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THERMAL BEHAVIOR OF THE KAOLINITE-HYDRAZINE INTERCALATION COMPLEX

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Abstract—The intercalation complex of a low-defect ("well-crystallized") kaolinite from Cornwall, England, with hydrazine was studied by high-temperature X-ray diffraction (HTXRD), differential thermal analysis (DTA), and thermogravimetry (TG). The X-ray pattern at room temperature indicated that intercalation of hydrazine into kaolinite causes an increase of the basal spacing from 7.14 to 10.4 Å, as previously reported. Heating between 25–200°C produces a structural rearrangement of the complex, which initially causes a contraction of the basal spacing from 10.4 to 9.6 Å. In a second stage, the basal spacing reduces to 8.5 Å. Finally, in a third stage, a reduction in spacing occurs through a set of intermediate phases, interpreted as interstratifications of intercalated and non-intercalated 1:1 layers. Evidence for these changes was observed by DTA, where three endothermic reactions are observed at low temperature. This behavior suggests that intercalated molecules occupy several well-defined sites in the interlayer of the kaolinite complex. The intercalated molecules deintercalate in an ordered fashion, which explains the successive and discontinuous contraction of the basal spacing of the complex. Heating between 200–400°C caused a limited increase in stacking order of the kaolinite structure, whereas dehydroxylation of kaolinite and the disappearance of its X-ray reflections occurred between 450–640°C.

Key Words—DTA-TG, HTXRD, Hydrazine, Intercalation Complex, Kaolinite.

INTRODUCTION

The kaolinite-hydrazine intercalation complex (K-H) was extensively studied by X-ray diffraction and spectroscopic methods. X-ray results indicated that hydrazine in the interlayer of the kaolinite structure produces a basal spacing of 10.4 Å (Weiss *et al.,* 1963), whereas the complex collapses to 7.1 Å when the hydrazine is removed by drying. The considerable broadening and decrease in intensity of the 7-Å diffraction peak were interpreted by Wada and Yamada (1968) as owing to partial fixation of hydrazine. Intercalation of kaolinite by hydrazine was proposed as a method to differentiate a 7-Å kaolin mineral from chlorite (14 Å) by X-ray diffraction (Wada and Yamada, 1968). The intercalation method can characterize kaolinite with various degrees of lattice disorder and intercalation reactivity (Range *et al.,* 1969; Fernández González *et al.,* 1976; Jackson and Abdel-Kader, 1978; Theng *et al.,* 1984; Gábor *et al.,* 1995). Hydrazine was also used to induce artificial disorder in kaolinite (Barrios *et al.,* 1977).

Most X-ray data of the K-H intercalation complex are limited to the angular range $2\theta = 2–15°$, where the more intense 001 and 002 reflections may be monitored. In addition, most studies involved examination of the intercalate at room temperature only. The interpretation of both the differential thermal analysis-thermal gravimetry (DTA-TG) curves and the infrared (IR) spectra of the K-H intercalate were deduced in part on the basis of these X-ray data. The X-ray study of this intercalation complex over a broad 2θ range and the structural modifications observed by high-temperature X-ray diffraction (HTXRD) are the aim of this work. The results suggest that the structural models of the K-H complex must be revised.

EXPERIMENTAL

The sample used for this study is a low-defect ("well-crystallized") kaolinite from Cornwall, England, with a Hinckley index of 1.00 (Hinckley, 1963). This sample contains mica impurities of <5%. The reagent was 99% pure hydrazine monohydrate (Probus S.A., Badalona, Spain). The K-H intercalation complex was obtained (Johnston and Stone, 1990) by: 1) immersing kaolinite in hydrazine for various lengths of time, followed by centrifugation, and 2) placing a few drops of hydrazine on an oriented preparation of kaolinite. Both natural kaolinite and the K-H intercalate were analyzed using HTXRD and DTA-TG.

The wet sample was spread on a Pt holder of a Siemens D-5000 diffractometer. The HTXRD patterns were obtained using CuKα radiation, 40 kV and 30 mA, and a step size of 0.02° at a counting time of 1 s. Heating rate was 4°C/s and a delay time of 600 s was used before any pattern was acquired. The diffractograms were obtained after variable temperature intervals (between 5–50°C) according to the expected modifications as indicated by the DTA-TG curves. Thermal analyses were performed in a Rigaku-Thermoflex apparatus (TG-8110) provided with a TASS 1000 station. Al_2O_3 was used as reference material. DTA and TG curves were recorded simultaneously in static air at a heating rate of 10°C/min.

