

THERMAL BEHAVIOR AND DECOMPOSITION OF INTERCALATED KAOLINITE

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Abstract—Intercalation complexes of a Hungarian kaolinite were prepared with hydrazine and potassium acetate. The thermal behavior and decomposition of the kaolinite-potassium acetate complex was studied by simultaneous TA-EGA, XRD, and FTIR methods. The intercalation complex is stable up to 300°C, and decomposition takes place in two stages after melting of potassium acetate intercalated in the interlayer spaces. Dehydroxylation occurred, in the presence of a molten phase, at a lower temperature than for the pure kaolinite. FTIR studies revealed that there is a sequence of dehydroxylation for the various OH groups of intercalated kaolinite. The reaction mechanism was followed up to 1000°C via identification of the gaseous and solid decomposition products formed: H₂O, CO₂, CO, C₃H₆O, intercalated phases with basal spacings of 14.1 Å, 11.5 Å, and 8.5 Å as well as elemental carbon, K₄H₂(CO₃)₃·1.5H₂O, K₂CO₃·1.5H₂O, and KAISiO₄.

Key Words—Infrared spectroscopy, Intercalation, Kaolinite, Thermal Analysis, X-ray powder diffraction.

INTRODUCTION

Clay minerals can interact with organic and inorganic materials by adsorption, intercalation, and cation exchange. The basic principles of intercalation reactions were reported earlier for kaolinite (Lagaly, 1984). The reactive guest molecules enter the interlayer spaces and expand the silicate layers. The reactive molecules were classified by Weiss *et al.* (1966) as follows: 1) compounds forming strong hydrogen bonds to the silicate layers, e.g., urea, formamide, acetamide, and hydrazine; 2) compounds with pronounced betaine-like character with the possibility of strong dipole interactions with the silicate layers, e.g., dimethyl sulphoxide; and 3) alkali salts of short-chain fatty acids, in particular acetic and propionic acids. Non-reacting guest compounds are entrained between the layers by reactive guest molecules.

Formation of intercalation compounds has been used as a sensitive method for distinction of different types of kaolinites according to Fernandez-Gonzales *et al.* (1976), Jackson and Abdel-Kader (1978), and Theng *et al.* (1984). Range *et al.* (1969) and Keller and Haenni (1978) showed kaolins to be commonly and intimately intermixed, containing microdomains with different chemical reactivity. It is difficult to detect such mixing by XRD and DTA methods. The maximum degree of reaction is not always 100% even after very long reaction times, as this depends on the type of kaolin, degree of structural order, and particle size (Wiewiora and Brindley, 1969; Weiss *et al.*, 1963a). The intercalation reactivity appears to be one of the important

factors that control technical applicability. The aim of the present work is to reveal the intercalation reactivity of a Hungarian kaolin that formed in a sandstone by kaolinitization (probably with a hydrothermal after-effect), to collect some data about the ordered-disordered structure of this kaolin by intercalation, and to study the thermal behavior and decomposition reactions of the kaolin-potassium acetate complex via the continuous monitoring of the reaction products.

Investigations were started by intercalation of hydrazine. It is known from different authors that hydrazine reacts readily with several types of kaolinite, being special among the amines in that the complex formed is particularly strong (van Olphen, 1963; Weiss *et al.*, 1963b; Thompson, 1985). The intercalation reactivities of the investigated kaolin towards hydrazine and potassium acetate were compared as well.

EXPERIMENTAL METHODS

Materials

The kaolin sample used in the investigations was from Sársáp, Hungary. The hydrazine hydrate used was 98% pure (Carlo Erba), while potassium acetate was of analytical purity (Reanal). The chemical composition of the kaolin is 57.7 wt. % SiO₂, 28.5 wt. % Al₂O₃, 10.0 wt. % H₂O, 1.3 wt. % Fe₂O₃, 0.7 wt. % TiO₂, 0.6 wt. % CaO, 0.2 wt. % MgO, 0.8 wt. % K₂O, 0.2 wt. % Na₂O and 0.2 wt. % organic carbon. The specific surface area of the sample investigated was 27.1 m²/g, as measured by the water vapor sorption

Table 1. Experimental conditions and degree of reaction for the kaolin-hydrazine complex.

