Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 279–289

THERMOANALYTICAL INVESTIGATION OF FORMAMIDE INTERCALATED KAOLINITES UNDER QUASI-ISOTHERMAL CONDITIONS

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(Received July 12, 2000; in revised form October 12, 2000)

Abstract

The thermal behaviour of fully and partially expanded kaolinites intercalated with formamide has been investigated in nitrogen atmosphere under quasi-isothermal heating conditions at a constant, pre-set decomposition rate of 0.20 mg $\min^{-1}$. With this technique it is possible to distinguish between loosely bonded (surface bonded) and strongly bonded (intercalated) formamide. Loosely bonded formamide is liberated in an equilibrium reaction under quasi-isothermal conditions at 118°C, while the strongly bonded (intercalated) portion is lost in an equilibrium, but non-isothermal process between 130 and 200°C. The presence of water in the intercalation solution can influence the amount of adsorbed formamide, but has no effect on the amount of the intercalated reagent. When the kaolinite is fully expanded, the amount of formamide hydrogen bonded to the inner surface of the mineral is 0.25 mol formamide/mol inner surface OH group. While the amount of surface bonded formamide is decreasing with time, no change can be observed in the amount of the intercalated reagent. With this technique the mass loss stages belonging to adsorbed and intercalated formamide can be resolved thereby providing a complex containing only one type of bonded (intercalated) formamide.

Keywords: CRTA, formamide, intercalation, kaolinite, quasi-isothermal thermogravimetry

Introduction

The application of kaolinite – an important industrial raw material – is closely related to its surface reactivity. The reactivity of kaolinite internal surfaces can be tested via the insertion of low molecular weight organic compounds (e.g. potassium acetate, hydrazine) between the kaolinite layers consisting of the two-dimensional arrange-

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1418–2874/2001/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

ments of tetrahedral (siloxane) and octahedral (gibbsitic) sheets [1, 2]. Such a process is known as intercalation. The mechanism of intercalation is not known with certainty, but it involves the disruption of the hydrogen bonding between the kaolinite layers and the formation of new hydrogen bonds between the kaolinite inner surface and the inserted molecule.

Molecules such as formamide and acetamide may connect to kaolinite inner surfaces either through the C=O group, the lone pair of nitrogen, or through the amide group. It was reported quite early that formamide readily intercalates kaolinite [3]. Based on the results of Raman microscopy and Fourier transform infrared (FTIR) microspectroscopy new models have been proposed for the intercalation of formamide in kaolinites [4].

Thermoanalytical studies showed that the removal of intercalated formamide below 300°C is a complex process and that the liberation of formamide from the complex takes place in two overlapping stages [5]. Later on it was also observed that higher amount of formamide can be connected to the clay if intercalation is carried out in the presence of water [6]. The complexity of the thermal decomposition patterns and the subtleties of the vibrational spectroscopic (FT-IR and Raman spectrometric) data [7] require a detailed study of the thermal decomposition mechanism. The objectives of this paper are, therefore: (i) to reveal the nature of formamide loosely and strongly bonded to kaolinite, (ii) to determine the exact amounts of differently bonded formamide, (iii) to clarify the role of water in the intercalation process, and (iv) to develop a method capable of providing intercalation complexes containing only one type of bonded formamide for further (structural) studies by infrared and Raman spectroscopic techniques.

Experimental

Preparation of intercalates

The clay minerals used in this study are highly ordered kaolinites from Királyhegy (Hungary) and Birdwood (Australia). While the former clay is highly reactive, the later one can only partially be intercalated. Formamide intercalation was carried out in a way that 500 mg of kaolinite were mixed with 10 cm^3 of analytical grade (Reanal, Hungary) formamide for 80 h at room temperature. In a parallel experiment the same amount of clay was mixed with 10 cm^3 of 1:1 ratio of formamide:water solution. The intercalates were separated from solution by centrifugation and allowed to dry at room temperature for five weeks.

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_α from a long fine focus Cu tube, operating at 40 kV and 25 mA.

