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Controlled rate thermal analysis of sepiolite

Ray L. Frost · János Kristóf · Erzsébet Horváth

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Abstract CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of a clay mineral such as sepiolite via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal changes in the sepiolite as the sepiolite is converted to an anhydride. In the dynamic experiment two dehydration steps are observed over the ∼20–170 and 170–350 °C temperature range. In the dynamic experiment three dehydroxylation steps are observed over the temperature ranges 201–337, 337–638 and 638–982 °C. The CRTA technology enables the separation of the thermal decomposition steps.

Keywords Attapulgite · Sepiolite · Palygorskites · Thermal analysis · CRTA · Thermogravimetry

R. L. Frost (✉)
Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, 2 George Street, G.P.O. Box 2434, Brisbane, QLD 4001, Australia
e-mail: r.frost@qut.edu.au

J. Kristóf
Department of Analytical Chemistry, University of Pannonia, P.O. Box 158, 8201 Veszprém, Hungary

E. Horváth
Department of Environmental Engineering and Chemical Technology, University of Pannonia, P.O. Box 158, 8201 Veszprém, Hungary

Introduction

The thermoanalytical studies of palygorskites are not new, even though the first reported studies were in 1947 [1–5]. A lack of recent studies is true of minerals such as palygorskite [6–9]. There is a need to undertake a systematic study using the latest technology of these minerals using thermo-analytical techniques including dynamic and controlled rate thermal analysis. Very few thermo-analytical and spectroscopic studies of the palygorskite have been forthcoming and what studies that are available are not new. To the best of the authors knowledge no recent thermo-analytical studies of sepiolites have been undertaken, especially in recent times, although differential thermal analysis of some related minerals has been published [10, 11]. The objective of this research is the study of the thermal decomposition of two selected sepiolites.

Sepiolites, attapulgites and various forms of 'Rocky mountain leather' all have a fibrous like morphology with a distinctive layered appearance [12–15]. Palygorskite has the structural formula $[(OH_2)_4(Mg,Al,Fe,)_5(OH)\cdot 2Si_8O_{20}]\cdot 4H_2O$ and sepiolite the formula $[(OH_2Mg_8(OH)\cdot 4Si_{12}O_{30}]\cdot 8H_2O$. The formulas are written as such to indicate the two types of water present, magnesium coordinated water and adsorbed water. The principal difference between the formula of sepiolite and palygorskite rests with the formula. Sepiolite $[Mg_8Si_{12}O_{30}\ (OH)_4\cdot(H_2O)_4\cdot 8H_2O]$ is a trioctahedral type mineral with three divalent magnesium cations filling the three positions of the octahedron. On the other hand palygorskite with the formula $[(OH_2)_4(Mg,Al,Fe,)_5(OH)\cdot 2Si_8O_{20}]\cdot 4H_2O$ has some of the magnesium cations replaced with trivalent cations such as Al or Fe, thus palygorskites tend towards a dioctahedral structure.

The dehydration and dehydroxylation of the palygorskite clays have been studied in detail by thermogravimetric techniques [4, 16, 17]. Differential Thermal Analysis (DTA) in combination with other techniques such as X-ray diffraction and Fourier Transform infrared spectroscopy (FTIR) proved most useful for the study of the dehydration process. It was found that dehydration of sepiolite and attapulgite take place in a series of four steps [18–20]. Up to 200 °C both hygroscopic and zeolitic water were lost. Between 250 and 450 °C bound water was lost; more strongly bound water was lost in the temperature range 450–610 °C; and coordinated water was lost in the temperature range 730–860 °C. All of the dehydration steps were endothermic in DTA. For both minerals, the partial dehydration of bound H_2O in the ranges 250–610 °C and 210–550 °C resulted in the formation of sepiolite anhydride and palygorskite anhydride, respectively. Dehydration of the bound H_2O in two steps was attributed to the difference in bonding position of H_2O in the structure of these minerals.

