

HIGH-TEMPERATURE X-RAY DIFFRACTION, DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRY OF THE KAOLINITE-DIMETHYLSULFOXIDE INTERCALATION COMPLEX

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Abstract—The intercalation complex of a kaolinite from Cornwall, UK, with dimethylsulfoxide (DMSO) was studied by high-temperature X-ray diffraction (HTXRD), differential thermal analysis (DTA) and thermogravimetry (TG). The X-ray pattern obtained at room temperature indicated that intercalation of DMSO into kaolinite caused an increase of the basal spacing of kaolinite from 7.14 to 11.19 Å. Heating between 25 and 300°C caused the removal of the DMSO, which occurred over several stages. In a first stage (25–125°C), an expansion (from 11.19 to 11.28 Å) followed by a contraction (from 11.28 to 11.19 Å) is observed, at the same time as the intensity of the basal reflection decreased and was replaced by a broad band extending from ~11 to ~7 Å. In a second stage (125–200°C), the loss of DMSO did not lead to changes in the HTXRD patterns; and finally, in a third stage, the loss of DMSO caused an important increase in intensity and sharpening of the basal reflections of the kaolinite. These stages were also shown by the DTA-TG curves for the complex. The TG curve indicated that the loss of ~15% of the intercalated DMSO occurs below 150°C, and caused the disruption of the structure. The remaining molecules, forming stronger bonds with the kaolinite surfaces, were lost between 150 and 300°C.

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

INTRODUCTION

The use of sheet silicates as selective catalysts for organic synthesis, based on the ability of these silicates to intercalate organic molecules, has received considerable attention (*e.g.* Thomas *et al.*, 1977; Pinnavia, 1983). Although most of the catalysts studied were smectites, it is important to know the processes of intercalation and release of the organic molecules in sheet silicates with simpler chemical composition, such as kaolin minerals.

Kaolinite has been observed to intercalate a relatively large number of polar organic compounds including dimethylsulfoxide (DMSO), formamide, dimethylformamide, N-methylformamide, acetamide, pyridine N-oxide, *etc.* (MacEwan and Wilson, 1980). The kaolinite-DMSO intercalation complex shows a basal spacing of 11.2 Å and has been studied extensively by X-ray, thermo-analytical and spectroscopic methods (*e.g.* González García and Sánchez Camazano, 1965; Olejnik *et al.*, 1968; Anton and Rouxhet, 1977; Adams and Waltl, 1980; Frost *et al.*, 1998, 1999a). The structure of the complex was determined by Thompson and Cuff (1985) using spectroscopic and X-ray and neutron powder diffraction data. In this structure, each DMSO molecule is triply hydrogen bonded above the octahedral vacancy in the gibbsite sheet of the kaolinite layer, and one methyl group is keyed into the ditrigonal hole of the tetrahedral sheet. The accommodation of the DMSO molecules causes a significant horizontal displacement of individual layers to achieve almost perfect overlap of

the octahedral vacancy by the adjacent ditrigonal hole.

Recently, based on Raman spectroscopic results, Frost *et al.* (1998, 1999b) undertook a molecular structural study of this complex and proposed a model in which water and DMSO are intercalated. Two types of DMSO, monomeric and polymeric, would be present in the intercalate in such a way that every inner-surface hydroxyl group would be individually hydrogen bonded to one DMSO molecule.

The results of the study of the kaolinite-DMSO complex by thermoanalytical methods (DTA-TG) indicated a ratio of kaolinite ($\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$):DMSO ranging from 1:0.7 to ~1:1, in samples with increasing degree of intercalation (*e.g.* Sánchez Camazano and González García, 1966; Weiss *et al.*, 1966; Olejnik *et al.*, 1968; Johnston *et al.*, 1984; Frost *et al.*, 1999a). Adams and Waltl (1980) studied the thermal decomposition of a kaolinite-DMSO intercalate by thermogravimetry. They determined two stages of mass loss, the first below 100°C and the second at 220°C, when the analysis was carried out in static air. Nevertheless, under flowing dry nitrogen gas, all the DMSO was removed below 175°C. The two stages of mass loss, which represent 1% and 19% of the initial mass, respectively, were ascribed to the loss of the loosely bound surface material and the intercalated DMSO. Adams and Waltl (1980) suggested that an exponential nucleation process rather than diffusion control is the determining step in the decomposition of the intercalate. Frost *et al.* (1998, 1999a) found three endotherms at 70, 113 and 168°C, and three stages of mass loss. They observed the loss of water at 70°C and the loss of DMSO at 113 and 160°C.

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Study of the thermal decomposition of a kaolinite-DMSO intercalate by HTXRD and DTA-TG provides new data on the decomposition process which have not been described previously.