Thermal analysis

Thermal decomposition of the intercalates was carried out in a Derivatograph PC-type thermoanalytical instrument (Hungarian Optical Works, Budapest, Hungary) in nitrogen atmosphere at a pre-set, constant decomposition rate of 0.20 mg min^{-1}. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 1°C min^{-1}.) The samples were heated in an open platinum crucible at a rate of 1°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. Some of the samples were heated in a labyrinth-type crucible (Hungarian Optical Works, Budapest) to provide a self-generated atmosphere and quasi-isobaric conditions during decomposition.

Results and discussion

The XRD patterns of the Királyhegy and Birdwood clay samples intercalated with formamide and a 1:1 formamide:water mixture are given in Fig. 1. Comparing the curves, it can be stated that the expansion of the Királyhegy kaolinite is practically complete (i.e. all particles in the sample reacted with the intercalating reagent) independently of the fact that the clay was mixed into pure formamide or into a solution of

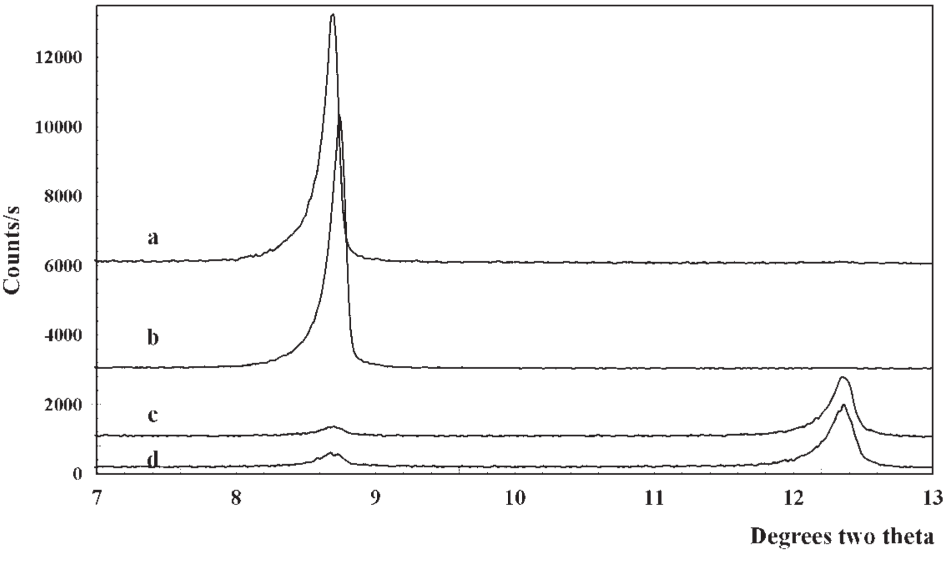

Fig. 1 XRD patterns of a: Királyhegy kaolinite intercalated with formamide, b: Királyhegy kaolinite intercalated with formamide/water mixture, c: Birdwood kaolinite intercalated with formamide, d: Birdwood kaolinite intercalated with formamide/water mixture

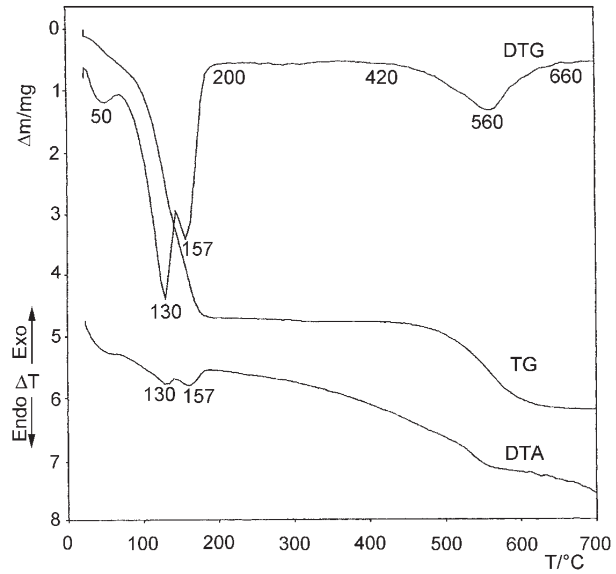

Fig. 2 Thermoanalytical curves of Királyhegy kaolinite intercalated with formamide recorded under dynamic heating conditions (sample mass is 31.81 mg)

