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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

THERMOANALYTICAL INVESTIGATIONS ON INTERCALATED KAOLINITES

J. Kristóf[1*], *R. L. Frost*[2], *E. Horváth*[3], *L. Kocsis*[3] *and J. Inczédy*[1]

[1]Department of Analytical Chemistry, University of Veszprém, H-8201 Veszprém,
PO Box 158, Hungary
[2]Centre for Instrumental and Developmental Chemistry, Queensland University of
Technology, 2 George Street, GPO Box 2434, Brisbane Queensland 4001, Australia
[3]Research Group for Analytical Chemistry, Hungarian Academy of Sciences
H-8201 Veszprém, PO Box 158, Hungary

Abstract

The thermal behaviour of ordered kaolinites from Hungary and Australia intercalated with potassium acetate, cesium acetate and urea has been investigated by simultaneous TG-DTG-DTA, TG-MS, Raman microscopy and XRD. Remarkable changes in the thermal decomposition pattern of the intercalates were obtained as a function of the nature of the intercalating reagents. Replacing the potassium cation to cesium leads to a change in the OH environments resulting in a more complicated dehydroxylation pattern. The urea intercalates can be decomposed completely without dehydroxylating the mineral, although further treatments are necessary to restore the original *d*-spacing.

Keywords: cesium acetate, intercalation, kaolinite, mass spectrometry, potassium acetate, Raman microscopy, thermal analysis, urea, X-ray diffraction

Introduction

Intercalation complexes of kaolinites and halloysites are formed in a way that the reactive guest molecules – e.g. urea, acetamide, hydrazine, potassium acetate – enter the interlayer spaces and expand the silicate layers [1, 2]. The intercalation reactivity of kaolinites is one of the important factors that control technical applicability in industrial processes, environmental decontamination, etc. Although the mechanism of intercalation (deintercalation) of kaolinites as well as the structure of clay-organic complexes has been investigated by highly sophis-

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[*] Author for correspondence. Fax: +36 88 421 869, e-mail: kristof@anal.venus.vein.hu

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ticated instrumental methods e.g. Raman microscopy [3, 4], FT-IR (DRIFT) spectrometry [5], thermal analysis [6, 7] etc., a more systematic study is necessary to understand in detail the processes of intercalation from the opening up of the layers to the formation of the expanded structure.

Also, it would be of high technological interest to convert by chemical treatment a disordered clay to an ordered one. Therefore, attention should be paid to any treatment that can increase or decrease structural order.

In the present study the potential of thermoanalytical methods is demonstrated – over and above the classical application of thermogravimetry and differential thermal analysis – in the study of ordered kaolinites intercalated with potassium acetate, cesium acetate and urea.

Experimental

Preparation of intercalates

The clay minerals used in this study are very highly ordered kaolinites from Királyhegy (Hungary) and Birdwood (Australia). The air dried kaolinites were intercalated according to Weiss *et al.* [8]. A 300 mg portion of the mineral was stirred in 30 cm^3 of 7.2 M potassium acetate solution or 5 M cesium acetate solution at room temperature for 80 h. Then the excess solution was removed by centrifugation. As to the urea intercalates, 300 mg of clay were mixed with 30 cm^3 of 10 M urea solution and stirred at 65°C for 80 h.

Thermal analysis

Simultaneous TG-DTG-DTA measurements of the intercalates were performed in a Derivatograph PC-type thermoanalytical instrument in nitrogen atmosphere at a heating rate of 5°C min^{-1}. TG-MS investigations were carried out by means of a Netzsch TG 209 thermobalance coupled with a Balzers MSC 200 Thermo-Cube type mass spectrometer connected via a fused silica capillary for sample introduction. Samples of a few milligrams were heated in nitrogen atmosphere at a rate of 10°C min^{-1}.

Raman microprobe spectroscopy

Raman spectra of the intercalated clay minerals were recorded at a resolution of 2 cm^{-1} using a Renishaw 1000 Raman microprobe system, which also includes a monochromator, a filter system and a charged coupled device (CCD) as a detector. Excitation was made by a Spectra-Physics model 127 He/Ne laser (633 nm). Band fitting was done using a Lorentz-Gauss cross product function with the minimum number of component bands used for the fitting process. The Gauss-

Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with correlation coefficients for r^2 greater than 0.995.