Thermal analysis using thermogravimetric techniques enables the mass loss steps, the temperature of the mass loss steps and the mechanism for the mass loss to be determined [21–27]. Thermoanalytical methods can provide a measure of the thermal stability of the clay minerals [21–46]. Controlled rate thermal analysis (CRTA) has proven extremely worthwhile in the study of the stability and thermal decomposition pathways of minerals and modified minerals such as mechanochemically activated kaolinite and intercalated kaolinites [26, 35, 47–52]. The application of CRTA technology to the study of the thermal stability of sepiolites has to the best of our knowledge never been reported. In this work we report the thermal analysis using both dynamic and controlled rate thermal analysis (CRTA technology) of sepiolite.

Experimental

Minerals

The clay minerals used in this research are (a) Clay Mineral Repository standard sepiolite from Nevada [SepNev-1] (b) sepiolite from Nairobi. Further details of these source clays can be found at the web site [http://cms.lnl.gov]. The chemical composition of the sepiolite from Nevada is in %: SiO_2: 54.0, Al_2O_3: 0.5, TiO_2: <.001, Fe_2O_3: 0.81, FeO: <0.1, MnO: 0.11, MgO: 23.3, CaO: 1.25, Na_2O: 2.1, K_2O: 0.15,P_2O_5: 0.02, LOI: 19.2. The chemical composition of the sepiolite from Nairobi in % is: SiO_2: 52.9, Al_2O_3: 2.56, TiO_2: <.001, Fe_2O_3:1.22, FeO: 0.3, MnO: 0.13, MgO: 23.6, CaO: <.01, Na_2O: <0.01, K_2O: 0.05,P_2O_5: 0.01, LOI: 20.8. The two sepiolites are reasonably close to the theoretical formula $Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$. The clays were analysed by X-ray diffraction for phase purity and dried in a desiccator to remove adsorbed water before being submitted for thermal analysis. The clay minerals were ground to a fine powder of <0.5 μm particle size for thermal analysis.

Thermal analysis

Dynamic experiment

Thermal decomposition of the sepiolite was carried out in a Derivatograph PC type thermoanalytical equipment (Hungarian Optical Works, Budapest, Hungary) capable of recording the thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves simultaneously. The sample was heated in a ceramic crucible in static air atmosphere at a rate of 5 °C min^{-1}.

Controlled rate thermal analysis experiment

Thermal decomposition of the sepiolites was carried out in a Derivatograph PC-type thermoanalytical instrument in a flowing air atmosphere (250 cm^3/min) at a pre-set, constant decomposition rate of 0.10 mg min^{-1} (below this threshold value the samples were heated under dynamic conditions at a uniform rate of 0.10 °C min^{-1}). The samples were heated in an open ceramic crucible at a rate of 0.10 °C min^{-1} up to 300 °C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage.

Results and discussion

Dynamic thermal analysis of sepiolite

The dynamic thermal analysis results for a sepiolite from Nevada and Nairobi are shown in Figs. 1 and 2. The figures

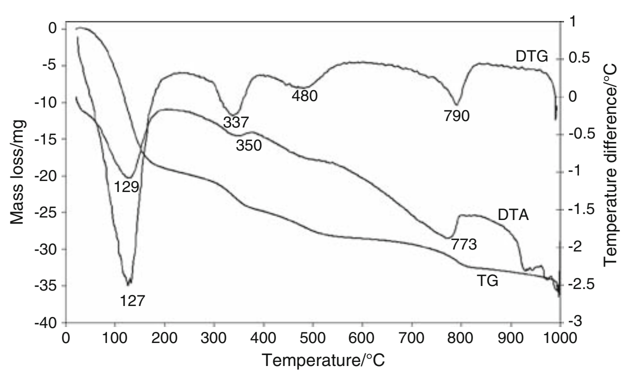

Fig. 1 The dynamic thermogravimetric and differential thermogravimetric analysis of sepiolite from Nevada—clay mineral reference standard SEPND-1

