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THERMAL BEHAVIOUR OF KAOLINITE INTERCALATED WITH FORMAMIDE, DIMETHYL SULPHOXIDE AND HYDRAZINE

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Abstract

The thermal behaviour of kaolinites intercalated with formamide, dimethyl sulphoxide and hydrazine has been studied by simultaneous TG-DTG-DTA-EGA and TG-MS techniques. The omplexes can be decomposed completely without dehydroxylating the mineral. It was found that he amount of intercalated guest molecules per inner surface OH-group is close to unity for the ormamide and dimethyl sulphoxide intercalates. For the intercalation of hydrazine it was found hat hydrazine is locked in the expanded mineral as hydrazine hydrate and its amount is somewhat higher than that obtained for the other two reagents. The thermal evolution patterns of the guest molecules revealed that all the three reagents are bonded at least in two different ways in the interlayer space.

Keywords: evolved gas analysis, intercalation, kaolinite, TG-DTG-DTA, X-ray powder diffraction

ntroduction

Kaolinite is an important industrial raw material having widespread application .g. in the manufacturing of paper (as a coating pigment and filler), in inks and paints as an extender) as well as as an additive in the production of rubber and polymers. The application of kaolinite is closely related to its surface reactivity. The reactivity of kaolinite internal surfaces can be tested via the insertion of low molecular mass organic reagents (e.g. potassium acetate, hydrazine, etc.) as guest molecules in between the layers consisting of the two-dimensional arrangements of a tetrahedral siloxane) and an octahedral (gibbsitic) sheet [1, 2].

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Although the process of intercalation (deintercalation) and the structure of the intercalation complex has already been studied e.g. by Raman microscopy [3], FTIR (DRIFT) spectrometry [4] and X-ray diffraction [5], a more detailed investigation is necessary to understand the structure of clay-organic complexes.

In spite of the fact that TG and DTA have long been used for the study of clay minerals, the application of these techniques to the investigation of intercalated kaolinites is rather limited [6–8]. In the present study the thermal behaviour of reactive kaolinites intercalated with dimethyl sulphoxide, formamide and hydrazine is discussed in detail.

Experimental

Preparation of intercalates

The clay minerals used in this study are highly reactive kaolinites from Királyhegy and Szeg (Hungary). Formamide intercalates were prepared in a way that 500 mg of kaolinite were mixed with 5 cm^3 of aqueous formamide (Reanal, Hungary) solution (diluted 1:1 with water) for 80 hours at room temperature. The excess solution was removed by centrifugation and the intercalate kept in a desiccator before analysis.

As to the dimethyl sulphoxide (DMSO) intercalate, a 500 mg portion of the mineral was stirred in 5 cm^3 of anhydrous dimethyl sulphoxide (Reanal, Hungary) in a closed vessel for 80 h at room temperature. Then the solid was separated from solution by centrifugation and air-dried for a week before analysis. Raman spectra showed the presence of water in the so-called anhydrous DMSO. For the preparation of kaolinite-DMSO complexes water-DMSO mixtures were used by previous authors [9]. In fact, Olejnik found that the optimum rate of intercalation occurred when the kaolinite was suspended in DMSO containing 9% water [10].

Hydrazine intercalates were prepared in a closed ampoule (a 500 mg portion of the clay was mixed with 5 cm^3 of 98% hydrazine hydrate (LOBA, Austria) solution for 80 h at room temperature) and the ampoule was opened – and the intercalate separated from solution – right before investigation.

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 copper tube, operating at 40 kV and 35 mA.

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}. For monitoring of evolved water, a continuous and selective water detector was connected to the Derivatograph and the EGA signal was recorded along with the TG-DTG-DTA curves [11]. 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 argon atmosphere at a rate of 10°C $\min^{-1}$.

Result and discussion

X-ray analyses

The X-ray diffraction analyses of the DMSO and hydrazine complexes showed and almost 100% intercalation rate (Fig. 1). With DMSO, the kaolinite layers expanded from 7.2 to 11.2 Å, while the incorporation of hydrazine into the interlamellar space resulted in an expansion to a *d*-spacing of 10.4 Å. As to the formamide intercalate, an expansion to 10.0 Å and an intercalation reactivity of ca 90% was observed.