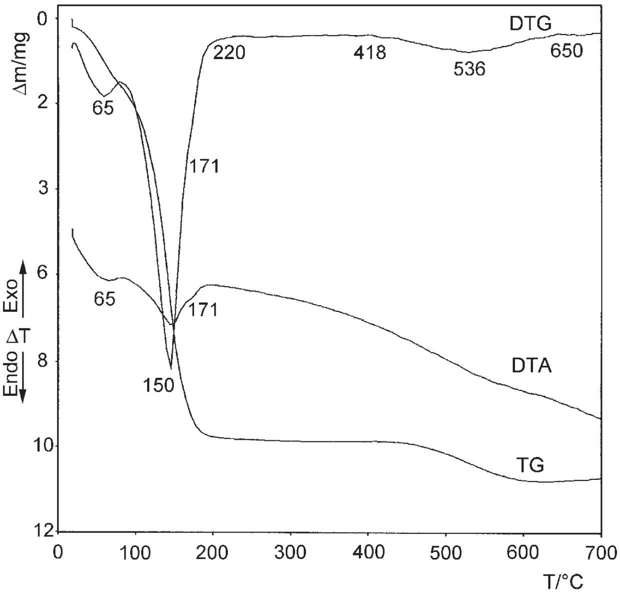

Fig. 3 Thermoanalytical curves of the Királyhegy kaolinite intercalated with a formamide/water mixture recorded under dynamic heating conditions (sample mass is 34.87 mg)

formamide/water mixture (curves a and b). As to the Birdwood kaolinite, only a moderate expansion could be observed, amounting to cca. 23% in formamide and cca. 28% in the formamide/water mixture (curves c and d).

The thermal behaviour of the Királyhegy clay intercalated with formamide and formamide/water mixture was reported earlier [6]. Under the conditions of dynamic heating (at a rate of 5°C min^{-1} in nitrogen atmosphere) the liberation of formamide took place in two overlapping stages at 130 and 157°C when pure formamide reagent was used (Fig. 2). When intercalation was made in a formamide/water mixture (Fig. 3), the amount of intercalated formamide (liberated in two closely overlapping stages at 150 and 171°C) increased by a factor of 3.1. The conclusion was made that, on the one hand, the intercalation complex contains two different environments for formamide connected to the clay and, on the other, the presence of water can significantly enhance the building of formamide molecules into the clay structure.

The thermoanalytical curves of the formamide intercalated Királyhegy kaolinite recorded under quasi-isothermal conditions are given in Fig. 4. According to TG-MS studies, the mass loss stage at 56°C belongs to the removal of 2.79% of water. Bonded formamide is released in two stages under quasi-isothermal conditions at 118°C (11.48%) and at 156°C (5.06%).

As to the thermal behaviour of the formamide/water intercalate (Fig. 5), the amount of water is 3.27%, while formamide is lost in a quasi-isothermal stage at 118°C (21.57%) and in a separate step at 153°C (4.24%). Comparing the results of Figs 4 and 5, significant differences can be observed in the thermal behaviour of differently bonded formamide molecules. While the first type of bonded formamide is