EXPERIMENTAL

The sample used for making the complex was a Cornwall kaolinite, supplied by Prof. E. Galán (University of Sevilla, Spain), with Hinckley index of 1.00 (Hinckley, 1963). The kaolinite contains <5% mica + quartz impurities. The reagent was 98% pure DMSO (PANREAC, Montplet and Esteban, S.A., Barcelona, Spain). The kaolinite-DMSO intercalation complex was obtained by placing an oriented sample of kaolinite in a DMSO atmosphere, at 50°C and for increasing time intervals. The degree of intercalation, calculated as $(I_{(001)\text{complex}} / (I_{(001)\text{complex}} + I_{(001)\text{kaolinite}})) \times 100$ (Wiewióra and Brindley, 1969), was time dependent but the maximum intercalation was obtained after 2–3 days. After 3 days the degree of intercalation remained practically unchanged. It should be noted that in preparation of the kaolinite-DMSO intercalate by previous workers (Anton and Rouxhet, 1977; Johnston *et al.*, 1984; Frost *et al.*, 1998), intercalation was achieved by direct mixing of kaolinite with DMSO.

Both natural kaolinite and the intercalate were analyzed using HTXRD, and thermoanalytical techniques: DTA and TG.

The HTXRD patterns were obtained with a Siemens D-5000 diffractometer, using $\text{CuK}\alpha$ radiation at 40 kV and 30 mA, step size = 0.02° and a counting time of 1 s per

step. The heating rate was 4°C/s and the samples heated to a particular temperature were held at that temperature for 600 s, prior to the XRD pattern being acquired. The diffraction patterns were obtained at varying temperature intervals (between 5 and 50°C) according to the expected modifications in the various temperature ranges, indicated by the DTA-TG curves. Thermal analyses were carried out using a Rigaku-Thermoflex instrument (TG-8110) equipped with a TASS 1000 station. Al_2O_3 was used as a reference material. The DTA and TG curves were recorded simultaneously in a static air atmosphere at a heating rate of 10°C/min.

RESULTS

Intercalation of DMSO into kaolinite resulted in the almost complete expansion of the clay (92%) from a basal spacing of 7.14 to 11.19 Å (Figure 1). This spacing agrees with those reported previously (González García and Sánchez Camazano, 1965; Olejnik *et al.*, 1968). The complex obtained displays a sharp 001 reflection as well as weaker higher-order 00 l reflections. The patterns also show the presence of non-basal reflections in the 18–23°2 θ and 35–40°2 θ zones of the diagrams, similar to those observed by Jacobs and Sterckx (1970) and Adams (1978). On the other hand, the intense reflection at 2.27 Å is due to the Pt holder.

The absence in Figure 1, of a band between 15 and 30°2 θ , as observed by Frost *et al.* (1998), interpreted as being due to the presence of a kaolinite-DMSO complex showing a certain degree of amorphicity, is noted. A similar band, due to the excess of reagent, was observed

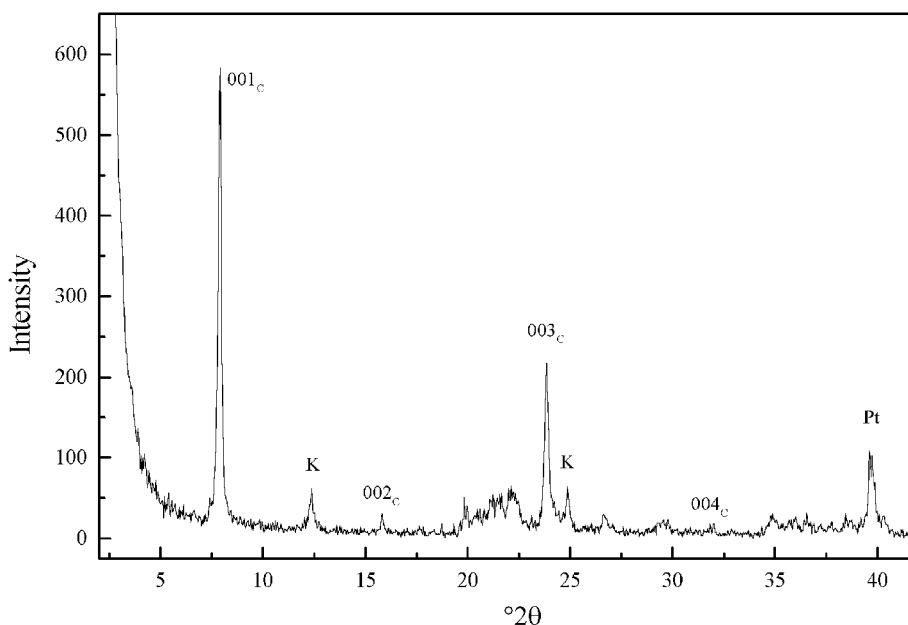


Figure 1. X-ray pattern of the oriented kaolinite-DMSO intercalation complex obtained at room temperature. The more intense reflections of the complex have been labeled as well as the Pt reflections. K: kaolinite; c: complex.

by Ruiz Cruz and Franco (2000a,b) in the X-ray pattern of the kaolinite-hydrazine intercalation complex. The lack of this band in the pattern of the kaolinite-DMSO complex probably indicates that the method used in this study for the intercalation considerably reduces the excess of reagent.

