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HYDRAZINE-HYDRATE INTERCALATED HALLOYSITE UNDER CONTROLLED-RATE THERMAL ANALYSIS CONDITIONS

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Abstract

The thermal behaviour of halloysite fully expanded with hydrazine-hydrate has been investigated in nitrogen atmosphere under dynamic heating and at a constant, pre-set decomposition rate of 0.15 mg min^{-1}. Under controlled-rate thermal analysis (CRTA) conditions it was possible to resolve the closely overlapping decomposition stages and to distinguish between adsorbed and bonded reagent. Three types of bonded reagent could be identified. The loosely bonded reagent amounting to 0.20 mol hydrazine-hydrate per mol inner surface hydroxyl is connected to the internal and external surfaces of the expanded mineral and is present as a space filler between the sheets of the delaminated mineral. The strongly bonded (intercalated) hydrazine-hydrate is connected to the kaolinite inner surface OH groups by the formation of hydrogen bonds. Based on the thermoanalytical results two different types of bonded reagent could be distinguished in the complex. Type 1 reagent (approx. 0.06 mol hydrazine-hydrate/mol inner surface OH) is liberated between 77 and 103°C. Type 2 reagent is lost between 103 and 227°C, corresponding to a quantity of 0.36 mol hydrazine/mol inner surface OH.

When heating the complex to 77°C under CRTA conditions a new reflection appears in the XRD pattern with a *d*-value of 9.6 Å, in addition to the 10.2 Å reflection. This new reflection disappears in contact with moist air and the complex re-expands to the original *d*-value of 10.2 Å in a few h. The appearance of the 9.6 Å reflection is interpreted as the expansion of kaolinite with hydrazine alone, while the 10.2 Å one is due to expansion with hydrazine-hydrate.

FTIR (DRIFT) spectroscopic results showed that the treated mineral after intercalation/deintercalation and heat treatment to 300°C is slightly more ordered than the original (untreated) clay.

Keywords: controlled rate thermal analysis, CRTA, halloysite, hydrazine, intercalation

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Introduction

The industrial application of kaolinite-type minerals is closely related to their reactivity and surface properties. Halloysite is a polytype of kaolinite ($Al_2(OH)_4[Si_2O_5]$) and differs mainly in the morphology of the crystals, which are curved or rolled [1–6]. Halloysite is a layer-structured mineral composed of siloxane and gibbsite-like layers. The siloxane layer is made of SiO_4 tetrahedra linked in a hexagonal array. The bases of the tetrahedra are almost coplanar and the apical oxygen atoms are linked to a second (gibbsitic) layer containing aluminium ions and OH groups. Because of the size differences between the siloxane tetrahedra and the aluminium octahedra, the halloysite surfaces are curved. This leads to structural disorder, particularly in layer stacking.

Halloysite contains water between the layers resulting in a water OH band at 3598 cm^{-1} in the infrared spectrum. In addition to this water band, four more OH stretching bands can be observed in the IR spectrum of halloysite. The band at 3620 cm^{-1} belongs to the inner OH groups located in the plane shared by the tetrahedral and octahedral sheets and pointing toward a cavity. The OH stretching bands at 3693, 3669 and 3652 cm^{-1} belong to the inner surface hydroxyl groups of the gibbsitic layer that lie at angles between 65 and 73° to the *ab* plane and form hydrogen bonds to the oxygens of the next adjacent siloxane layer [7–8]. Dissimilarly to kaolinites, the 3669 and 3652 cm^{-1} bands show a broad profile.

Halloysites occur naturally as expanded phases with *d*(*001*) spacing of ~10.0 Å due to the incorporation of water. On heating dehydration occurs in an irreversible process and a *d*-spacing of 7.1 Å results. Because halloysite is a layer-structured mineral, most of its surfaces are internal (referred to as inner surface). When low molecular weight organic compounds react with these inner surfaces, an expansion occurs along the *c*-axis. Such a process is known as intercalation. The intercalating guest molecules disrupt the hydrogen bonds holding the layers together and form new hydrogen bonds with the inner surface hydroxyls. In this way a nano-structured mineral is formed.

Molecules such as formamide and acetamide may connect to kaolinite and halloysite inner surfaces either through the C=O group, the lone pair of nitrogen, or through the amide group.

The possibility to intercalate hydrazine into kaolinite is known for a considerable length of time. Ledoux and White reported the expansion of kaolinite from 7.2 to 10.4 Å upon introducing hydrazine in the kaolinite structure [9]. Mild heating resulted in deintercalation accompanied with the partial collapse of the structure to 9.4 Å. Johnston and Stone showed the effect of evacuation on the kaolinite-hydrazine complex with the subsequent collapse of the structure from 10.4 to 9.6 Å [10]. A new model was proposed for hydrazine intercalation based on the insertion of a hydrazine-water unit by Frost *et al*. [11].