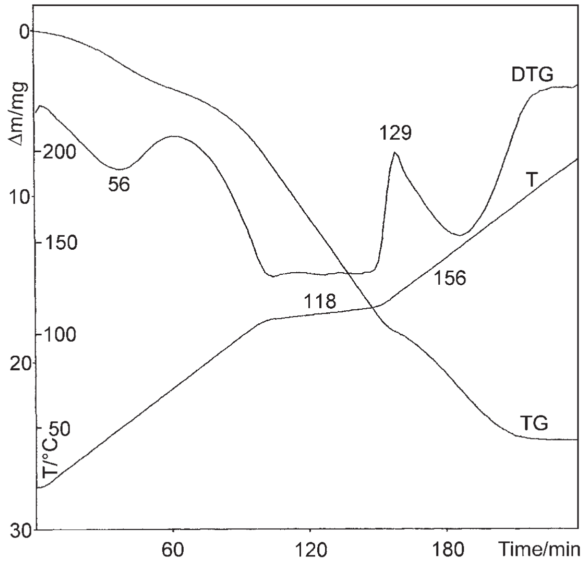

Fig. 4 Thermoanalytical curves of the formamide intercalated Királyhegy kaolinite recorded under quasi-isothermal conditions (sample mass is 127.75 mg)

lost under quasi-isothermal conditions at 118°C, the second type of formamide molecules exhibits a drastically different behaviour on heating. The observation that the temperature remained spontaneously constant during the first formamide mass loss stage indicates an equilibrium reaction. Stabilisation of sample temperature in an

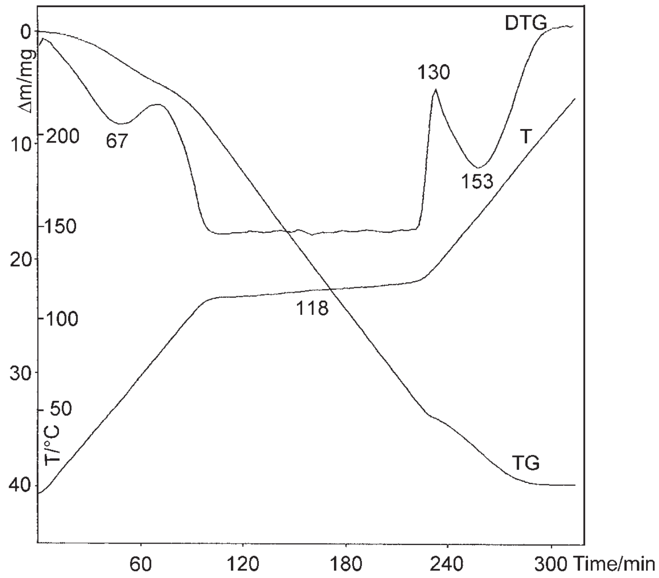

Fig. 5 Thermoanalytical curves of the formamide/water intercalated Királyhegy kaolinite recorded under quasi-isothermal conditions (sample mass is 136.55 mg)

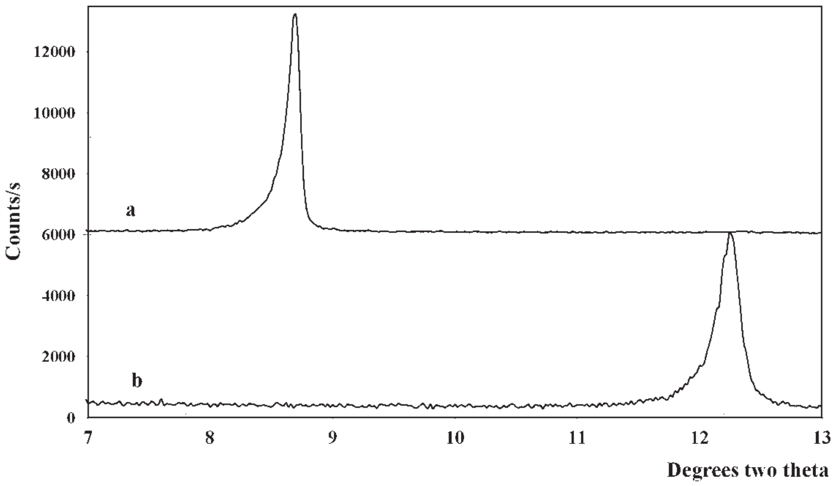

Fig. 6 XRD patterns of formamide/water intercalated Királyhegy kaolinite heat treated under quasi-isothermal conditions to a: 130°C and b: 300°C