HTXRD study

The HTXRD patterns obtained at increasing temperatures are shown in Figure 2 which reveals a slight increase in intensity of the complex reflections between room temperature and 50°C, due to the loss of adsorbed molecules (water + DMSO). This probably leads to a

better order in the packing of the kaolinite-DMSO complex. From this temperature upwards, the evolution of DMSO occurs over several stages: (1) In the range 60–125°C, partial removal of the DMSO causes a gradual decrease in intensity of the reflections of the complex, especially for the reflections 001 and 003 (Figures 2 and 3). Nevertheless, this intensity decrease is not accompanied, as expected (Adams and Waihl, 1980), by the concomitant increase in the intensity of the kaolinite reflections. A slight dilation of the structure perpendicular to the layers (from 11.19 to 11.28 Å) is observed between room temperature and 70°C. On the contrary, between 70 and 90°C, a contraction of the

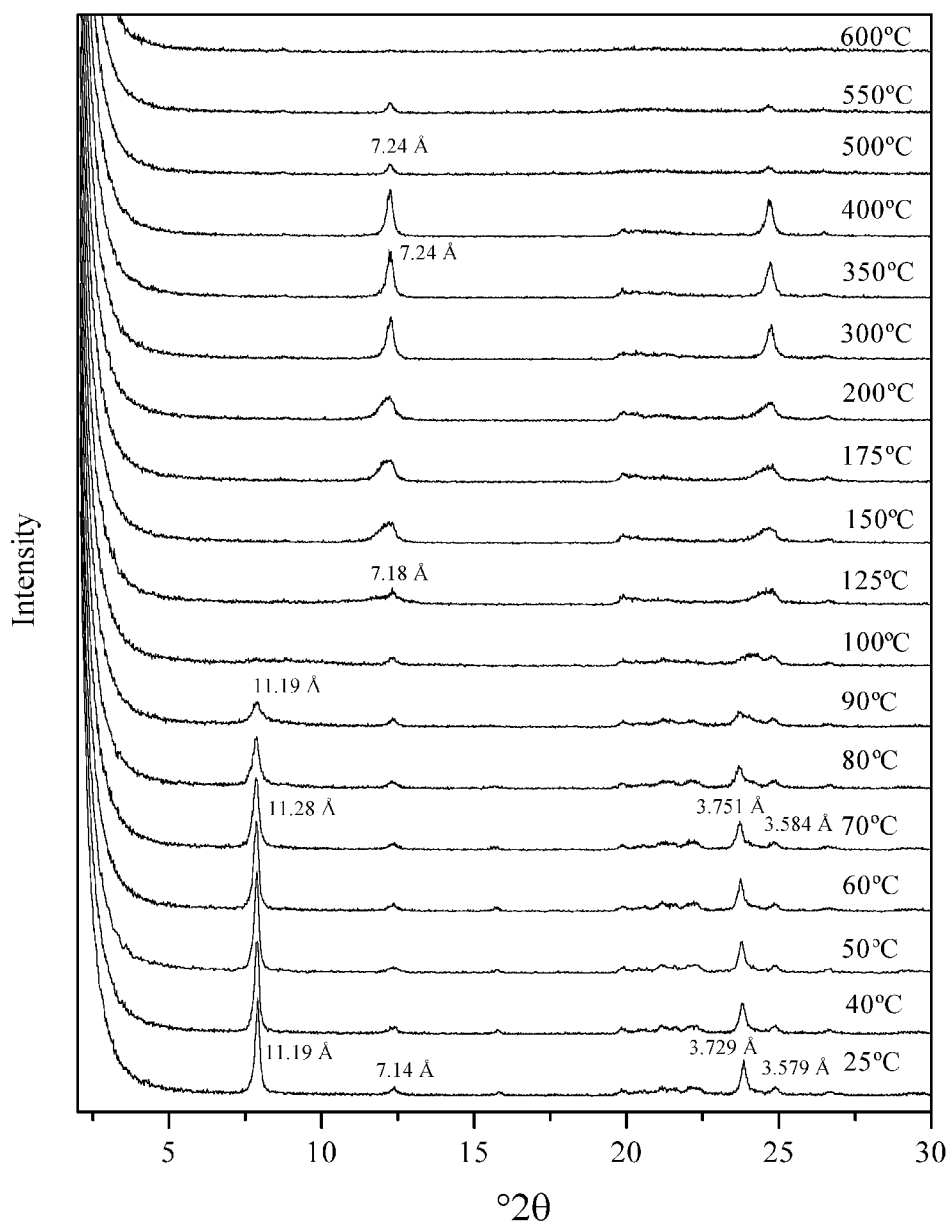


Figure 2. Selected HTXRD patterns obtained after heating in the range 25–600°C.

basal spacing from 11.28 to 11.19 Å occurred (Figure 3). The disappearance of the reflections of the complex between 100 and 125°C indicates the destruction of the ordered structure, and causes a wide band between ~11 and ~7 Å. This process is also revealed by the loss of definition of the non-basal reflections. (2) In the range 150–200°C, all the patterns show a very similar aspect, where the band of the complex is hardly visible, and the intensity of the kaolinite reflections remains almost unchanged (Figures 2 and 4). This behavior indicates a slow loss of DMSO, but does not, however, restore the kaolinite reflections. (3) A notable increase in intensity and sharpening of the kaolinite reflections is observed in the patterns obtained between 200 and 300°C, which suggests a new loss of DMSO (Figures 2 and 4). In this temperature interval, the better definition of the non-basal reflections also reveals the structural rearrangement of the kaolinite.