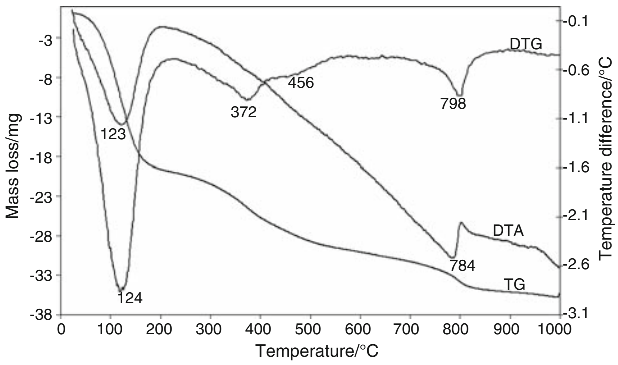

Fig. 2 The dynamic thermogravimetric and differential thermogravimetric analysis of sepiolite from Nairobi

report the DTG, DTA and TG curves. Four distinct mass losses are observed in the thermogravimetric and differential thermogravimetric curves in Fig. 1 at 127, 337, 480 and 790 °C with % mass losses of 12.4, 3.2, 2.5, 2.7 and 1.6%. In the DTA curve endotherms are observed at 129, 350, 480 and 773 °C. The results are similar for the thermal analysis of the sepiolite from Nairobi (Fig. 2). Peaks in the DTG curves occur at 124, 372, 456 and 798 °C. The % mass losses are 10.9, 3.5, 1.8, 2.9 and 0.4%. The endotherms for the DTA pattern for this sepiolite are not as distinct with endotherms observed at 123, 370, 460 and 798 °C.

Nagata et al. proposed a set of steps for the dehydration and dehydroxylation of a sepiolite [16, 53]. These steps correspond to (a) the loss of adsorbed water (b) the loss of hydration water (c) the loss of coordination water (d) the loss of water through dehydroxylation. Such a scheme is represented by the following chemical equations:

$$Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O \rightarrow Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4 + 8H_2O \text{ Step 1 at } {\sim}124\,^\circ C$$

$$Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4 \rightarrow Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_2 + 2H_2O \text{ Step 2 at } {\sim}337\,^\circ C$$

$$Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_2 \rightarrow Mg_8Si_{12}O_{30}(OH)_4 + 2H_2O \text{ Step 3 at } {\sim}480\,^\circ C$$

$$Mg_8Si_{12}O_{30}(OH)_4 \rightarrow 8MgSiO_3 + 4SiO_2 + 2H_2O \text{ Step 4 at } {\sim}790\,^\circ C$$

Such a scheme is an apparent oversimplification as each of these steps may be subdivided into component mass loss steps. If one uses the formula ($Mg_8Si_{12}O_{30}$ $(OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$) for sepiolite then the theoretical mass loss for step 1 should be 11.0%. The % mass loss observed for the DTG curve for sepiolite from Nevada was 12.4%. The theoretical mass loss for step 2 is 2.76% compared with the observed value of 3.2% which is in excellent agreement with the theoretical value. The third step theoretical mass loss also should be 2.76% and a value of 2.5% is observed. The final mass loss step should be 5.21%; 4.3% mass loss is found. Thus there is excellent agreement with the predicted and the observed mass loss values. The observation that the experimentally determined mass loss step is less than that predicted is an indication that some dehydroxylation may have taken place in the previous steps with the evolution of the bound water. It has been found that sepiolite folds to the anhydride like form when about half the H_2O of coordination is removed, at <200 °C in vacuum or at approximately 300 °C in air [18–20]. Removal of the remaining H_2O at 530 °C under reduced pressure produces little further structural change. Infrared evidence suggests that partially dehydrated sepiolite is a folded structure with H_2O of coordination trapped in hexagonal holes. The remaining H_2O is lost, without significant structural change, at ~500 °C under vacuum to give a true anhydride [21–24]. A previous thermo-analytical study by the author found similar results for a wide range of sepiolites and palygorskites [51].