equilibrium reaction also means the constant concentration (partial pressure) of gaseous decomposition products in the space among the particles in the open crucible used and the establishment of an equilibrium between the opposite diffusion processes of formamide vapour leaving the sample and nitrogen replacing formamide vapour [8]. The fact that the amount of formamide lost in the first step from the formamide/water intercalate is actually twice as much than that released from the formamide intercalate (21.57 and 11.48%, respectively) does not have any effect on the quasi-isothermal decomposition pattern when the reaction rate is controlled to a set value of 0.20 mg min^{-1}. The liberation of strongly bonded formamide takes place in a similar fashion and at practically the same temperature (156 and 153°C) indicating the similar mechanism of formamide bonding to the clay structure. Since the best separation of the overlapping formamide decomposition stages can be obtained at 129 (130°C), heating was stopped in a separate experiment at 130°C. The sample was cooled to room temperature and the quenched sample was X-rayed (Fig. 6 curve a). In another experiment the heating was stopped at 300°C and the cooled residue was also subjected to XRD analysis (Fig. 6 curve b). The X-ray results show that after the removal of loosely bonded formamide (at 130°C) the expanded structure (with a *d*-value of 10.16 Å) still exists, while at 300°C a complete deintercalation takes place and the structure collapses to its original *d*-value of 7.20 Å.

When the thermal decomposition of the formamide/water intercalate was carried out under quasi-isothermal, quasi-isobaric conditions (i.e. in a labyrinth-type crucible and a self-generated atmosphere), a similar pattern was observed. The only difference

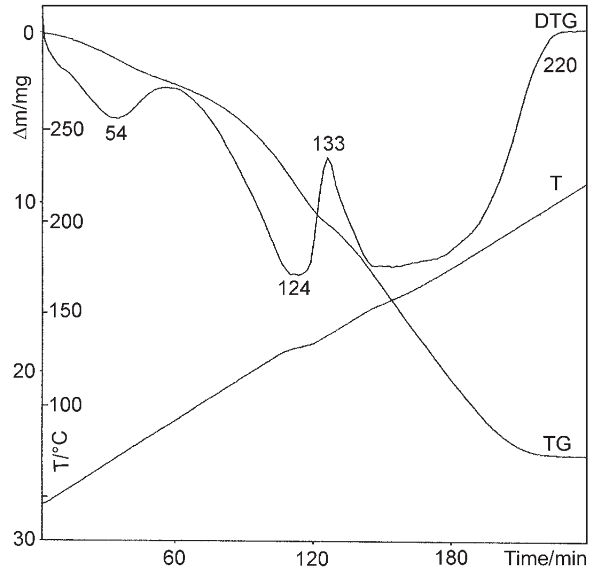

Fig. 7 Thermoanalytical curves of formamide intercalated Királyhegy kaolinite recorded 6 months after preparation under quasi-isothermal conditions (sample mass is 239.63 mg)

is that the decomposition temperatures were significantly higher (148°C for the removal of water and 182 as well as 247°C for the liberation of loosely bonded and strongly bonded formamide, respectively). Repeated experiments with lower decomposition rates (set to 0.1 and 0.05 mg min^{-1}) did not result in any change in the decomposition pattern.