Above 400°C the gradual decrease in intensity of the basal reflection of the kaolinite indicates the beginning of the dehydroxylation process (Figures 2 and 5).

DTA-TG study

The DTA-TG curves of the kaolinite-DMSO complex and the DTA curve of the untreated kaolinite are shown in Figure 6. Heating the complex at a continuous rate causes, as a first stage, an intense loss of mass, which is accompanied by an endothermic system. This system includes two well defined endothermic effects, centered at 65 and 200°C, respectively, and a third, weak endothermic effect, at ~100°C, which appears as a shoulder on the first endothermic effect. The first endotherm corresponds to a slow loss of mass (at 30–84°C) which represents ~3.74% of the initial mass. In the second stage (at 84–150°C) the mass loss is also slow and represents ~3.36% of the initial mass. In the third stage the loss of mass is quicker and represents ~19% of the initial mass. Assuming that the first mass loss (<100°C) corresponds to the loss of adsorbed molecules, the TG curve allows us to estimate a molar ratio for kaolinite:DMSO of ~1:1.05 after this stage of mass loss. This ratio becomes 1:0.9 after heating at 150°C.

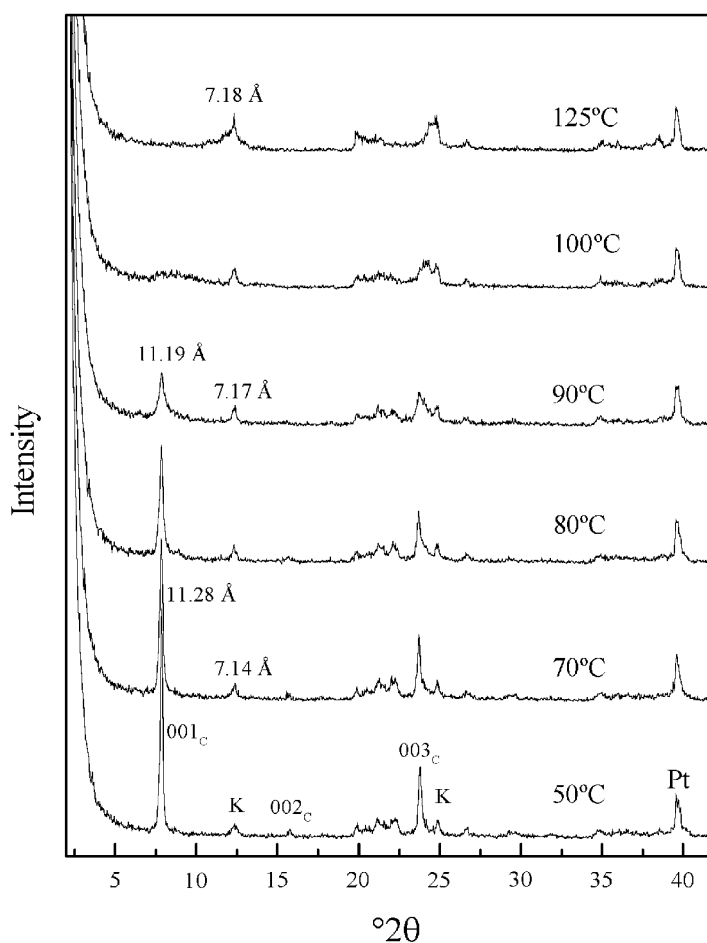


Figure 3. Selected HTXRD patterns obtained after heating in the range 50–125°C. The more intense reflections of the complex have been labeled. K: kaolinite; c: complex.

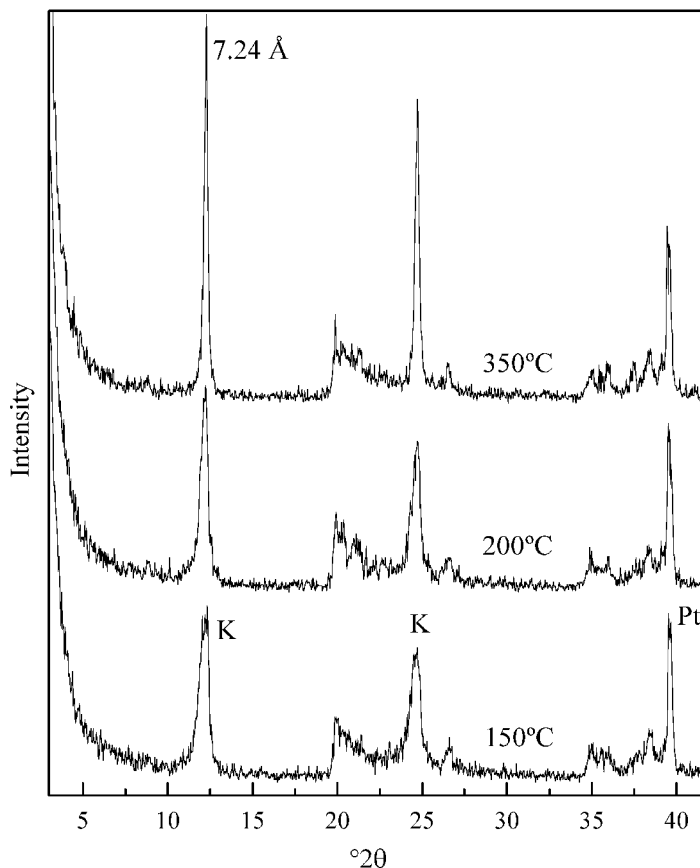


Figure 4. Selected HTXRD patterns obtained in the range 150–350°C, showing the behavior of the basal reflections of kaolinite. K: kaolinite.