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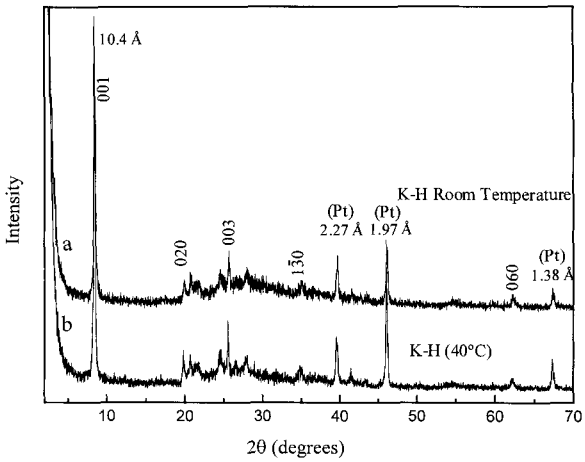


Figure 1. Oriented X-ray patterns of the K-H intercalation complex obtained at room temperature (a) and after drying at 40°C (b). The more intense reflections of the complex have been labeled as well as the Pt reflections.

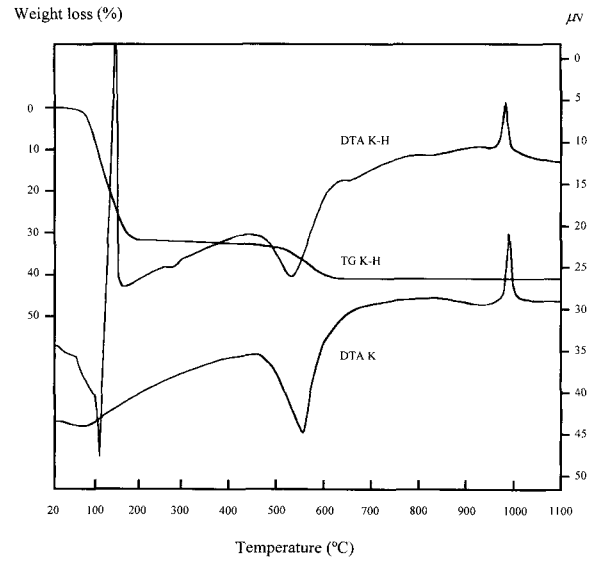


Figure 2. DTA-TG curves of the kaolinite-hydrazine intercalation complex (K-H), and DTA curve of untreated kaolinite (K).

RESULTS

Intercalation of hydrazine into kaolinite resulted in clay expansion from a basal spacing of 7.14 to 10.4 Å (Figure 1, curve a). This expansion agrees with those reported previously (Weiss *et al.,* 1963; Wada and Yamada, 1968; Johnston and Stone, 1990; Gábor *et al.,* 1995). Intercalation of hydrazine was almost complete after 1-h treatment, independently of the method used for preparation. The obtained complex shows a sharp 001 reflection as well as weaker higher-order 00*l* reflections, with $l = 2n + 1$. Lack of complete orientation is indicated by the presence of non-basal reflections. The position of the non-basal reflections with $l = 0$ (020, 130, and 060) suggests that the *a* and *b* parameters of the complex are similar to those of the untreated kaolinite. This pattern also shows a wide diffraction band centered at ~26 °2θ, probably related to the excess of hydrazine. The X-ray pattern obtained after heating at 40°C (Figure 1, curve b) reveals that this band is notably less intense, although two bands, centered at ~22 and 25 °2θ, persist after drying. These bands may be tentatively ascribed to poorly ordered Si and Al-rich oxyhydroxides, which show scattering bands in this region of the patterns (Lapaquellerie, 1987; Ruiz Cruz and Moreno Real, 1991). Intense reflections at 2.27, 1.97, and 1.38 Å are from the Pt holder.

DTA-TG results

The DTA curve of the K-H complex shows a large S-shaped low-temperature endothermic-exothermic peak system, an endothermic peak at 532°C, and an exothermic peak at 983°C (Figure 2). The low-temperature endothermic system includes a sharp endothermic effect, at 110°C, which shows two inflections, at 60 and 95°C, that indicate the presence of two broad endothermic effects. This DTA system is accounted for by a large weight loss from 40 to 210°C, observed in the TG curve. This weight loss suggests an estimated kaolinite/(water + hydrazine) ratio of about 1:2 in the initial complex, although the estimation of the ratio of adsorbed to intercalated molecules was not possible.

The low-temperature endothermic system, which suggests that the loss of water + hydrazine occurs in three separated stages, is almost immediately followed by an intense exothermic effect, which corresponds to hydrazine oxidation. A weak endothermic effect observed at 280°C is probably related to loss of residual, strongly bonded interlayer molecules.