In this study a combination of controlled-rate thermal analysis with X-ray diffraction and FT-IR (DRIFT) spectroscopy is used to follow the structural changes in hydrazine-intercalated kaolinite on heating. The objective of this work is to distinguish between differently bonded hydrazine molecules in the complex as well as to reveal the role of water in the intercalation process.

Experimental

Preparation of intercalates

The halloysite mineral used in this study is from Szeg in Hungary. The intercalate – using the 2–20 µm sized fraction of the clay – was prepared by mixing 500 mg of the halloysite with 10 cm^3 of an analytical grade, 85% hydrazine-hydrate aqueous solution (Reanal Budapest, Hungary) for 80 h at room temperature, magnetically stirred in a closed vessel. Immediately before analysis, the excess solution was decanted and the paste-like complex was dried under flowing nitrogen until a powdery material was obtained.

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 25 mA.

Diffuse reflectance Fourier-transform infrared spectroscopic (DRIFT) analysis

FT-IR (DRIFT) spectra of the samples heated to different temperatures were recorded by means of a Bio-Rad FTS 60A-type spectrometer. 512 scans were co-added at a resolution of 2 cm^{-1}. Approximately 3 mg sample was dispersed in 100 mg oven-dried, spectroscopic grade KBr. Reflected radiation was collected at ~50% efficiency. Background KBr spectra were obtained and spectra rationed to the background. The DRIFT accessory used is of the so-called 'praying monk' design accommodating powdery samples mixed with KBr in the sample cap (3 mm deep, 6 mm in diameter). The reflectance spectra expressed as Kubelka–Munk unit *vs.* wavenumber curves are very similar to absorbance spectra and can be evaluated accordingly.

Thermal analysis

Thermal decomposition of the intercalate was carried out in a Derivatograph PC-type thermoanalytical instrument (Hungarian Optical Works, Hungary) in a flowing nitrogen atmosphere (250 cm^3 min^{-1}) at a pre-set, constant decomposition rate of 0.15 mg min^{-1}. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 0.5°C min^{-1}). The samples were heated in an open platinum crucible at a rate of 0.5°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

The thermal behaviour of the hydrazine-hydrate intercalated halloysite in nitrogen atmosphere under dynamic heating conditions (5°C min^{-1} heating rate) is shown in Fig. 1. By comparing the curves, it can be concluded that hydrazine-hydrate is lost in

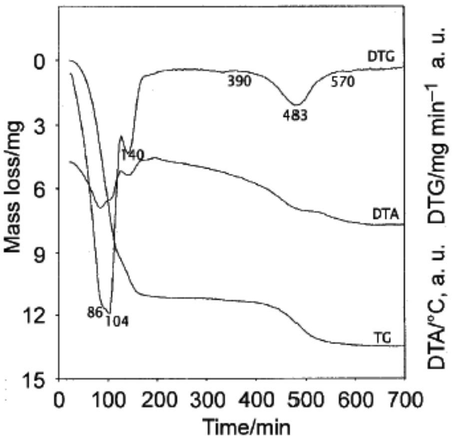

Fig. 1 Thermoanalytical curves of hydrazine-hydrate intercalated halloysite under dynamic heating at 5°C min^{-1} in nitrogen atmosphere

two closely overlapping mass loss stages at 86 and 104°C. A third (well-separated) step is also observed at 140°C, followed by the dehydroxylation of the thermally deintercalated mineral between 390 and 570°C. Based on our earlier findings with hydrazine-intercalated kaolinites, it is most likely that in the decomposition stage at 140°C hydrazine is liberated alone, i.e. without much water [12]. Due to the close overlap of the gas evolution processes and also to the fact that a standard starting condition can hardly be defined, an accurate quantitative evaluation in terms of mole bonded reagent per mole inner surface hydroxyl is not possible. With the use of the quasi-isothermal, quasi-isobaric option of the instrument, however, it is possible to increase resolution and to establish standardized conditions for comparison. Therefore, controlled-rate thermogravimetric experiments were performed providing time enough for the inherently slow transport of heat between the sample and the furnace chamber and for the establishment of an equilibrium between gas phase diffusion processes of opposite direction (transporting decomposition products from the sample to the furnace chamber and nitrogen to the sample to replace gas phase decomposition products). When a constant rate of decomposition (a straight line in the DTG signal) is attained, the state of equilibrium in the opposite gas phase diffusion processes has been reached as well.