The low-temperature endothermic system is followed almost immediately by two weak exothermic effects, at 350 and 360°C, which probably correspond to a reorganization of the kaolinite layers.

The endothermic effect observed in the range 470–620°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 the untreated kaolinite (Figure 6).

The results are similar but not identical to those published by Frost *et al.* (1999a). The differences are mainly related to both the temperature of the endothermic effects and the relative intensity of these, which can be related to the different methods of preparation of the complex and to the different rate of heating.

DISCUSSION

For the correct interpretation of the HTXRD and the DTA-TG data, there is a question about the possible presence of water molecules in the intercalate, as proposed by Frost *et al.* (1998, 1999a,b). It is difficult to prove the presence or the absence of water in the

intercalate, even using spectroscopic methods, since small amounts of adsorbed water are usually present in the spectra of clay minerals obtained in atmospheric air. A series of FTIR spectra of the kaolinite-DMSO complex obtained at increasing temperatures reveal that a band representing a small amount of water is present in the spectrum obtained at 25°C whereas the water band (at 1639 cm⁻¹) decreased notably in the spectra obtained above this temperature. These results, which are in accordance with those of Frost *et al.* (1998, 1999a) do not prove, however, that water is intercalated.

The loss of a monolayer of water molecules, present in the model established by Frost *et al.* (1998, 1999a) would cause a contraction of the basal spacing of the order of 1 Å, as observed, *e.g.* during the loss of water from the kaolinite- and dickite-hydrazine complexes (Ruiz Cruz and Franco, 2000a,b) in which the water loss leads to the formation of dehydrated complexes with well-defined basal spacings. This behavior is not observed during heating of the kaolinite-DMSO complex suggesting that intercalated water, if it exists, must be filling holes between the DMSO molecules.

Our interpretation is based on the hypothesis that water (adsorbed or intercalated) is lost in the first stage of

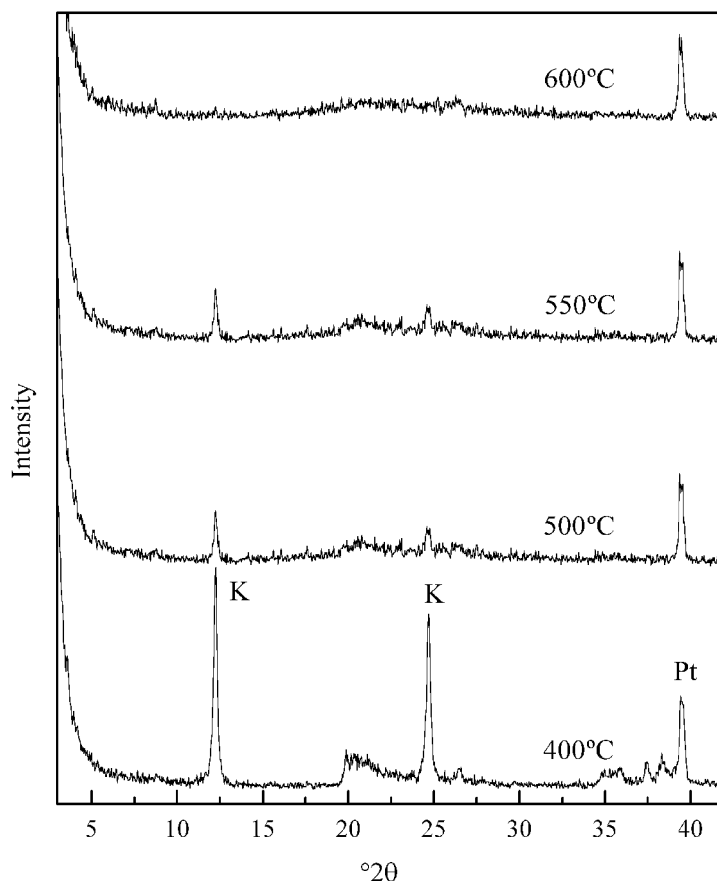


Figure 5. Selected HTXRD patterns obtained in the 400–600°C range. K: kaolinite.

heating whereas from 60–70°C only DMSO is lost. This interpretation is also based on the data by Frost *et al.* (1999a), which indicated that the most water is lost below 80°C. The high-temperature X-ray patterns (Figures 2–5) as well as the DTA-TG data (Figure 6) indicate that removal of the DMSO occurs over several stages.