The endothermic effect observed in the range 450–640°C corresponds to dehydroxylation of kaolinite, as indicated by the mass loss observed in the TG curve. This effect appears at a slightly lower temperature than that observed in the DTA curve of untreated kaolinite.

HTXRD results

HTXRD patterns obtained at intervals after temperatures were increased (Figure 3) reveal that loss of the guest molecules was apparently complete between 200–300°C. This is in agreement with the temperature deduced from the TG curve of the K-H complex (Figure 2). Loss of the guest molecules occurs through three well-defined stages: 1) Partial removal of the intercalated molecules begins between 25–60°C, as indicated by reduction of the basal spacing of the complex from 10.4 to 9.6 Å. Both the 10.4-Å and the 9.6-Å reflections are visible in the pattern obtained at

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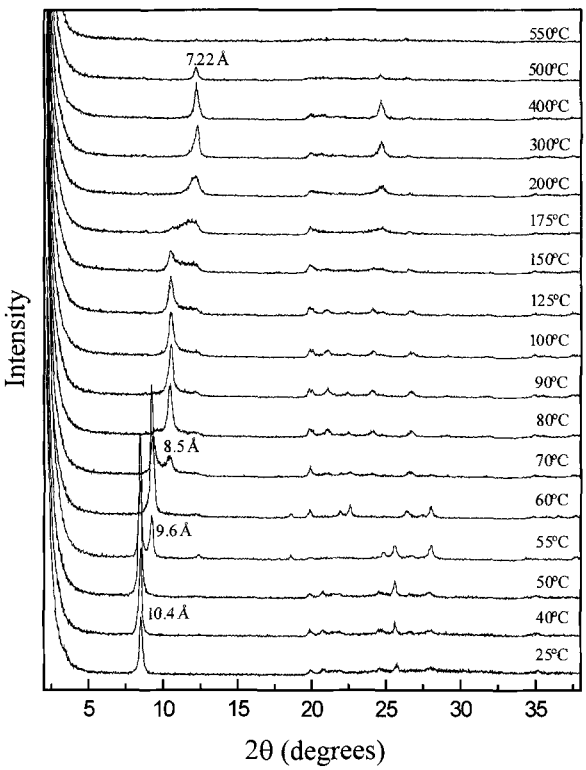


Figure 3. Selected HTXRD patterns obtained after heating in the range 25–600°C.

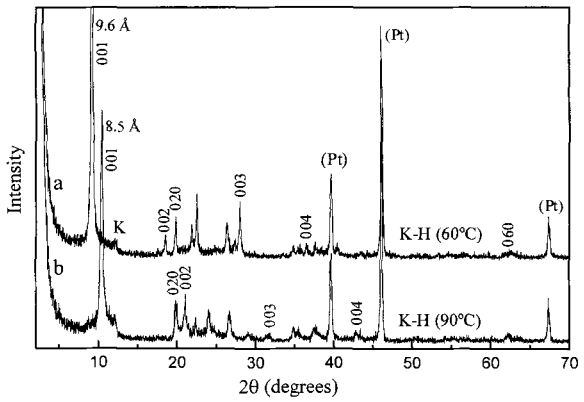


Figure 4. HTXRD patterns obtained after heating at 60°C (a) and 90°C (b). The more intense reflections of the 9.6-Å and 8.5-Å complexes are labeled respectively in (a) and (b). K: kaolinite reflections.

55°C. 2) Desorption between 60–90°C causes reduction of the basal spacing to 8.5 Å. The reflections of both complexes, at 9.6 and 8.5 Å, are observed in the pattern of the sample heated to 70°C. 3) From 90 to 400°C, the loss of the intercalated molecules causes the continuous broadening and shift of the 8.5-Å reflection to 7.22 Å. This transition is seen as a broadening of the 8.5-Å peak from 90 to 125°C, an undefined peak at 150°C, a broad 7.22-Å peak from 175 to 200°C, and sharpening of the 7.22-Å peak from 200 to 400°C.

The X-ray pattern obtained at 60°C (Figure 4, curve a) reveals that the 9.6-Å complex shows a set of basal reflections (both odd and even), as well as non-basal reflections, some of which, with $l = 0$, show similar or slightly higher d-values than those present in the pattern of the 10.4-Å complex. Another set of well-defined peaks probably correspond to *hkl* reflections with $l \neq 0$. The X-ray pattern obtained at 90°C (Figure 4, curve b) permits the observation of the basal reflections of the 8.5-Å complex, which show an increase of the even reflections and a decrease of the odd ones in intensity, relative to the 9.6-Å complex. The position of the non-basal reflections with $l = 0$ also suggests that the lattice parameters, other than c, remain unchanged in this phase. The presence of the kaolinite reflections, which increase in intensity between 60–90°C, suggests that the poorly crystalline Al-Si-rich oxyhydroxides contributed to the formation of kaolinite. In contrast to the structural modifications observed between 25–90°C, the reduction of the basal spacing occurs gradually from 125 to 200°C, and causes a broad X-ray trace between 8.4–7.3 Å (Figure 5a).