Particle size of the kaolinite (μm)	Concentration of the hydrazine solution (M)	Time of reaction (in h)	Degree of reaction (α) at 65°C (%)
Under 2	20	1	90
		24	94
30	10	1	90
		24	92
	20	24	92
		24	93
	24	94	

method (Gál, 1967; Juhász, 1982). Kaolinite was isolated from raw material by sedimentation. Samples with particle sizes of 30 μm and under 2 μm were used for the experiments.

Methods

The chemical analysis was made by means of a Perkin Elmer 5000 atomic absorption spectrometer. XRD measurements were performed with a Philips PW-1050/25 powder diffractometer at 45 kV and 35 mA using $\text{CuK}\alpha$ radiation. IR spectra of samples in KBr pellets were taken by a BIO-RAD Digilab FTS 45 type spectrometer in the 4000–400 cm^{-1} range. The thermal behavior of the reaction products was investigated by a Derivatograph C type instrument (Hungarian Optical Works, Budapest) connected to selective water, carbon dioxide, and carbon monoxide monitors (Kristóf *et al.*, 1991, 1990; Kristóf and Inczédy, 1993). Thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermal analysis (DTA), and temperature (T) curves were recorded simultaneously in nitrogen atmosphere at a heating rate of 5°C/min. DTA curves were obtained using Al_2O_3 as a reference material. The gaseous decomposition products formed during heating were also investigated by the TG-MS technique (a Perkin Elmer TGS-2 thermobalance was coupled with a Balzers QMG-511 mass spectrometer).

The air-dried kaolinite was treated with 20 M and 10 M hydrazine hydrate solutions according to Weiss *et al.* (1963b). Here 300 mg kaolin was put in an ampoule and filled with 30 cm^3 hydrazine solution, sealed immediately, and kept at 65° \pm 1°C in a thermostat. After opening the ampoule, the excess liquid was removed, and the wet reaction products were immediately examined by XRD. Other aliquots of kaolin (300 mg each) were treated with 30 cm^3 7.2 M (saturated) and 3.6 M potassium acetate solutions (pH about 8). The samples were shaken for 1, 8, 24 and 80 h at room temperature or kept at 65° \pm 1°C in a thermostat-controlled water bath. The excess liquid was removed by centrifuging, and the wet clay was stored in a humid atmosphere obtained with saturated solutions of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ until XRD investigation. A portion of the wet

Table 2. Experimental conditions and degree of reaction for the kaolin-potassium acetate complex.

Particle size of the kaolinite (μm)	Concentration of the potassium acetate solution (M)	Time of reaction (in h)	Degree of reaction (α) (%)		
			at 25°C	at 65°C	
Under 2	7.2	1	62	63	
		8	70	71	
		24	72	70	
		80	82	79	
		3.6	1	56	—
			8	59	60
30	7.2	24	62	61	
		80	65	—	
		8	86	87	
		24	84	84	
		3.6	24	78	76

clay was exposed to air. The air-dried samples were examined by FTIR and TA methods.

The degree of reaction (α) of kaolin with hydrazine and with potassium acetate was determined by XRD. The value of α is taken from the intensity of the (001) reflection of kaolinite and that of the intercalation compounds (Fenoll Hach-Ali and Weiss, 1969).

RESULTS

Reactivity of kaolinite

The XRD patterns showed that the investigated kaolin sample contains mainly medium-ordered kaolinite, less than 10% sericite-muscovite, and about 20% quartz.

The results of XRD investigations of the intercalation products formed are presented in Tables 1 and 2. The basal spacing of the kaolin-hydrazine complex is 10.5 Å and that of the kaolin-potassium acetate one is 14.1 Å. After 1 h at 65°C the degree of reaction with 20 M and 10 M hydrazine hydrate solutions is rather high (about 90%) for the kaolinite with particle size under 2 μm (Table 1). The reaction rate increased with time, especially in the case of the 20 M solution. The degree of reaction was maximum 94%. The reproducibility of intercalation was found to be ± 1 wt. % in parallel investigations.