Controlled rate thermal analysis of sepiolite

The controlled rate thermal analysis of the sepiolites from Nevada and Nairobi are shown in Figs. 3 and 4. The results

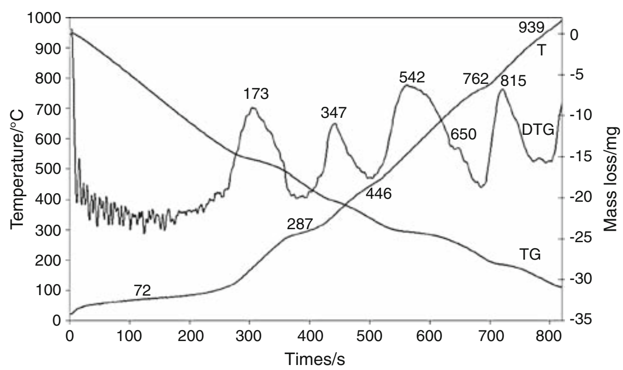

Fig. 3 The controlled rate thermal analysis of sepiolite from Nevada

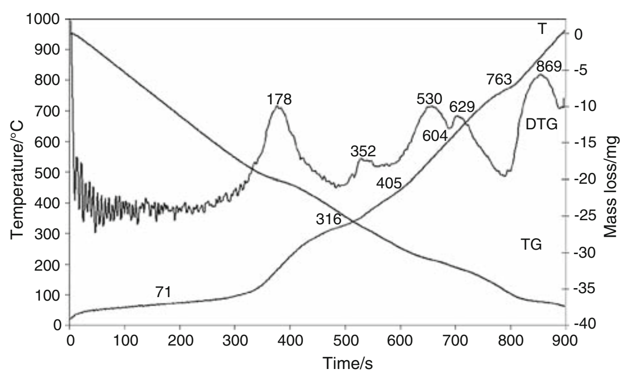

Fig. 4 The controlled rate thermal analysis of sepiolite from Nairobi

Table 1 Decomposition stages of sepiolites under CRTA conditions

Decomposition process	Sepiolite, Nevada (sample mass: 152.31 mg)			Sepiolite, Nairobi (sample mass: 196.89 mg)		
	Temp. range/°C	Mass loss		Temp. range/°C	Mass loss	
		mg	%		mg	%
Dehydration	22–171	15.3	10.0	22–178	20.1	10.2
	171–347	5.0	3.3	178–352	6.3	3.2
Dehydroxylation	347–542	3.8	2.5	352–530	4.5	2.3
	542–815	4.0	2.6	530–627	1.2	0.6
	815–989	2.8	1.8	627–871	4.7	2.4
				871–957	0.6	0.3

of the thermal analysis are reported in Table 1. The first two steps are assigned to the dehydration of the sepiolite and the next three steps to dehydroxylation of the clay. In the CRTA experiment water is lost in a quasi isothermal step at 72 °C followed by a non-isothermal step at 287 °C. In the first step 10.0% of the total mass is lost and 3.3% in the second step. If one uses the formula ($Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$) for sepiolite then the theoretical mass loss for step 1 should be 11.0%. The % mass loss observed for the CRTA curve for sepiolite from Nevada was 10.0%. The theoretical mass loss for step 2 is 2.76% compared with the observed value of 3.3% which is in excellent agreement with the theoretical value. For the Nairobi sepiolite a similar set of results is obtained. For the dehydroxylation mass losses of 10.2 and 3.2% are observed. For the sepiolite from Spain, mass losses of 7.3 and 4.1% were found (Fig. 5).

The OH units appear to be lost in three or four non-isothermal steps at 446, 762 and 939 °C. In the first three steps for the Nevada sepiolite over the 347–542, 542–815 and 815–939 temperature ranges, 2.5, 2.6 and 1.8% mass losses are found. Using the formula ($Mg_8Si_{12}O_{30}(OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$) for sepiolite, the theoretical mass loss for first dehydroxylation step is 2.76% compared with the observed value of 2.5% which is in excellent agreement with the theoretical value. The second dehydroxylation step, theoretical mass loss also should be 2.76% and a value of 2.6% is observed. The third mass loss step should be 5.21%. However, only 1.8% mass loss is found. In Fig. 3 an additional dehydroxylation step at 650 is observed. For the sepiolite from Nairobi in the CRTA experiment, four dehydroxylation steps are observed over the 352–530, 530–627, 627–871, 871–957 temperature range with mass losses of 2.3%, 0.6%, 2.4% and 0.3%.