The thermoanalytical curves of 248.9 mg hydrazine-hydrate intercalated halloysite heated at a pre-set rate of 0.15 mg min^{-1} are given in Fig. 2. When the set rate of decomposition was attained (a straight line in the DTG signal), the temperature remained essentially constant at approx. 46°C. On prolonged heating (after about 200 min) the temperature increased and then remained almost constant again at about 64°C for some 100 min. On further heating a decrease of the decomposition rate and an increase of the temperature was observed resulting in two minima in the DTG curve at 77 and 103°C. With further heating the complex is completely decomposed between 103 and 227°C. The deintercalated sample was heated to 700°C in order to determine the amount of water re-

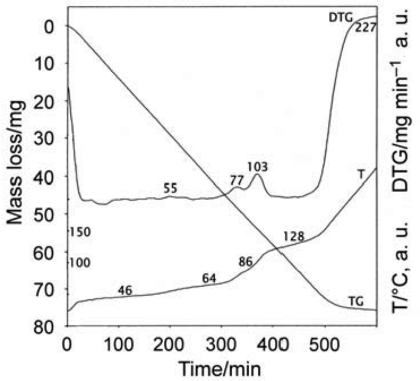

Fig. 2 Controlled rate thermal analysis experiment of hydrazine-hydrate intercalated halloysite dried under nitrogen before CRTA analysis

leased during dehydroxylation of the mineral between 390 and 570°C. The thermal behaviour of the halloysite fully expanded by hydrazine-hydrate (as evidenced by X-ray diffraction measurements) can be interpreted as follows. Adsorbed (surface-bonded) hydrazine-hydrate is lost in a quasi-isothermal, equilibrium step until 55°C. The adsorbed reagent amounting to 0.31 mol hydrazine-hydrate per mol inner surface hydroxyl is connected to the outer and inner surfaces of the fully expanded mineral. Weakly bonded hydrazine can be connected to the siloxane layer through the hydrogen atoms, can be present as a space filler or inserted into the ditrigonal cavity of the siloxane layer [10]. The quantity of the weakly bonded reagent liberated between 55 and 77°C is 0.20 mol hydrazine hydrate per mol inner surface hydroxyl. The mass loss stages between 77 and 103°C as well as between 103 and 227°C belong to strongly bonded hydrazine lost in equilibrium, but non-isothermal processes. The amount of the two types of strongly bonded (intercalated) reagent is 0.07 mol hydrazine-hydrate and 0.36 mol hydrazine per mol inner surface OH group, respectively. These hydrazine molecules form hydrogen bonds with the inner surface OH groups. Based on earlier results with FT-IR and Raman spectroscopy, the inner surface OH groups are infrared active and Raman inactive in a kaolinite intercalation complex with hydrazine-hydrate. Based on this observation, the intercalation of a hydrazine-water unit (as $[NH_2{-}NH_3]^+OH^-$) was proposed [11]. TG-MS results also showed that water and hydrazine are lost simultaneously but with an 'off-set' from the heated complex (water is released at a lower temperature than hydrazine, resulting in the presence of water-free hydrazine in the last stage of decomposition [12]).

In a parallel experiment heating was stopped at 77°C and the quenched sample was immediately subjected to XRD analysis (Fig. 3a). The XRD pattern of the partially heated complex showed two reflections with *d*-values of 10.2 and 9.6 Å. When the sample was exposed to room air for 1 h, the 9.6 Å reflection almost disappeared and the complex re-expanded to the original *d*-value of 10.2 Å (Fig. 3b). This phenomenon can be explained by the uptake of water. Considering the results of Johnston and Stone with the intercalation of water-free hydrazine resulting in an expansion of kaolinite to 9.6 Å [10],

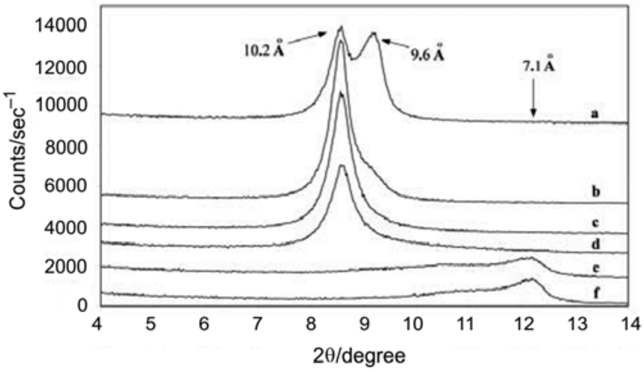

Fig. 3 X-ray diffraction patterns of hydrazine-hydrate intercalated halloysite CRTA treated to 77°C (a) and then exposed to air for 1 h (b), 1 day (c), 2 days (d), 7 days (e) and 20 days (f)