The reactivity of the kaolinite in potassium acetate solutions is moderate. The maximum degree (about 86%) was found with the higher concentration potassium acetate solution (7.2 M) for the sample with 30 μm particle size, as in the reaction with hydrazine (Table 2). The degree of interaction was not affected significantly by the temperature but it increased with time, especially with more concentrated solutions. The stability of the kaolin-potassium acetate compound was followed, too. A sample with 82% intercalation was exposed to air for half a year. After this interval the degree of intercalation determined by XRD investigation was still 82 \pm 1 wt. %.

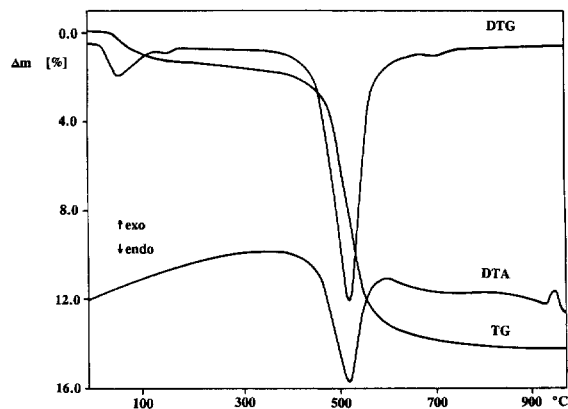


Figure 1. Thermoanalytical (TG, DTG, DTA) curves of the Hungarian kaolinite.

The effect of heating the intercalation complex of potassium acetate with kaolinite

Thermoanalytical results. Figure 1 shows the thermoanalytical curves of the Hungarian kaolinite. The onset of the dehydroxylation reaction is at about 380°C, and the reaction reaches a maximum at 520°C as indicated by the DTG curve.

The thermoanalytical and evolved gas analysis curves of the intercalated kaolin-potassium acetate sample (Figure 2) prove the strongly hygroscopic nature of the compound. The amount of adsorbed water is quite high and is completely removed until 200°C. At 298°C a sharp endothermic DTA peak was observed with no mass change at all. This peak indicates the melting of the intercalated potassium acetate. Decomposition of the intercalated compound takes place in two stages, at 430°C and 480°C, according to the DTG and DTA curves.

The water detector curve (curve H₂O in Figure 2) indicates that dehydroxylation occurs in the lower temperature range along with the formation of carbon dioxide as a product of acetate decomposition (Gábor *et al.*, 1989), while in the second stage carbon monoxide is formed together with other organic products. Carbon monoxide is also liberated in a slow reaction up to about 800°C due to the reaction of the potassium carbonate obtained and elemental carbon formed by cracking.

FTIR results. The structural changes of the kaolin and the kaolin-potassium acetate complex at elevated temperatures were followed by FTIR spectroscopy. The samples were heated to 350°, 400°, 500°, and 600°C in a nitrogen atmosphere and cooled back to room temperature. The heat-treated samples were then investigated in KBr pellets at a resolution of 2 cm⁻¹ and 64 scans. In the case of kaolinite (Figure 3), the four OH bands represent stretching vibration frequencies at 3697, 3671, 3654, and 3621 cm⁻¹. Upon increasing

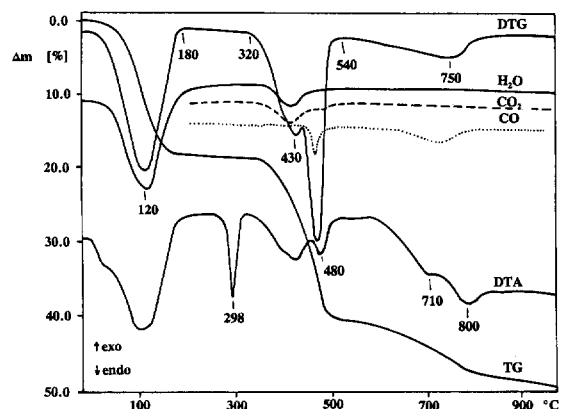


Figure 2. Thermoanalytical (TG, DTG, DTA) and evolved gas analysis (H₂O, CO₂, CO) curves of the kaolin-potassium acetate complex.

the temperature, the ratio of the bands does not change significantly. At 600°C, all the OH bands disappear.