Heating between 25 and 50°C (Figures 2 and 3) causes the loss of the DMSO + water molecules loosely bonded at the surface of the particles. This loss causes an increase in intensity of the complex reflections and gives rise to a well defined endothermic effect, centered at 65°C. This DTA peak shows a very variable intensity in the DTA curves obtained from complexes with several kaolinites and dickite, suggesting that the amount of adsorbed molecules depends heavily on the particle size.

The X-ray patterns obtained after heating between 50–125°C (Figure 3) reveal, in the first stage (50–70°C), a dilation of the structure (from 11.19 to 11.28 Å), which is followed, at ~90°C, by a slight contraction (from 11.28 to 11.19 Å), at the same time as the reflections decrease in intensity. The observed contraction may be related to the loss of ~3.4% of the initial mass, which would cause a different arrangement of the DMSO molecules in the interlayer space of the

kaolinite, as observed Raupach *et al.* (1987) in the kaolinite-DMSeO intercalate. The weak endothermic effect observed at ~100°C reflects these changes. It is also possible, as suggested by Yariv (pers. comm., 2001) that the ordered kaolinite-DMSO intercalation complex is only stable when it contains the necessary amount of water. The loss of the basal reflection of the complex probably indicates that the kaolinite now forms a single-layer complex.

The X-ray patterns obtained between 150–200°C (Figures 2 and 4) reveal that the modifications are scarce in this temperature range, where the kaolinite reflections remain unchanged. An intensity increase of the kaolinite reflections is, however, observed from 200°C. This behavior can be explained on the basis of the DTA-TG curves, although some differences in the temperature intervals, ascribed to the different thermal regimes, are observed. The TG curve indicates that the loss of the intercalated species in the temperature range 100–150°C is small, whereas an increase in slope is observed from 170°C. This later stage of mass loss, which represents 19% of the initial mass, concludes at ~350°C, and is shown in the DTA curve, by the presence of a new, well defined endothermic effect.

Thus, the HTXRD patterns and the DTA-TG curves indicate that the loss of the intercalated molecules occurs over a number of well differentiated stages. During the two first stages, the mass loss is only ~3.5% of the initial mass, but it causes the disruption of the structure of the complex. It is important to note that, in contrast to the kaolinite-DMSeO complex, where an ordered structure with a kaolinite:DMSeO ratio of 1:0.5 has been identified (Raupach *et al.*, 1987), in the case of the kaolinite-DMSO complex, the disappearance of the ordered structure occurs when the kaolinite:DMSO ratio is 1:0.9, near the ideal ratio determined in the ordered complex (Thompson and Cuff, 1985). However, this process does not lead to the restoration of the kaolinite structure. On the contrary, this restoration is observed from 200°C, when ~40% of the intercalated DMSO has been lost.

These stages of removal of DMSO suggest either the presence of two, structurally different, DMSO molecules in the initial complex, as proposed by Frost *et al.* (1998, 1999a,b) or a change in bond strength, after the loss of part of the intercalated species. In any case, it seems that the ordered kaolinite-DMSO intercalation complex is only stable when all the positions are occupied.

Heating above 300°C (Figure 5) causes the progressive ordering of kaolinite, as revealed by both the sharpening and the increase in intensity of the basal kaolinite reflections. Nevertheless, these reflections are notably broader than those of the untreated kaolinite, even in the pattern obtained at 400°C (Figure 7). This

shows that the number of layers in the fundamental domains, calculated using the Scherrer formula (Cullity, 1956), decreased notably (from ~59 to ~37 layers per diffraction domain) as a consequence of the intercalation-deintercalation process. On the basis of our data, and as indicated by the broadening of the basal reflections and the shape and definition of the non-basal ones (Plançon and Zacharie, 1990), the structural modifications of kaolinite appear to be more important than previously assumed (*e.g.* Olejnik *et al.*, 1968). Similarly, kaolinite dehydroxylation occurs in a temperature range lower (by ~20°C) than that observed for the untreated kaolinite (Figure 6), in accordance with the reported trend in kaolinites with different degrees of ordering (Mackenzie, 1970) as well as in kaolinite-K acetate intercalates (Gábor *et al.*, 1995; Ruiz Cruz and Franco, 1999) and kaolinite-hydrazine intercalates (Ruiz Cruz and Franco, 2000a,b).

CONCLUSIONS

The HTXRD patterns and the DTA-TG curves of the kaolinite-DMSO intercalation complex indicate that removal of the intercalated species occurs over several stages, which cause: (1) the slight contraction of the basal spacing (at ~90°C); (2) the formation of disordered structures (between 70 and 125°C), probably consisting of interstratification of intercalated and non-intercalated layers; and (3) an increase in intensity and sharpening of the kaolinite reflections (from 200°C). This behavior