When the intercalates were kept for a longer period of time (approx. 5 months after the air-dry condition was attained) a considerable change was observed in the thermal decomposition pattern. For example, for the formamide intercalated kaolinite (Fig. 7) the amount of loosely bonded formamide decreased drastically. In addition, the intercalate shows a more 'powdery' structure (e.g. the amount of sample necessary to fill up the same type of crucible was almost double). The fact that the removal of loosely bonded formamide in an equilibrium process under isothermal conditions takes place at 124°C (rather than at 118°C) also indicates a more compact material imposing a higher control on the rate of gas phase diffusion. The strongly bonded (intercalated) formamide is lost in a temperature range between 133 and 220°C. This stage represents a non-isothermal equilibrium process. A non-isothermal equilibrium reaction means that higher and higher energy (i.e. higher temperature) is necessary to maintain the same (constant) rate of decomposition (i.e. the same equilibrium between the concentrations of formamide vapour leaving the sample and nitrogen replacing formamide among the particles). The temperature increase attained spontaneously during the course of reaction is due to the gradual collapse (deintercalation) of the clay structure providing less and less space for gas molecules leaving/entering the interlayer space. When heating is continued to dehydroxylate the deintercalated mineral, the quantity of dehydroxylation water can be determined and

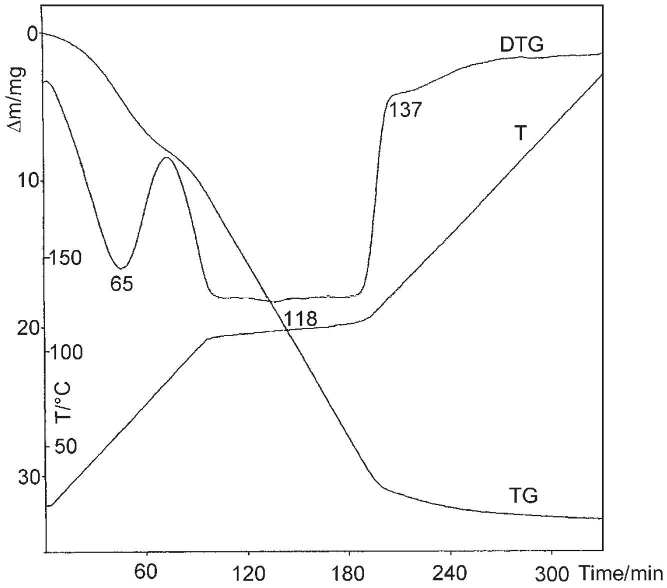

Fig. 8 Thermoanalytical curves of formamide intercalated Birdwood kaolinite recorded under quasi-isothermal conditions (sample mass is 125.53 mg)

used to calculate the amount of formamide moles bonded to each mole of inner surface hydroxyls. This quantity is 0.24 mol formamide/mol inner surface OH. Since this figure is – within measurement error – the same as that obtained for the fresh sample (0.25 mol formamide/mol inner surface OH), it can be concluded that the intercalation complex is a stable one and can be stored for an extended period of time without any significant change regarding the amount of strongly bonded/intercalated formamide. It should be noted that the Királyhegy kaolinite contains a significant amount of quartz, as well. The presence of this impurity, however, does not influence the intercalation behaviour of the clay and the reliability of the thermoanalytical study of the complex formed.

The thermoanalytical curves of 125.53 mg of the Birdwood clay intercalated with formamide alone and heated under quasi-isothermal conditions are given in Fig. 8. After the removal of water (6.37%) at 65°C, a quasi-isothermal decomposition stage follows at 118°C, similarly to the case with the Királyhegy clay. Although the amount of the loosely bonded formamide is higher (18.46%) than that for the completely expanded Királyhegy kaolinite, no other differences can be observed in the mechanism of the thermal decomposition process. The liberation of the loosely bonded formamide is finished by 137°C, while the low amount of the strongly bonded reagent (1.29%) is released up to about 200°C.

Intercalation with the formamide/water mixture shows a similar pattern (Fig. 9) resulting in the liberation of water (2.09%) at 67°C, loosely bonded formamide (17.13%) under quasi-isothermal conditions at 118°C, and strongly bonded formamide (1.30%) between 146 and 200°C.