Figure 4 shows the absorption bands of the kaolin-potassium acetate complex at 25°C (spectrum a). In addition to the four OH bands, a new (hydrogen-bonded) band appeared at 3604 cm⁻¹. Upon increasing the temperature, the hydrogen-bonded OH group disappears first at 350°C (spectrum b) and the bands of the outer hydroxyls (3667 and 3648 cm⁻¹) merge together. At 400°C (spectrum c) only inner hydroxyls (3619 cm⁻¹) and inner surface hydroxyls (3696 cm⁻¹) are present. At 500°C, no OH groups could be detected.

XRD results. Portions of the intercalated kaolin were preheated at 240°C (i.e., before the melting of intercalated potassium acetate), at 315°C (i.e., after the melting of KAc but before decomposition), as well as at 460°, 540°, 700°, and 1000°C. These temperature values were selected based on the DTG and DTA curves (Figure 2).

The results are summarized in Table 3 and in Figure 5. After intercalation at 25°C, the silicate layers expand

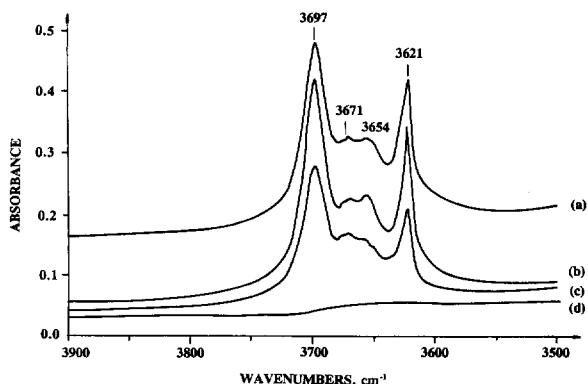


Figure 3. IR spectra of kaolin heated a) up to 350°C, b) up to 400°C, c) up to 500°C, and d) up to 600°C.

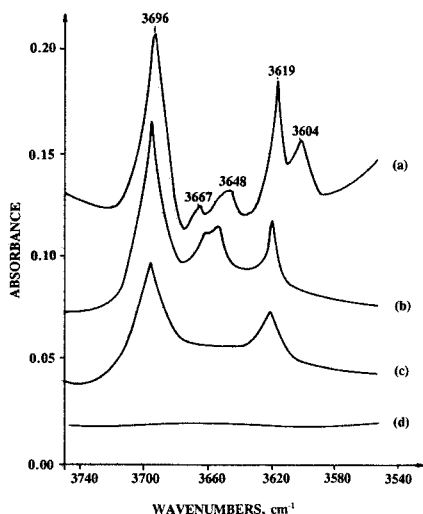


Figure 4. IR spectra of the kaolin-potassium acetate complex at a) room temperature and after heating to b) 350°C, c) 400°C, and d) 500°C.

from 7.1 Å to 14.1 Å, and a small amount of unreacted kaolinite is present (curve b). Until the melting of potassium acetate (298°C), no significant changes can be observed (curve c). In the narrow temperature range (about 20°) between the melting of intercalated acetate and the beginning of decomposition, however, two new reflections appear at 11.5 Å and 8.5 Å at the expense of the 14.1 Å reflection (curve d). At 460°C (curve e), the reflections of expanded kaolinite disappear and new products are formed: $K_4H_2(CO_3)_3 \cdot 1.5H_2O$ (ref. data ASTM 20-889) and $K_2CO_3 \cdot 1.5H_2O$ (ref. data ASTM 11-655). The amount of these compounds increases with the increasing temperature. The formation of $KAlSiO_4$ was observed at a rather low temperature (700°C). The degree of structural order and the amount of the latter compound also increase with temperature. At 1000°C, this is the only crystalline product observed. A small amount of sericite-muscovite is present in the samples until about 900°C.