X-ray diffraction

The X-ray diffraction analyses were carried out on a Philips PW 1050/25-type vertical goniometer equipped with a graphite diffracted beam monochromator. The radiation used was CuK$_\alpha$ from a long fine focus Cu tube, operating at 40 kV and 35 mA.

Results and discussion

The TG and DTG curves of the Királyhegy kaolinite (1), the Királyhegy + potassium acetate intercalate (2) as well as the Királyhegy kaolinite intercalated with cesium acetate (3) are shown in Fig. 1. Comparing the curves, it can be concluded that the insertion of the intercalating agents drastically change the decomposition pattern of the clay. While the pure mineral can be dehydroxylated in one step at 610°C, the potassium acetate intercalate decomposes in two steps: at 376°C and in a slow process over a wide temperature range between 400 and 550°C. Due to previous experience, early dehydroxylation is due to the removal of inner surface hydroxyls which are hydrogen-bonded to the intercalating ace-

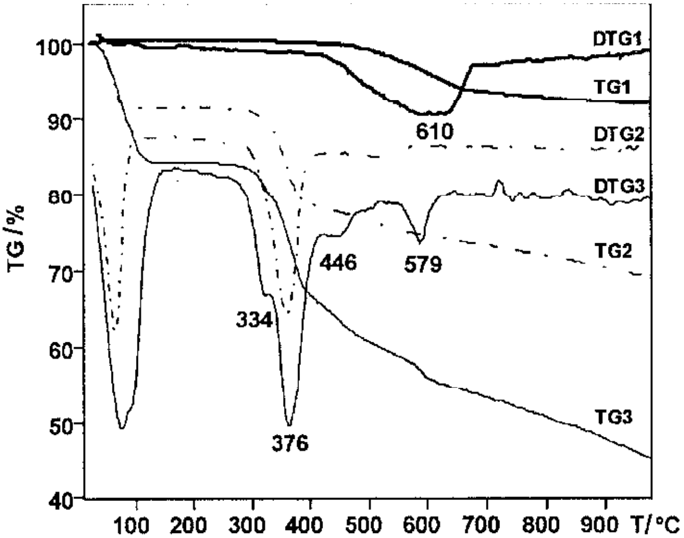

Fig. 1 TG and DTG curves of the Királyhegy kaolinite (1), the Királyhegy kaolinite intercalated with potassium acetate (2) and the Királyhegy kaolinite intercalated with cesium acetate (3)

tate ions [6], while the second step of dehydroxylation is due to the removal of hydroxyls which are not hydrogen-bonded to the acetate (i.e. to the non-reacted mineral).

Dehydroxylation is accompanied with the decomposition of the interlayer potassium acetate as well. Since the thermal decomposition of the intercalating agent does not result in the formation of water, the processes of dehydroxylation and decomposition can easily be separated by the selective detection of water vapour released in the thermolysis process using e.g. a simple device connected to the thermobalance [9].

As to the decomposition of the cesium acetate intercalate, however, a much more complicated decomposition pattern can be experienced. An additional decomposition step can be observed in the dehydroxylation range at 334°C, indicating the complexity of the process. In addition, the mass loss stage at 579°C – which does not belong to the liberation of water – cannot be explained based solely on the TG and DTG curves. Therefore, a mass spectrometric analysis carried out simultaneously with the thermogravimetric investigation is absolutely necessary. The TG and mass spectrometric ion intensity curves of H_2O (m/z=18), CH_3 (m/z=15) and CO_2 (m/z=44) recorded during a TG-MS run are shown in Fig. 2.

A comparison of the curves provides information sufficient for the understanding of the processes of both dehydroxylation and acetate decomposition. The step at 334°C in the DTG curve of Fig. 1 belongs to an additional dehydroxylation stage as indicated by the H_2O^+-ion intensity curve. The water curve con-