HTXRD patterns obtained in the range 200–550°C (Figures 3 and 5b) reveal a gradual sharpening and intensity increase of the basal reflections of kaolinite, which reaches a maximum at 400°C. At temperatures above 400°C, a decrease in intensity of the kaolinite reflections is observed. The X-ray pattern obtained at 400°C shows a notable broadening of the basal reflections of the kaolinite, relative to those of the untreated kaolinite (Figure 6), at the same time that the loss of orientation is revealed by the intensity increase of the non-basal reflections relative to the intensity of the basal reflections. The decrease in intensity of the kaolinite reflections above 400°C is also in accordance with the DTA-TG results (Figure 2), which reveal that dehydroxylation begins at 450°C.

DISCUSSION

The X-ray patterns of the K-H complex obtained at room temperature (Figure 1) indicate that intercalation of hydrazine in kaolinite produces a complex with a 10.4-Å spacing. The partial destruction of the kaolinite structure apparently leads to the simultaneous formation of poorly crystalline phases, probably Si-Al-rich oxyhydroxides. The presence of well-defined, non-basal reflections suggests, as in the case of the dickite-formamide and kaolinite-dimethylsulfoxide complexes, the formation of a three-dimensionally ordered intercalate (Adams and Jefferson, 1976; Adams, 1978; Thompson and Cuff, 1985).

Heating between 25–60°C (Figure 3) causes the shift of the basal reflections of the complex from 10.4 to 9.6 Å (Figure 4). This reduction is, on the basis of

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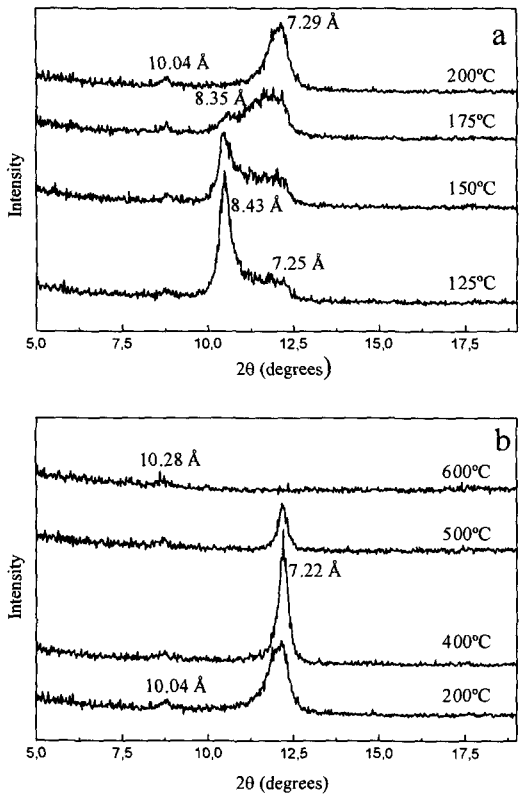


Figure 5. (a) Selected HTXRD patterns obtained in the range 125–200°C, which show the gradual shift of the basal reflection of the intercalate. (b) Selected HTXRD patterns obtained between 200–600°C, showing the behavior of the basal reflections of kaolinite.

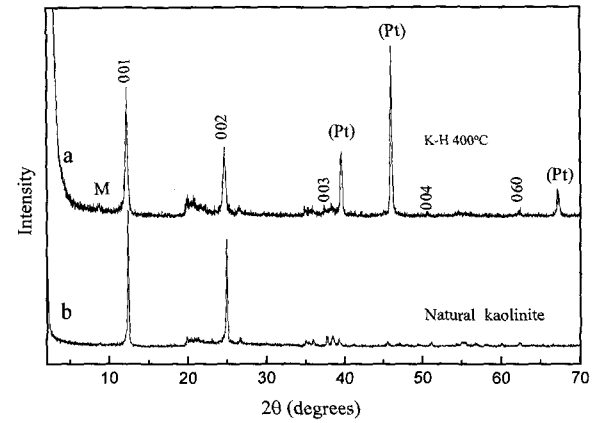


Figure 6. Oriented X-ray patterns of kaolinite after desorption (a) and untreated kaolinite (b). The intensity scale has been modified in (a) to facilitate the comparison of both patterns. M: Mica.

