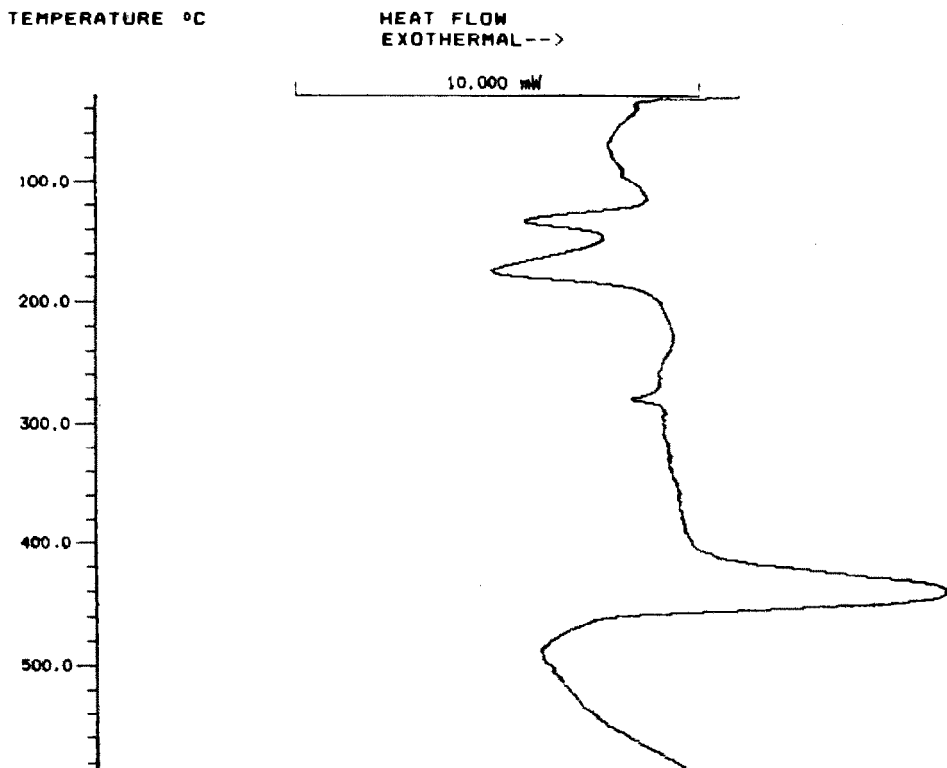


Fig. 2. DSC curve.

nm, swell more or less strongly when the sample is solvated with ethylene-glycol, which suggests the presence of traces of smectite.

The DSC curve shows two endothermic peaks at 138 and 280°C (Fig. 2), which we attribute to dehydration processes in the smectite, as revealed in the TG curve.

The first peak is due to the loss of water bonded to the basal oxygens, with a ΔH value of 25.16 J g^{-1} . The second less intense peak ($\Delta H = 3.06 \text{ J g}^{-1}$), corresponds to loss of the hydration water of the exchange cations.

We have applied our previously reported method [2-6] to the kinetic study of the two dehydration processes of smectite.

With the data obtained from the DSC curve and using the mechanisms most usually reported in the literature for the thermal decomposition of solids [9] (see Table 1), we have plotted $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1 - \alpha)]$ versus $[\Delta(1/T)]/[\Delta \ln(1 - \alpha)]$. From these representations, we can calculate the activation energy of the processes. Tables 2 and 3 show the results for r (correlation coefficient), m (slope), i (intercept value) and E_a (activation energy) obtained for the seven mechanisms studied and for both processes.

