Journal of Thermal Analysis, Vol. 49 (1997) 1441-1448

STUDY OF THE STRUCTURE AND THERMAL BEHAVIOUR OF INTERCALATED KAOLINITES

J. Kristóf[1], M. Tóth[2], M. Gábor[3], P. Szabó[4] and R. L. Frost[5]*

[1]University of Veszprém, Department of Analytical Chemistry, H-8201 Veszprém,
P.O. Box 158
[2]Research Laboratory of Geochemistry of the Hungarian Academy of Sciences,
H-1112 Budapest, P.O. Box 132
[3]Institute of Inorganic and Analytical Chemistry, L. Eötvös University, H-1518 Budapest,
P.O. Box 32
[4]Research Laboratory of Inorganic Chemistry, Hungarian Academy of Sciences,
H-1112 Budapest, P.O.Box 132, Hungary
[5]Centre for Instrumental and Developmental Chemistry, Queensland University of Technology,
2 George Street, G.P.O. Box 2434, Brisbane Q 4001, Australia

Abstract

Intercalation complexes of three different Hungarian kaolinites with hydrazine and potassium acetate were investigated by FT-IR (DRIFT) spectrometry, X-ray diffraction, and thermogravimetry combined with mass spectrometry. Differences were found in the thermal behaviour of the complexes as well as in the rehydration – reexpansion patterns of the heated intercalates. An XRD method is proposed for the distinction of kaolinite and 7.2 Å halloysite present in the same mineral.

Keywords: diffuse reflectance FT-IR spectrometry, intercalation, kaolinites, thermal analysis, X-ray powder diffraction

Introduction

The ability of kaolinite and halloysite to intercalate certain organic and inorganic compounds has been recognised independently by Wada [1] and Weiss [2] in 1962. The reactive guest molecules – e.g. urea, acetamide, hydrazine, alkali salts, short-chain fatty acids (in particular acetic and propionic acids) – enter the interlayer spaces and expand the silicate layers. Although the structure and behaviour of clay intercalation complexes are not well understood, several authors investigated the mechanism of kaolinite intercalation [3–7] .

The intercalation reactivity of kaolinite appears to be one of the important factors that control technical applicability [8]. The use of kaolinite intercalates in industrial processes, environmental decontamination, etc. depends strongly on the ease of their formation. The aim of the present study is to reveal the nature of the

---

* Author to whom all correspondence should be addressed.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

interlayer structure, the intercalation reactivity as well as the thermal behaviour and stability of three different Hungarian kaolinites intercalated with hydrazine and potassium acetate.

Experimental

Materials

The investigated kaolinites have some genetic differences. The Királyhegy kaolinite (K) was formed under hydrothermal conditions, while the Sárisáp one (S) formed in sandstone by kaolinitization with a hydrothermal after-effect. The Szegilong kaolinite (SZ) was redeposited from a colloidal solution. The chemical composition of kaolinite K is 80.5% (*w/w*) SiO_2, 12.6% Al_2O_3, 0.02% Fe_2O_3, 0.09 % TiO_2, 0.03% MgO, 0.01% CaO, 0.05% K_2O, 0.02% Na_2O and 5.8% H_2O. Kaolinite SZ contains 47.3% SiO_2, 32.6% $A1_2O_3$, 3.1% Fe_2O_3, 0.2% CaO, 0.5% K_2O, 0.1% Na_2O and 14.8% H_2O. The chemical composition of kaolinite S has already been reported [7] .

Analytical grade potassium acetate (Reanal) and hydrazine hydrate of 98% purity (Carlo Erba) were used as intercalating reagents.