Table 3. Phases identified in the kaolinite-potassium acetate (K-KAc) complex heated to different temperatures.

Heat treated up to (°C)	Main crystalline phases found
20	
240	K-KAc, kaolinite, muscovite, quartz
315	Decomposition products of K-KAc (11.5 Å, 8.5 Å), kaolinite, muscovite, quartz, K-KAc (14.0 Å).
460	Muscovite, quartz, $K_4H_2(CO_3)_3 \cdot 1.5H_2O$, $K_2CO_3 \cdot 1.5H_2O$
540	$K_4H_2(CO_3)_3 \cdot 1.5H_2O$, $K_2CO_3 \cdot 1.5H_2O$, muscovite, quartz
700	$KAlSiO_4$ and all phases at 540°C
1000	$KAlSiO_4$

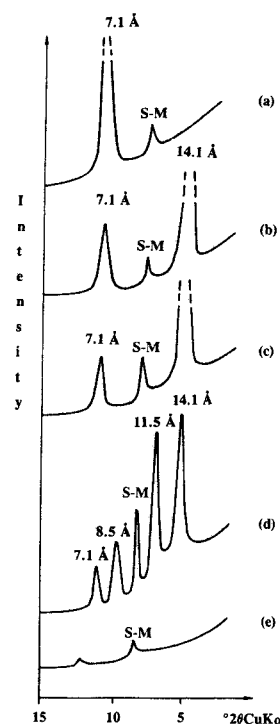


Figure 5. XRD patterns of a) kaolin, b) kaolin-potassium acetate and kaolin-potassium acetate heated to c) 240°C, d) 315°C and e) 460°C. S-M = sericite-muscovite.

Identification of the phases found was based on the following peaks (ASTM): 7.14 Å - 2.56 Å - 2.49 Å kaolinite; 10.0 Å - 4.98 Å - 4.44 Å sericite-muscovite; 4.27 Å - 3.34 Å - 1.54 Å quartz; 6.93 Å - 2.79 Å - 2.77 Å - 2.74 Å $K_2CO_3 \cdot 1.5H_2O$; 3.83 Å - 2.90 Å - 2.48 Å - 2.31 Å $K_4H_2(CO_3)_3 \cdot 1.5H_2O$; and 4.49 Å - 3.11 Å - 2.59 Å $KAlSiO_4$. The kaolinite-potassium acetate complex (14.0 Å) and the decomposition products of the complex (11.5 Å and 8.5 Å) were identified according to Weiss *et al.* (1963a, 1966), and Theng *et al.* (1984).

DISCUSSION

The investigated kaolin is mostly a reactive type of kaolinite that reacts readily with the guest molecules. The degree of intercalation of hydrazine is rather high (90%) even after a reaction time of one hour, as compared with literature data obtained for different types of kaolinite (Range *et al.*, 1969; Theng *et al.*, 1984). The basal spacing of the Hungarian kaolin-hydrazine complex was 10.5 Å. No intermediate intercalation complex with a lower basal spacing was identified by the XRD method. The rate of intercalation increased slightly with reaction time (24 h) and is practically independent of the particle size.

The degree of intercalation of potassium acetate is only 82% even after a long reaction time (80 h). This result is similar to that obtained by Theng *et al.* (1984),

which suggests that the extent of intercalation depends on the molecular weight of the guest compounds.

According to Range *et al.* (1969) and Douglas *et al.* (1980), there is a group of kaolins that undergoes fast and quantitative reaction with hydrazine to give an intercalation compound with a basal spacing of 10.4 Å. These kaolins are characterized by relatively little disorder. Some kaolins contain a component which reacts with hydrazine to give intercalation compound with a basal spacing of 9.5–9.6 Å. Furthermore, kaolinites with medium to strong disorder do not react quantitatively with hydrazine.