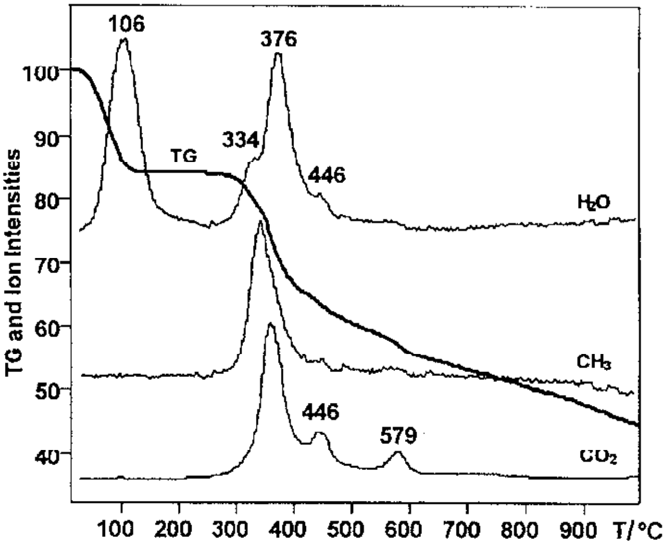

Fig. 2 TG and mass spectrometric ion intensity curves of the Királyhegy kaolinite intercalated with cesium acetate

firms the second dehydroxylation stage of hydrogen-bonded OH groups at 376°C and that of the non-reacted clay at 446°C. The CH_3^+-ion intensity curve – along with that of CO_2 – shows that the acetate decomposition takes place simultaneously with dehydroxylation. It is interesting to observe CO_2 liberation in a separate process at 579°C. It can be supposed that at this temperature cesium carbonate decomposes – in molten phase – to cesium oxide accompanied with the liberation of CO_2. The final product of the thermolysis process is $CsAlSiO_4$ as identified by X-ray diffraction. The most interesting feature of the cesium acetate intercalate is the double dehydroxylation step of the hydrogen-bonded inner surface hydroxyls. It can be supposed that in the cesium acetate intercalate two different environments exist for the OH groups accessible by the intercalating acetate ions. This difference can be due to the cesium cation, since – due to its larger size – it does not fit into the ditrigonal whole of the tetrahedral layer. FT-Raman microscopy can support this supposition as well. Band component analysis of the Raman spectrum of the cesium acetate intercalate shows that two hydrogen-bonded OH bands (ν_6 and ν_7) appear at 3598 and 3606 cm^{-1} which make up 16.6 and 26.3% of the total normalised band intensities (Fig. 3). The results obtained by TG-MS and Raman spectroscopy are in perfect harmony with respect to the existence of different OH environments.

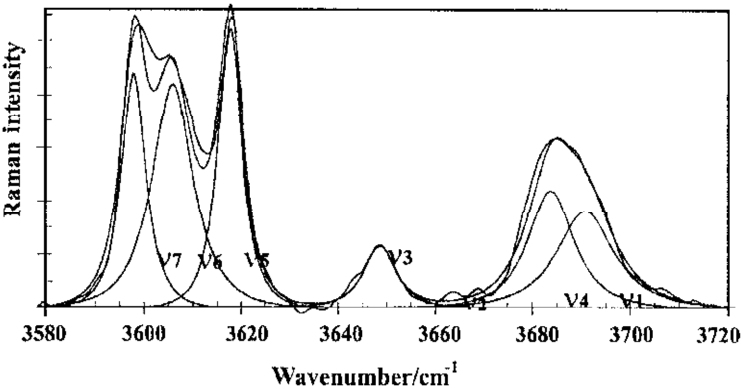

Fig. 3 Raman spectrum of the hydroxyl stretching region of the Királyhegy kaolinite – cesium acetate intercalate

Incorporation of urea between the kaolinite layers takes place according to a completely different pattern. While the acetate ions are connected not only to the inner surface hydroxyls but also to the tetrahedral sheet of the next layer, urea is connected – via hydrogen-bonding – to the tetrahedral layer only [10]. The expansion of the Királyhegy clay from 7.2 to 10.9 Å is practically complete as a result of urea intercalation (over 97% of the clay was reacted). Heating 53.40 mg of this intercalate to 700°C in nitrogen atmosphere in the Derivatograph, the melting of urea takes place at 134°C followed by the decomposition and com-