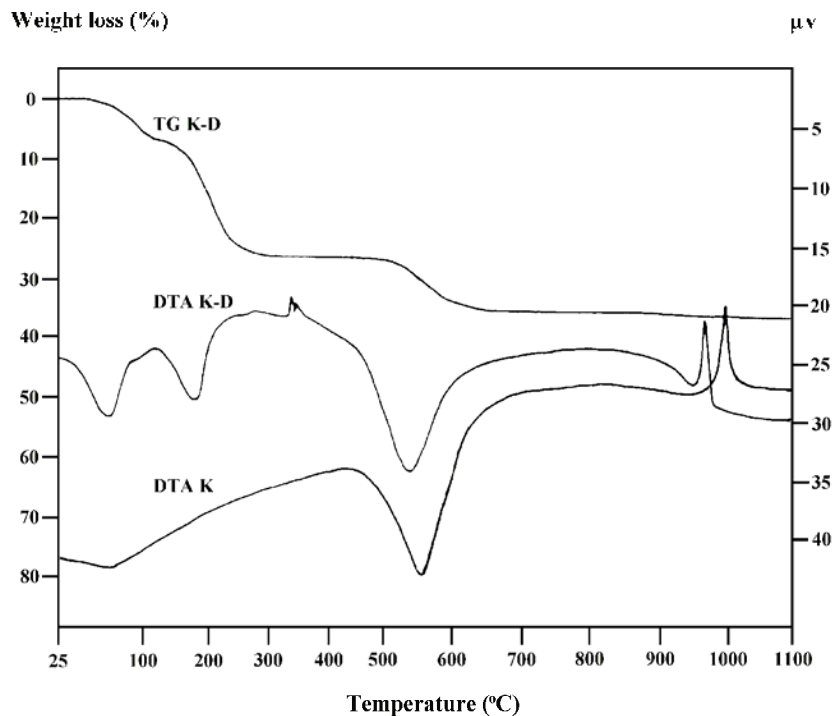


Figure 6. DTA and TG curves of the kaolinite-DMSO (K-D) intercalation complex, and DTA curve of untreated kaolinite (K).

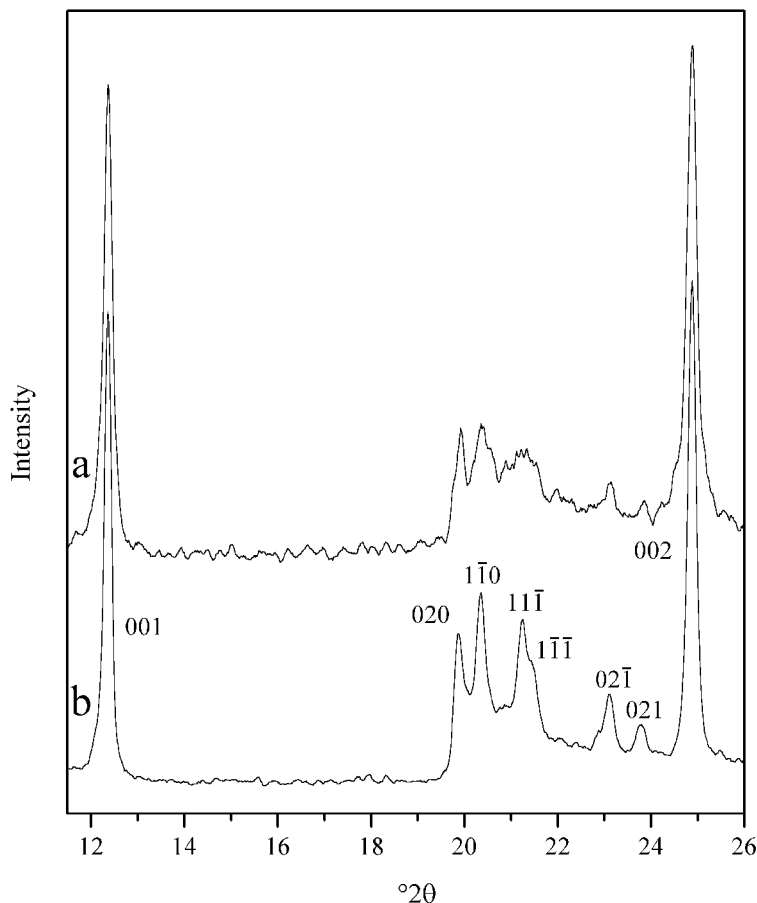


Figure 7. X-ray patterns of unoriented deintercalated kaolinite (a) and untreated kaolinite (b). The intensity scale has been modified in trace a to facilitate comparison of the two patterns.

indicates that the loss of a small amount of the intercalated molecules causes the disruption of the ordered structure of the complex at the same time as the remaining molecules form stronger bonds with the kaolinite surfaces.