The Hungarian kaolin investigated reacts quickly but not quantitatively with hydrazine resulting in a basal spacing of 10.5 Å. Therefore, it may be considered as a type with a disordered, nonreactive part, i.e., a mixture of well and poorly ordered kaolinite (Wiewiora and Brindley, 1969). On the other hand, these authors found no simple correlation between intercalation and the degree of structural order in clays studied by them.

The thermal behavior and decomposition of intercalated kaolin is not well understood, although the alteration of the properties of kaolinite by intercalation has been known for a long time. Only the effect of heating the intercalation complex of potassium acetate with kaolinite was studied, because the complex of hydrazine oxidizes very quickly when exposed to air. The thermoanalytical investigations revealed that the potassium acetate-kaolinite complex is stable at least up to 300°C; only the adsorbed water is released from the substance below this temperature. Decomposition of the intercalated compound begins only after melting of the potassium acetate intercalated in the interlayer spaces, indicating that the reactions occur in the presence of a molten phase. In the first stage of thermal decomposition, dehydroxylation of kaolinite takes place with the formation of water along with the decomposition of the molten salt. The gaseous products of the acetate decomposition are mainly CO₂, CO, and acetone (identified by MS). The thermal stability of the kaolinite decreased significantly as a result of intercalation. The maximum rate of dehydroxylation of the intercalation complex is observed at 430°C, instead of 520°C for the pure kaolinite sample. Reactions in the presence of a molten phase are rather complex processes (e.g., the formation and reduction by elemental carbon of K₂CO₃ and the formation of KAlSiO₄). The DTA curve at 960°C indicates no spinel formation for the intercalated sample. Probably the solid potassium compound obtained prohibits the formation of a crystalline spinel phase.

According to FTIR results, the structural changes of the kaolinite-potassium acetate complex as a function of the temperature are different from those of the pure kaolinite. Upon increasing the temperature, the ratio of the four OH bands in the case of the pure kaolinite is virtually unchanged, indicating that none of the var-

ious OH groups is preferred for dehydroxylation. The new absorption band (3604 cm⁻¹) of the kaolin-potassium acetate complex at 25°C is proof of the intercalated acetate. This can be due to the fact that acetate ions are situated in interlayer positions (Ledoux and White, 1964). The strong negative oxygens of the acetate anions should form hydrogen bonds with inner surface hydroxyls shifting their frequencies towards lower values. Inner hydroxyls are not significantly affected by the interlayer anions since their dipoles point toward empty octahedral sites.

Upon increasing the temperature, the hydrogen-bonded OH groups disappear first (by 350°C), followed by all the outer hydroxyls by 400°C. Dehydroxylation is complete at 500°C, while in the case of the pure kaolinite most inner OH groups are still present at this temperature. There is a sequence of dehydroxylation of various OH groups in the case of intercalated kaolinite.

After melting of potassium acetate, a partial collapse of the complex takes place resulting in new basal spacings of 11.5 Å and 8.5 Å. Besides these two reflections, a part of the 14.1 Å basal spacing still exists. Analogous observations were made by Weiss *et al.* (1963a) and Deeds *et al.* (1966). Upon exposure of the heated complex to the atmosphere, these basal spacings disappear within a few hours and the 14.1 Å reflection is restored due to the uptake of water by the interlayer potassium acetate. At 460°C, all reflections of the expanded kaolinite disappear and crystalline potassium hydrogen carbonate can be detected. It is surprising that this phase still exists at high temperature. The stability of this compound may be due to the fact that acetate ions between the silicate layers form hydrogen bonds with the hydroxyl groups. Some of these strong bonds should exist at high temperature besides the decomposition of intercalated potassium acetate. Potassium hydrogen carbonate could not be detected during the thermal decomposition of pure potassium acetate (Gábor *et al.*, 1989). In accordance with the thermoanalytical results, no spinel formation was detected in the temperature range investigated.

CONCLUSION

The investigation of the thermal behavior of intercalated kaolinite in the function of the temperature requires the use of less common and highly sophisticated measurement techniques such as continuous and selective gas monitors and FTIR spectrometry. The multimethod approach proposed here would provide data that are equally important and complementary to each other.

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