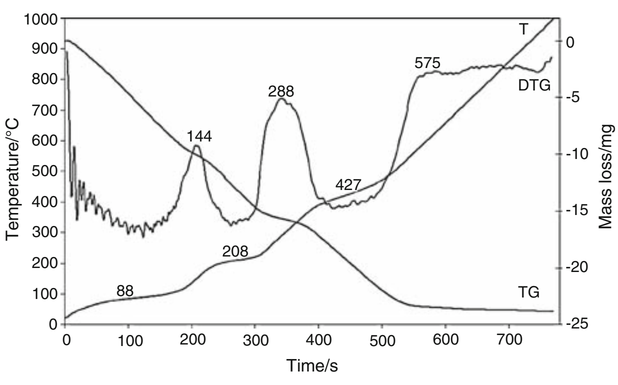

Fig. 5 The controlled rate thermal analysis of sepiolite from Spain

Conclusions

The number of steps in the thermal analysis of sepiolites are greater compared with previous published results when using dynamic high resolution DTG and CRTA techniques. The CRTA experiment enables the separation of mass losses for the dehydration steps of sepiolite minerals. Two dehydration steps for sepiolite are observed. These occur around 70–90 °C, and 210–320 °C. Three dehydroxylation steps for sepiolite are observed in the CRTA experiment. A low temperature mass loss at 350–400 °C and a higher temperature mass loss above 500 °C. Significant differences in the results as determined by the dynamic and CRTA experiment are observed.

CRTA technology offers better resolution and a more detailed interpretation of the decomposition processes of a clay mineral such as sepiolite via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal partial collapse of the layers of sepiolite as the sepiolite is converted to an anhydride, since in this cases a higher energy (higher temperature) is needed to drive out gaseous decomposition products through a decreasing space at a constant, pre-set rate. The CRTA experiment proves the thermal decomposition of sepiolites from different sources are almost identical. The CRTA technology offers a mechanism for the study of the thermal decomposition of minerals such as sepiolite.

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Appendix

Calculation of water content for Sepiolite, Nevada:

Composition: $Mg_4Si_6O_{15}(OH)_2 * xH_2O$

Removing water up to 347 °C: 20.30 mg that is 1.127 mmol

Remaining dehydrated mineral up to 347 °C: 132.01 mg that is 0.245 mmol

Molar mass of dehydrated mineral: 539.80 g/mol

Calculation of x:

1 mol dehydrated mineral − x mol H_2O

0.245 mol dehydrated mineral − 1.127 mol H_2O

$x = 4.6–5$ mol

Formula: $Mg_4Si_6O_{15}(OH)_2 * 5H_2O$

Steps of water liberation according to the decomposition steps up to 347 °C:

1. step: 3.45 mol
2. step: 1.15 mol

Calculation of water content for Sepiolite, Nairobi:

Composition: $Mg_4Si_6O_{15}(OH)_2 * xH_2O$

Removing water up to 352 °C: 26.40 mg that is 1.465 mmol

Remaining dehydrated mineral up to 352 °C: 170.49 mg that is 0.316 mmol

Molar mass of dehydrated mineral: 539.80 g/mol

Calculation of x:

1 mol dehydrated mineral − x mol H_2O

0.316 mol dehydrated mineral − 1.465 mol H_2O

$x = 4.63–5$ mol

Formula: $Mg_4Si_6O_{15}(OH)_2 * 5\ H_2O$

Steps of water liberation according to the decomposition steps up to 352 °C:

1. step: 3.53 mol
2. step: 1.10 mol

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