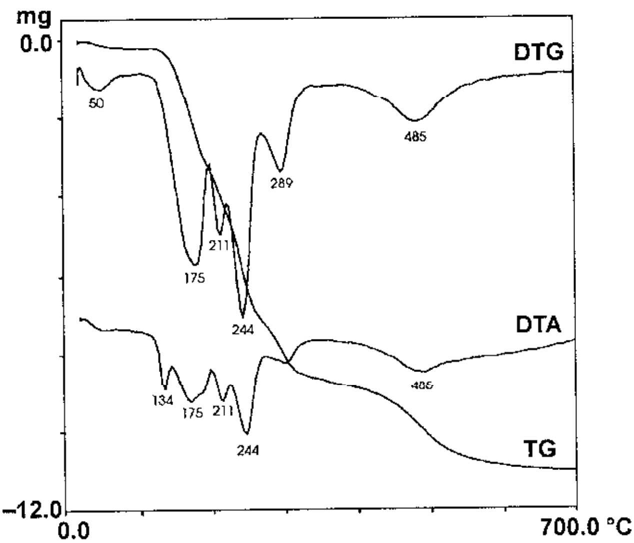

Fig. 4 TG-DTG-DTA curves of the Királyhegy kaolinite – urea intercalate

plete removal of the intercalating reagent by cca. 350°C (Fig. 4). Although the temperature ranges of urea removal and kaolinite dehydroxylation are completely separated, a decrease of cca. 100°C in the dehydroxylation peak temperature (as compared to that of the untreated mineral) indicates that a structural change has occurred in the mineral. A comparison in Fig. 5 between the X-ray diffraction pattern of the original intercalate (curve A) and that heated to 350°C (curve B) shows that although the expanded structure no longer exists, the original structure was not regained. Mixing the heated intercalate to water and stirring gently for 2 h results in the appearance of a new reflection at 10.1 Å (curve C) indicating as if a 10 Å – halloysite were formed. Further heating the washed sample to 120°C (curve D), the 10.1 Å reflection disappears and several new reflections appear centered at 8.3, 7.7 and 7.2 Å. It means that further treatments are still necessary to regain the original structure.

The highly ordered Birdwood kaolinite (with a Hincley index of 1.31) cannot be intercalated with urea under identical experimental conditions. The reason for this is not understood but it can be supposed that the kaolinite surface is coated with a single layer of smectite preventing intercalation. Therefore, the Birdwood clay + urea "intercalate" is a physical mixture of clay and urea adsorbed on the clay particles when the solid is separated from the urea solution by centrifugation. The thermal behaviour of 31.85 mg of this physical mixture is shown in Fig. 6. Again, a decrease of cca. 20°C in the dehydroxylation temperature – as compared to that of the untreated mineral – can be observed in the DTG (and DTA) curves. Since this decrease is too much to be merely a consequence of the

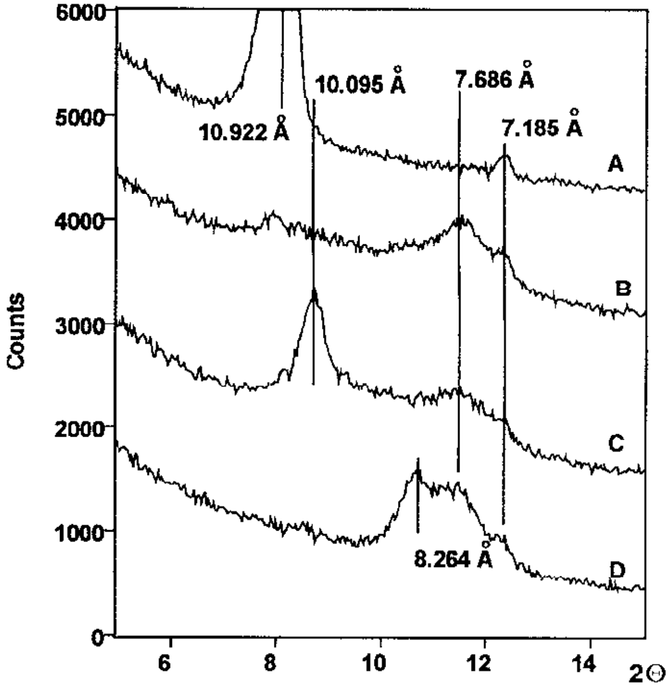

Fig. 5 X-ray diffraction patterns of the Királyhegy kaolinite – urea intercalate (curve A), the intercalate heated to 350°C (curve B), the 350°C intercalate treated with water (curve C) and the water-treated 350°C intercalate reheated to120°C (curve D)

changing particle size distribution or packing density, it is reasonable to suppose that some interaction of urea and the clay occurred during heating. The X-ray analysis of the original mixture and that heated to 350°C indicates an intensity decrease of the 001 reflection as a result of the thermal treatment (curves A and B in Fig. 7). When the mixture was heated to 140°C only (i.e. to the melting temperature of urea) and cooled back to room temperature, an intercalation rate of cca. 8% could be calculated from the diffraction pattern (curve C). It means that urea penetrates the smectite layers and gets into the kaolinite in a molten phase and after an extended period of time.