Methods

Thermoanalytical investigations were carried out in argon atmosphere in a Perkin Elmer TGS-2 thermobalance coupled with a Hiden HAL 3F/PIC type mass spectrometer at a heating rate of 20°C min^{-1} and 70 eV electron energy. XRD measurements were performed in a Philips PW-1050/25 type powder diffractometer operated at 45 kV and 35 mA using CuK_α radiation. Diffuse reflectance FT-IR (DRIFT) spectra of samples were taken by a BIO-RAD Digilab FTS 60A type spectrometer (256 spectra were coadded at a resolution of 2 cm^{-1})

Kaolinites were isolated from the raw minerals by sedimentation. Samples under 30 μm were used for all experiments. 300 mg portions of air-dried kaolinites were stirred in 30 cm^3 saturated (7.2 *M*) potassium acetate solution for 80 h at room temperature. The excess liquid was removed by centrifugation and the wet clay was air-dried for a week before investigation. Aliquots of kaolinites were treated with 11 *M* hydrazine hydrate solution according to Weiss *et al.* [9]. Here 300 mg kaolinite was put in an ampoule and filled with 30 cm^3 hydrazine solution, sealed immediately and kept at 65±1 °C in a temperature controlled water bath. After opening the ampoule, the excess liquid was removed and the wet reaction products were immediately examined by XRD.

The degree of intercalation of kaolinites (α) was determined by XRD. The value of α was taken from the intensities of the 001 reflection before and after intercalation according to Wiewiora and Brindley [10]. An aliquot of the K kaolinite intercalated with potassium acetate was stirred in distillated water and portions of the clay sampled at specified time intervals were analyzed by XRD and DRIFT.

Potassium acetate intercalates of the three kaolinites were heated to the melting temperature of the intercalated acetate (293 °C) in a Mettler TA-1 thermoanalyser under N_2 at a heating rate of 6°C min^{-1} and cooled to room temperature. Then the samples were exposed to air for different times and examined by XRD method.

Results and discussion

Intercalation reactivity of different kaolinites

The XRD results proved that the Hungarian clays contain well-crystallized kaolinite, quartz and a small amount of illite. The investigated kaolinites differ from each other in terms of their ordered-disordered structure. Kaolinite K is highly ordered, S is medium ordered and SZ is disordered along the b-axis.

All the three kaolinites reacted with saturated potassium acetate solution at room temperature. Their XRD patterns show the intercalation of potassium acetate, indicated by a basal spacing of 14.1 Å. The degree of intercalation was 94% in the case of the highly ordered K kaolinite and the medium ordered S kaolinite, and 88% for the disordered SZ kaolinite. The reproducibility of intercalation was found to be ±1% in parallel investigations. Several authors mentioned about commonly and intimately intermixed kaolinites containing microdomains of different chemical reactivity [11, 12]. The quantities of intercalated fractions indicated the high reactivity of the three clays, dissimilarly to the disordered type Georgia kaolinite where a reactivity of about 58% could be attained by potassium acetate [5]. The XRD patterns also prove that the coherently scattering domain size of the investigated kaolinites increased and the deformation decreased as a result of intercalation [13].

To understand the high reactivity of the disordered SZ kaolinite, the intercalation of the three clays and the Georgia kaolinite was made with 11 *M* hydrazine solution and the products were investigated by XRD. The basal spacing of the formed hydrazine complexes is 10.4 Å, except for the SZ clay which expands to a *d*-value of 10.3 Å (Fig. 1A). The hydrazine complexes were then leached with water after

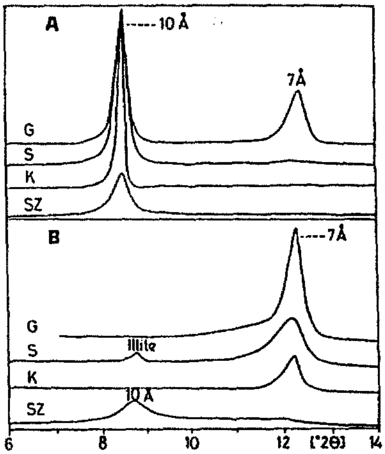

Fig. 1 XRD patterns of kaolinite-hydrazine complexes before (A) and after (B) leaching with water (G: Georgia kaolinite, S: Sárisáp kaolinite, K: Királyhegy kaolinite, SZ: Szegilong kaolinite)