In all cases the correlation coefficients are close to unity, in agreement with the results of Criado et al. [10]. Nevertheless, the straight line passes

TABLE 1

Kinetic equations for the seven mechanisms

Mechanism (rate-controlling process)	$f(\alpha)$
D1 (one-dimensional diffusion)	$(1/2\alpha)$
D2 (two-dimensional diffusion)	$[-\ln(1-\alpha)]^{-1}$
D3 (three-dimensional diffusion: Jander equation)	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{-1/3}]^{-1}$
D4 (three-dimensional diffusion: Ginstling-Brounshtein equation)	$3/[2(1-\alpha)^{1/3}-1]$
F1 (random nucleation)	$(1-\alpha)$
R2 (phase-boundary reaction: cylindrical symmetry)	$2(1-\alpha)^{1/2}$
R3 (phase-boundary reaction: spherical symmetry)	$3(1-\alpha)^{2/3}$

TABLE 2

Results obtained for the plot of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1-\alpha)]$ vs. $[\Delta(1/T)]/[\Delta \ln(1-\alpha)]$ using the seven mechanisms, for the first dehydration process of smectite

Mechanism	r	m	i	E_a (kJ mol ⁻¹)
D1	-0.99881	-88140.38	2.38925	732
D2	-0.99908	-89049.39	2.01319	740
D3	-0.99905	-88944.73	1.49901	739
D4	-0.99905	-88944.67	1.83234	739
F1	-0.99999	-36704.90	0.00910	305
R2	-0.99999	-36704.91	0.50910	305
R3	-0.99999	-36704.93	0.34243	305

TABLE 3

Results obtained for the plot of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1-\alpha)]$ vs. $[\Delta(1/T)]/[\Delta \ln(1-\alpha)]$ using the seven mechanisms, for the second dehydration process of smectite

Mechanism	r	m	i	E_a (kJ mol ⁻¹)
D1	-0.99938	-257914.9	1.65987	2144 ± 8
D2	-0.99935	-260518.3	1.27189	2166 ± 8
D3	-0.99936	-260218.1	0.75906	2163 ± 8
D4	-0.99936	-260217.5	1.09238	2163 ± 8
F1	-0.99999	-115400.3	0.01000	959 ± 5
R2	-0.99999	-115400.3	0.51000	959 ± 5
R3	-0.99999	-115400.3	0.34333	959 ± 5

TABLE 4

Results obtained for the plot of $[\Delta \ln \alpha' - \Delta \ln f(\alpha)]/[\Delta \ln(1 - \alpha)]$ vs. $[\Delta(1/T)]/[\Delta \ln(1 - \alpha)]$ using the seven mechanisms, for the first dehydration process of illite

Mechanism	r	m	i	E_a (kJ mol ⁻¹)
D1	-0.99941	-33418.35	1.53064	277 ± 3
D2	-0.99949	-33777.40	1.14397	280 ± 3
D3	-0.99949	-33735.77	0.63094	280 ± 3
D4	-0.99949	-33735.67	0.96428	280 ± 4
F1	-0.99999	-14918.35	0.00912	124 ± 4
R2	-0.99999	-14918.35	0.50910	124 ± 2
R3	-0.99999	-14918.32	0.34243	124 ± 2

through the origin only when the analyses of the two dehydration processes are performed using an F1 (random nucleation) mechanism.

Therefore we conclude that the two dehydration processes of smectite are controlled by an F1 mechanism with activation energy values $E_a = 305.18$ kJ mol⁻¹ for the first process and $E_a = 959.49$ kJ mol⁻¹ for the second.

On the DSC curve, between 142 and 208°C, there is an endothermic process with a ΔH value of 80.08 J g⁻¹. This process can be attributed to the loss of hygroscopic water from illite.

Table 4 shows the results obtained from the DSC curve for the process. It can be seen that only the F1 mechanism (random nucleation) has an intercept value close to zero, with an E_a value of 124.04 kJ mol⁻¹.

Finally, several exothermic peaks appear on the DSC curve above 400°C, which, on the TG and DTG curves, correspond to the dehydroxylation of all the phyllosilicates present in the sample. Because of the overlapping of these peaks, it was impossible to carry out a kinetic study of them.

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