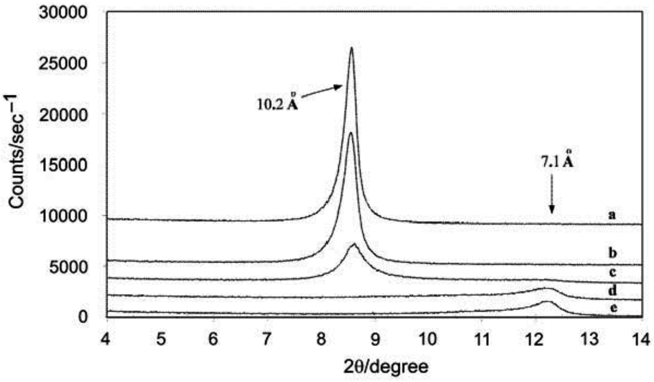

Fig. 4 X-ray diffraction patterns of hydrazine-hydrate intercalated halloysite exposed to air for 0 h (a), 2 h (b), 1 day (c), 7 days (d) and 19 days (e)

the following conclusion can be drawn. When hydrazine-hydrate is intercalated, the halloysite expands to 10.2 Å. When the clay reacts with pure hydrazine, or water is removed from the complex by heating an expansion (or partial collapse) of the kaolinite to 9.6 Å occurs. After about a week in contact with room air (Figs 3e and 3f), the expanded structure no longer exists (hydrazine is lost completely).

When the fresh intercalate is subjected to X-ray diffraction analysis, a single peak can only be observed with a *d*-value of 10.2 Å (Fig. 4a). Upon exposure to room air, the complex decomposes gradually, and the original structure with a *d*-value of 7.2 Å is restored. This band, however, is broad and extended on the higher 2Θ side indicating the presence of several expanded structures. It can be concluded that a partially hydrated halloysite structure is obtained after the decomposition of the complex. Thermogravimetric analyses showed that the residual water amounts to 3.60 % and is liberated up to 300°C.

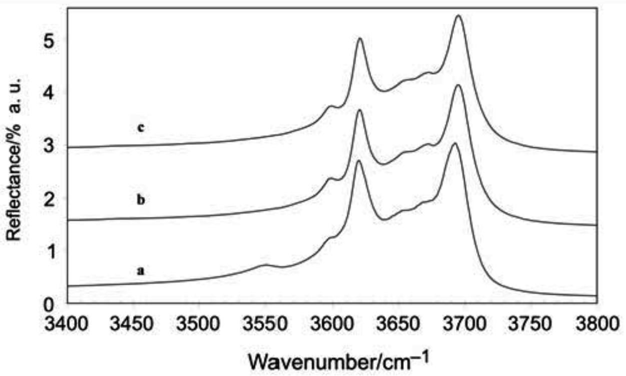

Fig. 5 DRIFT spectra of the O–H stretching region of: a – halloysite; b – hydrazine-hydrate intercalated halloysite CRTA-treated to 77°C, exposed to air for 20 days and heated to 300°C; c – hydrazine-hydrate intercalated halloysite exposed to air for 19 days and heated to 300°C

A comparison of the FT-IR spectra of the original halloysite and the spontaneously decomposed intercalate can be made in Fig. 5. While the ν_1 inner surface OH stretching band appears at 3693 cm^{-1} in the original mineral (Fig. 5a), this band shifts to 3696 cm^{-1} in the treated sample. It is interesting to observe that the other two inner surface OH stretching bands at 3669 and 3652 cm^{-1} are slightly more resolved in the treated sample. Also, the original mineral contains two types of water resulting in water OH stretching bands at 3598 and 3551 cm^{-1}. In the water deformation vibration range two bands appear at 1652 and 1622 cm^{-1}, as well. The treated mineral does not contain the loosely bonded water giving an OH stretching band at 3551 cm^{-1}.

Conclusions

- With the use of controlled-rate thermal analysis, the presence of two different types of hydrogen-bonded reagent can be identified – and distinguished from the adsorbed and weakly bonded part – in a halloysite structure fully expanded by hydrazine-hydrate.
- The occurrence of the 9.6 Å reflection in the partially decomposed complex is due to the presence of hydrazine hydrogen-bonded directly to the inner surface OH groups. The presence of the 10.2 Å reflection is explained by the connection of hydrazine molecules to the OH groups through water (i.e. in the form of hydrazine-hydrate).
- The intercalation of hydrazine into halloysite is complex and shows the different types of interactions of the reagent with the mineral (outer and inner) surfaces.
- With intercalation (and deintercalation) of hydrazine in the halloysite structure a slight increase in structural order can be observed.

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