Range *et al.* [11] for distinguishing differences in the reactivity of kaolinites (Fig. 1B). The XRD patterns showed that the intercalated hydrazine complexes collapsed to their original basal spacing of 7.2 Å, except for the disordered SZ sample from which an aqueous complex was formed with a 10.0 Å basal spacing typical of halloysite. Thus, it can be concluded that the clay from Szegilong contains halloysite with 7.2 Å spacing and that is the reason for the high reactivity of the disordered sample. This is a good example for the case when a distinction between a disordered kaolinite and a halloysite with the same 7.2 Å basal spacing by XRD can only be made after intercalating the clay and leaching with water. However, with FT-IR spectroscopy the halloysite structure can be identified directly via the hydrogen bonded OH band observed at 3600 cm^{-1} (Fig. 2).

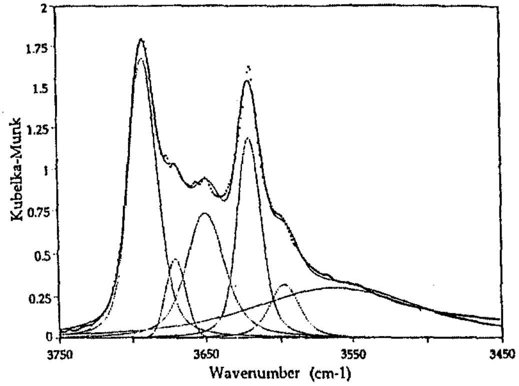

Fig. 2 FT-IR spectrum of the Szegilong kaolinite

Thermal behaviour of potassium acetate complexes

The thermal behaviour of the potassium acetate complexes shows also differences. The TG-DTG-MS curves of the acetate complex of the highly ordered K kaolinite (Fig. 3) give two distinct DTG peaks at 380 and 490°C. The main gaseous reaction product at 380°C is water indicating the dehydroxylation of the intercalated kaolinite, accompanied with a small amount of acetate decomposition products. The dehydroxylation temperature is lower by about 280°C than that of the pure kaolinite sample. At 490°C the main decomposition products of intercalated acetate could be detected along with a small amount of water indicating the dehydroxylation of the non-intercalated part of kaolinite.

The TA pattern of the intercalation complex of the SZ kaolinite (Fig. 4) differs from that of the K one. The DTG curve shows only one peak at 410°C. These data show that the dehydroxylation of the intercalated SZ kaolinite does not separate well from the decomposition of the acetate, as compared to the case with the K complex. All the three acetate complexes are stable to 300°C in argon atmosphere, and their thermal stability does not depend on the ordered-disordered structure of the original clay. Decomposition of the intercalates begins only after the melting of the potassium acetate intercalated in the interlayer spaces. The TG-MS patterns showed that dehydroxylation occurs

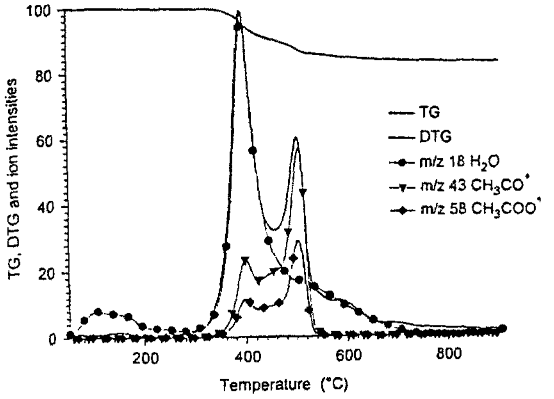

Fig. 3 TG, DTG and ion intensity curves of the Királyhegy kaolinite intercalated with potassium acetate

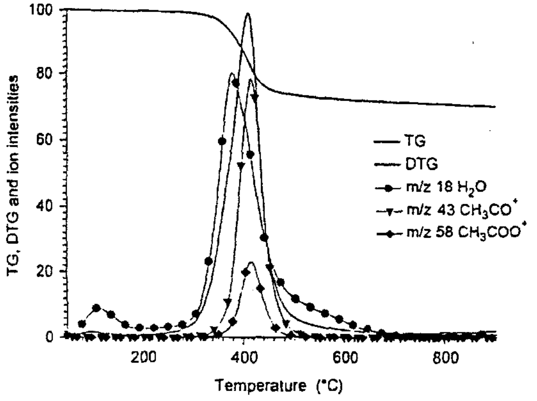

Fig. 4 TG, DTG and ion intensity curves of the Szegilong kaolinite intercalated with potassium acetate

in the first stage of decomposition for all the clays investigated. As a general rule, the thermal stability decreases significantly as a result of intercalation.