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REFERENCES

- Adams, J.M. (1978) Unifying aspect of the 3-D structures of some intercalates of kaolinite. *Clays and Clay Minerals*, **33**, 291–295.
- Adams, J.M. and Walth, G. (1980) Thermal decomposition of a kaolinite:dimethyl sulfoxide intercalate. *Clays and Clay Minerals*, **28**, 130–134.
- Anton, O. and Rouxhet, P.G. (1977) Note on the intercalation of kaolinite, dickite and halloysite by dimethyl-sulfoxide. *Clays and Clay Minerals*, **25**, 259–263.
- Cullity, B.D. (1956). Diffraction I: The directions of diffracted beams. Pp. 78–103 in: *Elements of X-ray Diffraction* (Morris Cohen, consulting editors). Addison-Wesley publishing company, Inc., USA.
- Frost, R.L., Kristof, J., Paroz, G.N. and Klopogge, J.T. (1998) Molecular structure of dimethylsulfoxide intercalated kaolinites. *The Journal of Physical Chemistry B*, **102**, 8519–8532.
- Frost, R.L., Kristof, J., Horvath, E. and Klopogge, J.T. (1999a) Deintercalation of dimethylsulphoxide intercalated kaolinites – a DTA/TGA and Raman spectroscopic study. *Themochimica Acta*, **327**, 155–166.
- Frost, R.L., Kristof, J., Horvath, E. and Klopogge, J.T. (1999b) Molecular structure of dimethyl sulfoxide in DMSO-intercalated kaolinites at 298 and 77 K. *The Journal of Physical Chemistry A*, **48**, 9654–9660.
- Gábor, M., Toth, M., Kristof, J. and Gábor, K.H. (1995) Thermal behavior and decomposition of intercalated kaolinite. *Clays and Clay Minerals*, **43**, 223–228.
- González García, S. and Sánchez Camazano, M. (1965) Complejos de adsorción de los minerales de la arcilla con dimetilsulfóxido. *Anales de Edafología y Agrobiología*, **24**, 495–520.
- Hinckley, D.N. (1963) Variability in ‘crystallinity’ values among the kaolin deposits of the coastal plain of Georgia and South Carolina. *Clays and Clay Minerals*, **11**, 229–235.
- Jacobs, H. and Sterckx, M. (1970) A contribution to the study of the intercalation of dimethyl sulfoxide in the kaolinite lattice. Pp. 154–160 in: *Proceedings of the Reunion Hispano-Belga de Minerales de la Arcilla, Madrid* (J.M.

- Serratos, editor). C.S.I.C., Madrid.
- Johnston, C.T., Sposito, G., Bocian, D.F. and Birge, R.R. (1984) Vibrational spectroscopic study of the interlamellar kaolinite-dimethyl sulfoxide complex. *The Journal of Physical Chemistry*, **88**, 5959–5964.
- MacEwan, D.M.C. and Wilson, M.J. (1980) Interlayer and intercalation complexes of clay minerals. Pp. 197–284 in: *Crystal Structures of Clay Minerals and their X-ray Identification* (G.W. Brindley and G. Brown, editors). Monograph **5**. Mineralogical Society, London.
- Mackenzie, R.C. (1970) Simple phyllosilicates based on gibbsite- and brucite-like sheets. Pp. 497–537 in: *Differential Thermal Analysis* (R.C. Mackenzie, editor). Academic Press, London.
- Olejnik, S., Aylmore, L.A.G., Posner, A.M. and Quirk, J.P. (1968) Infrared spectra of kaolin mineral-dimethylsulfoxide complexes. *The Journal of Physical Chemistry*, **72**, 241–249.
- Pinnavia, T.J. (1983) Intercalated clay catalysts. *Science*, **220**, 365–371.
- Plançon, A. and Zacharie, C. (1990) An expert system for the structural characterization of kaolinite. *Clay Minerals*, **25**, 249–260.
- Raupach, M., Barron, P.F. and Thompson, J.G. (1987) Nuclear magnetic resonance, infrared, and X-ray powder diffraction study of dimethylsulfoxide and dimethylselenoxide intercalates with kaolinite. *Clays and Clay Minerals*, **35**, 208–219.
- Ruiz Cruz, M.D. and Franco, F. (1999) New data on the kaolinite-potassium acetate complex. *Clay Minerals*, **34**, 565–577.
- Ruiz Cruz, M.D. and Franco, F. (2000a) Thermal behavior of the kaolinite-hydrazine intercalation complex. *Clays and Clay Minerals*, **48**, 63–67.
- Ruiz Cruz, M.D. and Franco, F. (2000b) Thermal decomposition of a dickite-hydrazine intercalation complex. *Clays and Clay Minerals*, **48**, 586–592.
- Sánchez Camazano, M. and González García, S. (1966) Complejos interlaminares de caolinita y haloisita con líquidos polares. *Anales de Edafología y Agrobiología*, **25**, 9–25.
- Thomas, J.M., Adams, J.M., Graham, S.H. and Tennakoon, D.T.B. (1977) Chemical conversion using sheet silicates intercalates. Pp. 298–315 in: *Solid State Chemistry of Energy Conversion and Storage*. Advances in Chemistry Series, **163**. American Chemical Society, Washington, D.C.
- Thompson, J.G. and Cuff, C. (1985) Crystal structure of kaolinite:dimethylsulfoxide intercalate. *Clays and Clay Minerals*, **33**, 490–500.
- Weiss, A., Thielepape, W. and Orth, H. (1966) Neue kaoliniteinlagerungsverbindungen. *Proceedings of the International Clay Conference, Jerusalem* (L. Heller and A. Weiss, editors). Israel Program for Scientific Translations, Jerusalem.
- Wiewióra, A. and Brindley, G.W. (1969) Potassium acetate intercalation in kaolinite and its removal; effect of material characteristics. Pp. 723–733 in: *Proceedings of the International Clay Conference, Tokyo*. Israel University Press, Jerusalem.

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