the DTA-TG data, caused by loss of some of the intercalated species. This intermediate intercalation complex was not observed by Gábor *et al.* (1995), whereas a similar shift in basal reflections was observed by Johnston and Stone (1990) during hydrazine loss at decreasing pressure. Johnston and Stone (1990) interpreted these results as owing to the structural rearrangement caused by the loss of a portion of the intercalated hydrazine. These authors assume, on the basis of the modifications observed in the OH-stretching region of the spectra, that strong H bonds were formed between the OH surface of the 1:1 layer and hydrazine. In their structural model, hydrazine molecules serve as molecular props between the 1:1 layers, resulting in the observed 10.4-Å spacing. Partial loss of hydrazine drives the remaining hydrazine molecules into the ditrigonal holes of the oxygen-atom surface of the 1:1 layer, resulting in the 9.6-Å spacing. Nevertheless, heating between 60–90°C causes an additional shift of the basal reflection from 9.6 to 8.5 Å, thus indicating that another structural modification occurred in this temperature range. This is in contrast to the continuous, or non-discrete change that occurs from a 8.5-Å to a 7.2-Å spacing when the K-H complex is heated.

Our data indicate that three main structural modifications occurred during the destruction of the hydrazine complex. Upon desorption, the changes are characterized by decreasing of the basal spacing and a change in the relative intensity of both odd and even basal reflections. Although the *c* axis is reduced during this process, the *a* and *b* parameters of the kaolinite structure appear to be unaffected. The first two modifications lead to structurally ordered complexes, which appear to be stable only within a narrow temperature interval, whereas complete loss of the intercalated species occurs through intermediate structures, probably consisting of random interstratifications of both intercalated and non-intercalated kaolinite layers.

These successive structural modifications suggest that the intercalated molecules, present in the complex obtained at room temperature, occupy well-defined positions in the interlayer of the kaolinite. The two discrete spacings observed during desorption are related to the proportion of intercalated molecules in the interlayer, and can probably be explained by the ordered sequence of desorption. The first stage of desorption (between 25–60°C) corresponds to loss of water and hydrazine adsorbed in the outer surface of the clay particles, as well as to the loss of weakly bonded molecules, as indicated by the low-temperature endotherm. From TG data, the mass loss is ~3.5% (in weight) of the total adsorbed species. Weight loss observed between 60–90°C represents the loss of ~40% of the absorbed molecules. The higher temperatures indicate slightly stronger bonds with kaolinite than those removed between 25–60°C. Finally, the mass loss of ~55% of the initial mass, corresponding to the third endothermic reaction (at 90–210°C), represents the loss of more strongly bonded molecules present in

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the 8.5-Å complex. Although the loss rate of both water and hydrazine cannot be estimated, the rate is probably different, favoring the formation of well-defined intercalation complexes with a different degree of hydration. To test this hypothesis, a detailed study of the IR spectra of the complex obtained at increasing temperatures is in preparation.

Heating in the range 200–400°C (Figures 3 and 5a) causes the progressive stacking ordering of kaolinite, as revealed by both the sharpening and the intensity increase of the basal kaolinite reflections. Nevertheless, these reflections are notably broader than those of untreated kaolinite, even in the pattern obtained at 400°C (Figure 6). Thus, the number of layers in the diffracting domains notably decreased as a consequence of the intercalation process, a relationship first noted by Barrios *et al.* (1977).

The HTXRD patterns obtained between 400–600°C (Figures 3 and 5b) reveal that kaolinite reflections gradually disappear between 400–550°C, whereas the weak 10-Å (mica impurity) reflection remains at 600°C. Kaolinite dehydroxylation occurs in a temperature range slightly lower than that observed for untreated kaolinite (Figure 2), in accordance with the reported trend in kaolinites with a different degree of stacking ordering (Mackenzie, 1970) as well as in kaolinite-potassium acetate intercalates (Gábor *et al.*, 1995; Ruiz Cruz and Franco, 1999).

CONCLUDING REMARKS

The HTXRD patterns of the K-H intercalation complex indicate that removal of the intercalated species between 50–90°C occurs through ordered complexes, which show sharp reflections at 9.6 and 8.5 Å. This behavior suggests that the intercalated molecules occupy well-defined positions in the interlayer of the kaolinite. The ordered loss of the intercalated molecules is based on bonding strength and this explains why a successive contraction of the basal spacing occurs. Above 90°C, desorption occurs, in contrast, through a continuous shift of the basal reflections, which indicates the presence of interstratifications of intercalated and non-intercalated layers.

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