Stability of the potassium acetate complex against water

The stability of the K kaolinite-potassium acetate complex against water was investigated in a way that the intercalate was continuously stirred in pure water, and portions at specified time intervals were analyzed – after centrifugation – by FT-IR and XRD techniques. The FT-IR patterns in Fig. 5 show the ν_a and ν_s bands of the acetate group (at 1621 and 1408 cm^{-1}, respectively) after 1 min, 30 min and 24 h of washing. It can be stated that traces of organics are still present even after 24 h, indicating the high stability of the complex against water. XRD results of the washed samples show a similar behaviour.

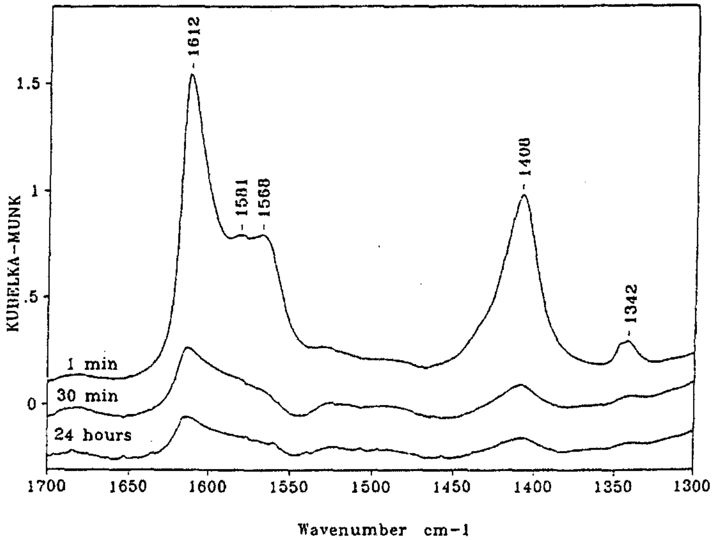

Fig. 5 FT-IR spectra of the Királyhegy kaolinite-potassium acetate complex washed with water for different times

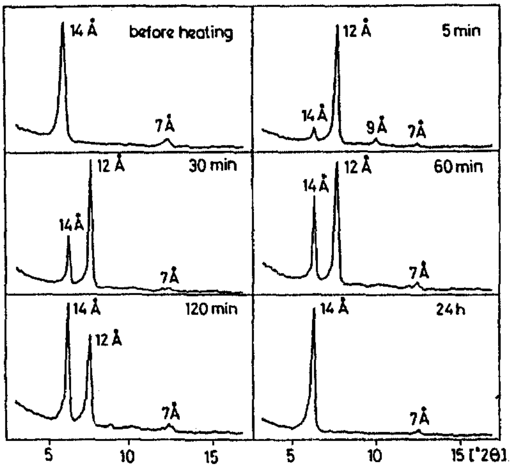

Fig. 6 *d*-values of the Királyhegy kaolinite-potassium acetate complex exposed to air after heating the sample to 293°C and cooling back to room temperature in N_2 atmosphere

Rehydration features of the preheated intercalates

It was previously reported that a partial collapse of the intercalate takes place on heating to the melting temperature of potassium acetate resulting in new reflections which gradually disappear when the sample is exposed to air [7] . The *d*-values of the heated K kaolinite–potassium acetate complex as a function of the exposure time are shown in Fig. 6. The new, strong XRD peak observed at 12 Å gradually decreases and finally diminishes after 24 h in contact with humid air. At the same time the complex gradually reexpands to its original *d*-value of 14.1 Å. On the contrary, the behaviour of the disordered SZ kaolinite is completely different (Fig. 7) since in this case the peak at 14.1 Å does not exist at all, and the 12 Å one is very weak as well. However, two strong, new peaks at 9.1 and 10.0 Å appear which diminish with time. The latter two peaks indicate the presence of potassium acetate hydrate (ASTM No. 20-845). The 12 Å reflection of the complex is built up gradually at the expense of the previously mentioned acetate peaks, and after 24 h the original structure of the complex is regained.