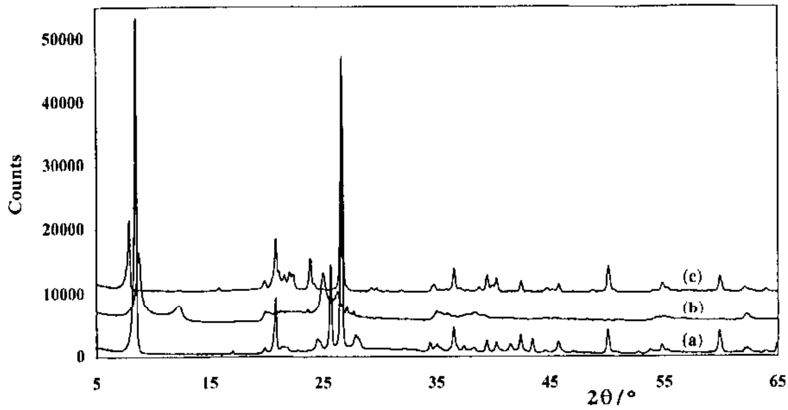

Fig. 1 XRD patterns of (a) Királyhegy kaolinite intercalated with hydrazine, (b) Szeg kaolinite intercalated with formamide, (c) Királyhegy kaolinite intercalated with dimethyl sulphoxide

Formamide intercalate

The thermoanalytical curves of 40.11 mg of formamide intercalated kaolinite are given in Fig. 2. The EGA analysis revealed the liberation of 4.84% water in the first mass loss step at 80°C. The removal of formamide from the complex was observed in two stages at 150 and 210°C. Taking into consideration that the amount of dehydroxylation water released between 360 and 565°C was 8.19%, it is possible to calculate the amount of formamide connected to the inner surface hydroxyls via hydrogen bonding. In this calculation it has to be taken into account that in the half unit cell of kaolinite there are three inner surface hydroxyls situated in the outer, un-

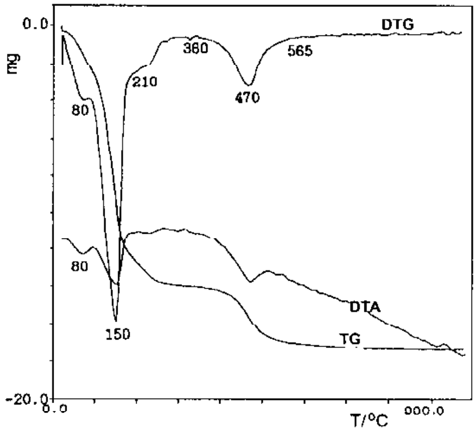

Fig. 2 Thermal behaviour of formamide intercalated Szeg kaolinite

shared plane, whereas the inner OH group is located in the lower, shared plane of the octahedral sheet. While the inner surface hydroxyls are accessible by the guest molecules, the inner hydroxyl which essentially lies parallel to the 001 plane and points toward the vacant dioctahedral site in the kaolinite structure [12] is not accessible at all. The calculation results show that each inner surface OH group can bind 0.98 formamide molecule, most likely through the C=O group, as evidenced by Raman spectroscopic measurements [13].

DMSO intercalate

The TG-DTG-DTA and EGA curves of 39.02 mg of DMSO intercalated kaolinite are shown in Fig. 3. By comparing the curves, the following can be concluded with respect to the thermal behaviour of this complex. The intercalate contains 6.20% water which is lost up to about 80°C. In addition, traces of water are released in the second step of decomposition at 173°C only, as indicated by the water detector signal. The amount of DMSO liberated in two stages at 117 and 173°C is 15.17 and 7.44%, respectively. Since the two mass loss stages represent a temperature difference of 56°C in the DTG peak positions, it is reasonable to suppose that the complex contains two types of bonded DMSO. Previous investigation by Raman microscopy [14] gave evidence for the presence of monomeric and polymeric DMSO molecules in the intercalate. Taking into consideration that the amount of dehydroxylation water released between 400 and 600°C was 3.95%, each inner surface OH-group binds 0.88 DMSO molecule. This means that – in spite of the complete expansion of the layers – some of the inner surface OH-groups remain free in the complex. This result is in harmony with Raman spectroscopic investigations [14] which showed that not all of the band intensities were lost upon intercalation. The two DMSO mass loss stages gave a ratio of 2:1 (67.1 and 32.9%), indicating that the amount of DMSO in monomeric form is twice as much as that in polymeric form.