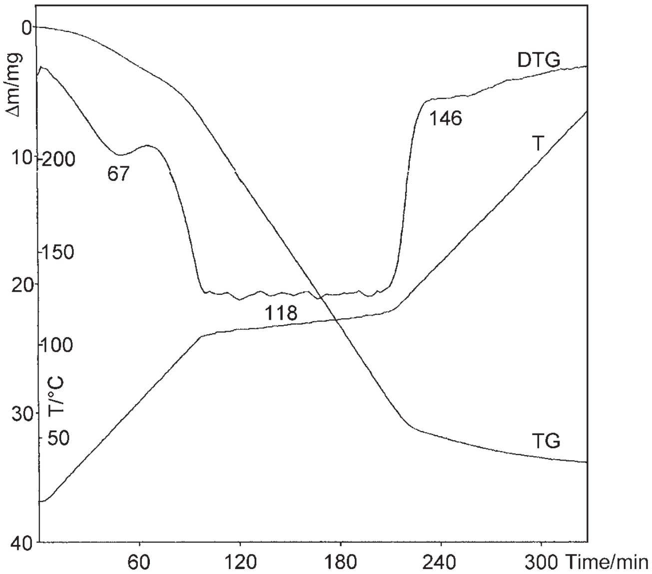

Fig. 9 Thermoanalytical curves of formamide/water intercalated Birdwood kaolinite recorded under quasi-isothermal conditions (sample mass is 165.06 mg)

Conclusions

1. The liberation of loosely bonded formamide takes place in an equilibrium reaction at a constant temperature of 118°C when thermal decomposition is carried out at a pre-set, uniform rate of 0.20 mg min^{-1}, independently of the type of kaolinite used and the amount of water present in the intercalation solution.
2. The amount of strongly bonded formamide is about 3.3–3.9 times higher in the completely expanded Királyhegy clay than in the partially intercalated Birdwood clay. The liberation of the strongly bonded formamide takes place in a non-isothermal, equilibrium process between cca. 130 and 200°C.
3. When the Királyhegy kaolinite is 100% expanded, the percentage amount of loosely bonded formamide is 1.87 times higher if intercalation is carried out in a formamide/water mixture, rather than in pure formamide. With the poorly expanding Birdwood kaolinite the presence of water in the intercalation solution has no significant effect on the amount of loosely bonded formamide.
4. After removal of the loosely bonded formamide, the completely expanded structure of the intercalated Királyhegy kaolinite still exists, i.e. no partial collapse of the structure results when some 70–80% of the reagent connected to the clay is removed.

Based on the above considerations a possible explanation for this unusual thermal behaviour of the intercalates studied is that the loosely bonded formamide is connected to the outer surface of the clay particles, while the strongly bonded portion is connected to the inside surface (i.e. this is the intercalated formamide). The question why water can influence the amount of loosely bonded (surface bonded) formamide when the clay is completely expanded and why it cannot if intercalation is incomplete, still remains unanswered.

Knowing the amount of dehydroxylation water liberated between 400 and 600°C from the heated intercalates, it is possible to calculate the amount of formamide connected to the inner surface OH groups (the inner OH groups are not accessible for the guest molecules). The calculation results show that in average each inner surface OH group is surrounded by 0.25 formamide molecule in the fully expanded Királyhegy kaolinite and 0.03 formamide molecule in the partially expanded Birdwood kaolinite. It should be noted that the rate of expansion of kaolinite and the amount of intercalated formamide cannot be directly related since a complete expansion does not necessarily means that all inner surface OH groups are in hydrogen bonding (like in the case of hydrazine intercalated kaolinite [9]). It is important to observe that the amount of loosely bonded (surface bonded) formamide is decreasing with time, while that of the strongly bonded (intercalated) reagent does not show any observable change (i.e. the intercalation complex is a stable one).

FT-IR (DRIFT) and Raman microscopic investigations of the samples heated to 130°C under quasi-isothermal conditions – i.e. containing only strongly bonded (intercalated) formamide – could be useful in an attempt made to reveal the subtle nature of formamide intercalated organoclay complexes.

This research was supported by the Hungarian Scientific Research Fund (under Grant No. T25171). The support of the Queensland University of Technology Centre for Instrumental and Developmental Chemistry is also gratefully acknowledged.

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