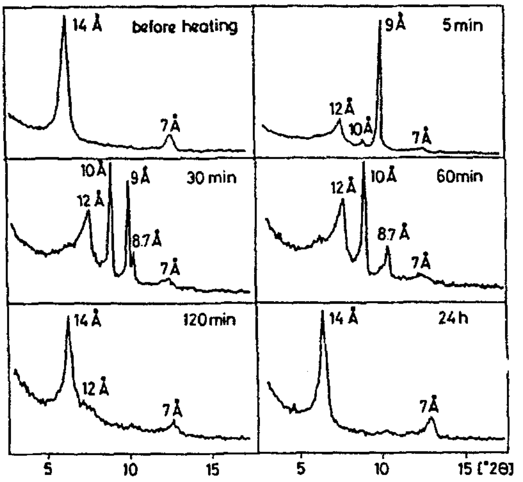

Fig. 7 *d*-values of the Szegilong kaolinite-potassium acetate complex exposed to air after heating the sample to 293°C and cooling back to room temperature in N_2 atmosphere

In the case of the medium ordered S kaolinite complex a new, strong peak appears after 5 min at 12 Å, in addition to the low intensity 14.1 Å one and the two acetate bands at 9.1 and 10.0 Å. The intensity of the 12 Å reflection decreases with time, but it is still observable after 24 h. The main difference between the highly ordered and disordered clay complexes is that the incorporation of free acetate in the kaolinite structure is hindered for a disordered kaolinite. In the case of the medium ordered S kaolinite the incorporation of hydrated acetate is moderated.

Conclusion

The combination of FT-IR, XRD and TG-MS techniques for the study of clay-organic complexes can be of an advantage in an attempt made to reveal small differences between kaolinites with regard to their structure, reactivity and thermal behaviour. The multi-method approach proved to be promising and can be recommended for the investigation of kaolinites of different origin.

* * *

The authors wish to thank Dr. E. Máttyás for providing the kaolinite samples and for carrying out their chemical analysis. Financial support from the Hungarian Scientific Research Fund under grant No. OTKA-014179 is gratefully acknowledged.

References

1 K. Wada, Am. Miner., 46 (1962) 78.
2 A. Weiss, Angew. Chem., 73 (1962) 736.
3 J. G. Thompson, N. Gabbitas and P. J. R. Uwins, Clays Clay Miner., 41 (1993) 73.
4 S. Yariv, A. Nasser, K. H. Michaelian, I. Lapides, Y. Deutsch and N. Lahav, Thermochim. Acta, 234 (1994) 275.
5 M. Gábor, L. Pöppl, V. Izvekov and H. Beyer, Thermochim. Acta, 148 (1989) 431.
6 J. Kristóf, J. Mink, E. Horváth and M. Gábor, Vibr. Spectrosc., 5 (1993) 61.
7 M. Gábor, M. Tóth, J. Kristóf and G. Komáromy-Hiller, Clays Clay Miner., 43 (1995) 223.
8 M. Fernandez-Gonzales, A. Weiss and G. Lagaly, Keram. Z., 28 (1976) 56.
9 A. Weiss, W. Thielepape, W. Ritter, H. Schäfer and G. Göring, Z. Anorg. Allg. Chem., 320 (1963) 183.
10 A. Wiewiora and G. W. Brindley, Proc. Int. Clay Conf. Tokyo, 1 (1969) 723.
11 K. J. Range, A. Range and A. Weiss, Proc. Int. Clay Conf. Tokyo, 1 (1969) 3.
12 W. D. Keller and R. P. Haenni, Clays Clay Miner., 26 (1978) 384.
13 M. Tóth et al., in preparation.