Conclusions

The application of thermal analysis techniques – combined with Raman spectroscopy and X-ray diffraction – can significantly improve the efficiency of research aimed at the understanding of the nature of clay-organic complexes.

This multi-method approach can be recommended to follow structural changes associated with kaolinite intercalation and deintercalation. Changes in-

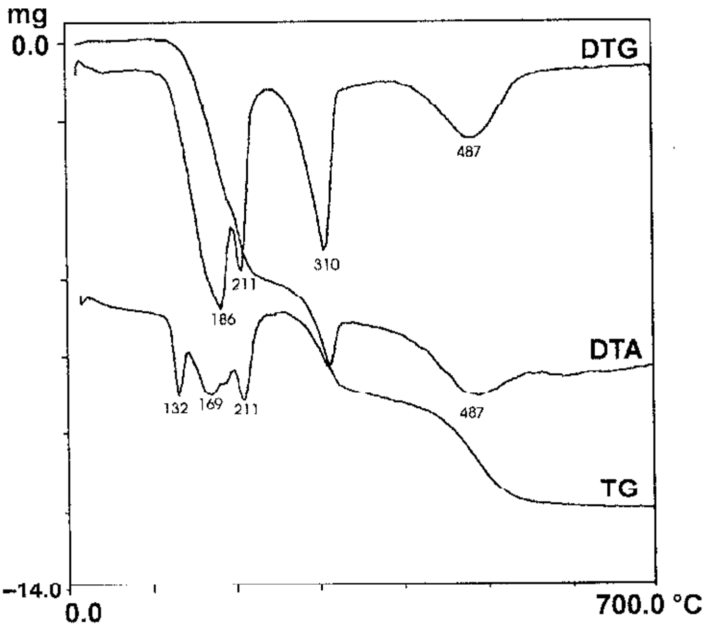

Fig. 6 TG-DTG-DTA curves of the Birdwood kaolinite – urea "intercalate"

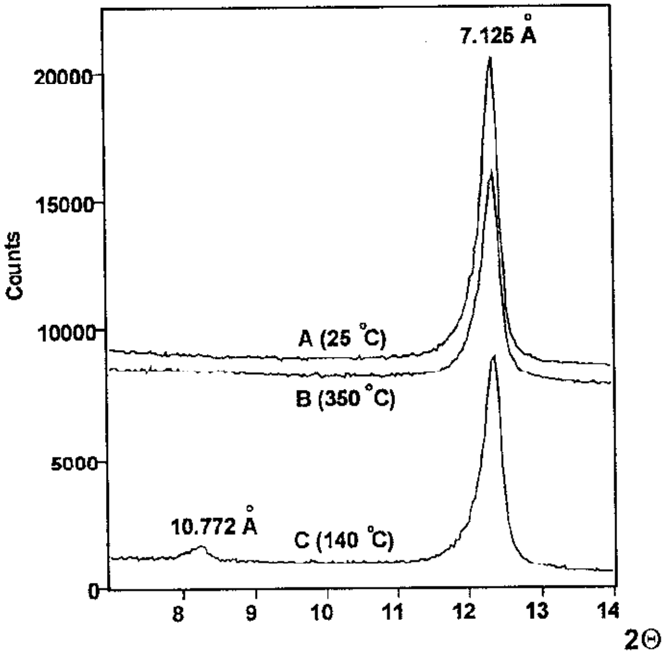

Fig. 7 X-ray diffraction patterns of the Birdwood kaolinite – urea "intercalate" (curve A), the intercalate heated to 350°C (curve B), and the intercalate heated to 140°C (curve C)

duced thermally in the mineral structure can contribute to the better understanding of small differences between kaolinites and needs to be studied in detail.

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