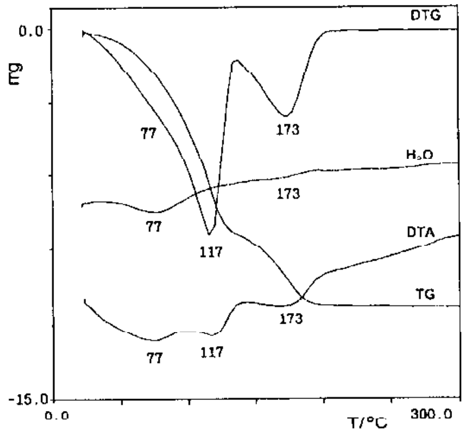

Fig. 3 Thermal behaviour of dimethyl sulphoxide intercalated Királyhegy kaolinite

Iydrazine intercalate

The thermoanalytical curves of 87.97 mg of the hydrazine intercalated kaolinite re given in Fig. 4. The EGA analysis showed the liberation of water throughout the ntire thermal decomposition range. A more detailed study of the gas evolution patrn was carried out by TG-MS technique. Figure 5 gives the ion intensity curves of I_2O^+ (m/z=18) and the NH^+ fragment (m/z=15) as a function of the temperature (the ater one represents the process of hydrazine evolution). Comparing the curves it can e concluded that water and hydrazine are simultaneously released up to about 70°C. t is supposed that in this temperature range (from ambient to 70°C) hydrazine hy-

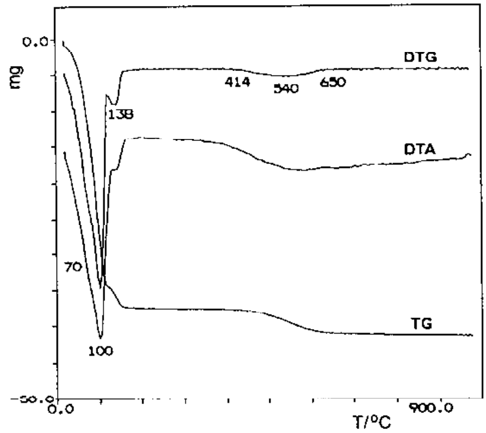

Fig. 4 Thermal behaviour of hydrazine hydrate intercalated Királyhegy kaolinite

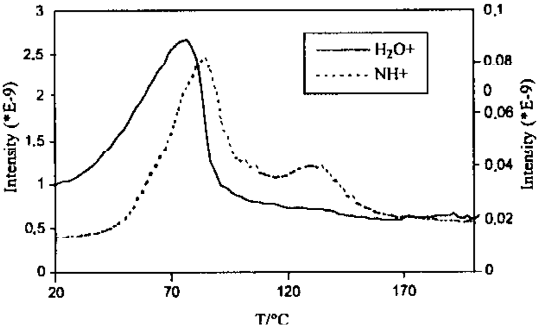

Fig. 5 Mass spectrometric ion intensity curves of hydrazine hydrate intercalated Királyhegy kaolinite

drate bonded to the outer surfaces of the clay particles was lost to the atmosphere. Above 70°C an offset can be seen in the peak maxima. Above 100°C the liberation of water is slowed down, while hydrazine shows a higher release rate. This behaviour can be explained in the following way. When the kaolinite is intercalated with hydrazine, it is actually intercalated with hydrazine hydrate. On heating both hydrazine and water are released from the complex, but water is less strongly bonded to the clay internal surface then hydrazine itself. The idea to suppose hydrazine hydrate intercalation is supported by FTIR (DRIFT) and Raman spectroscopic measurements as well [15]. Based on the quantitative evaluation of the TG and DTG curves, a figure corresponding to 1.3–1.5 mole hydrazine hydrate per mole inner surface OH can be obtained in parallel investigations. Similarly to the case with the formamide or DMSO intercalate, part of the intercalated hydrazine is more strongly bonded to the kaolinite internal surface and, therefore, is lost at a higher temperature (138°C).

Conclusions

The common feature of the three types of intercalation complexes of kaolinite is that the guest molecules are volatile liquids at room temperature. Therefore, except for the hydrazine intercalate which decomposes on exposure to air, the air-dried complexes can be considered as expanded minerals having guest molecules in between the kaolinite layers, only. The fact that these compounds are of low boiling point liquids supports the idea of having no (or limited) adsorption on the outer surface of the clay particle. In addition, the particle surface area is negligible as compared to that of the inner surfaces. Thus, the idea to calculate the amount of intercalated reagent per inner OH-group seems to be justified. This calculation shows that the amount of guest molecules per inner surface OH-group is close to unity for the formamide and DMSO intercalates. As to the intercalation complex with hydrazine, this figure is somewhat higher and can be determined with a lower precision due to the close overlap of the surface-bonded and intercalated hydrazine mass loss stages.

Due to the inherent advantage of thermal analysis, it is possible to reveal differences in the bonding strength of the intercalating reagent in all the three cases. The identification of differently bonded reagent molecules indicates the complexity of the system and can contribute substantially to the reliable identification of the structure of these complexes by XRD, FTIR and Raman spectroscopic techniques.

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