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X-RAY STUDY OF THE THERMAL INTERCALATION OF ALKALI HALIDES INTO KAOLINITE

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Abstract

Intercalation complexes of kaolinite with a series of alkali halides (NaCl (trace amounts), KCl, RbCl, CsCl, NaBr, KBr, CsBr, KI, RbI and CsI) were obtained by a thermal solid state reaction between the kaolinite-dimethylsulfoxide intercalation complex and the appropriate alkali halide. The ground mixtures (1:1 weight ratio) were pressed into disks that were gradually heated up to 250°C for different times. X-ray diffractograms of the disks were recorded after each thermal treatment. At the end of the thermal treatment the disks were ground and basal spacings of the powders obtained. As a result of thermal treatment, alkali halide ions diffuse into the interlayers, replacing the intercalated dimethylsulfoxide molecules. Such a replacement may take place only if the thermal diffusion of the penetrating species is faster than the evolution of the intercalated organic molecule. With increasing temperature the intercalated salt diffused outside the interlayer space or underwent a thermal hydrolysis which resulted in the evolution of hydrogen halides from the interlayer space. Consequently, the amounts of intercalation complexes decreased at elevated temperatures.

Keywords: intercalation, kaolinite-alkali halides comlexes, kaolinite-dimethylsulfoxide complex

Introduction

Minerals from the kaolin group can intercalate certain inorganic salts and a variety of organic compounds [see e.g. 1–5]. The salts or organic compounds penetrate the interlayer space of kaolin-like layers and so expand the crystal basal spacing from 0.72 nm to about 1.00–1.44 nm. The penetrating species that break the strong electrostatic and van der Waals interactions between the layers may form hydrogen bonds with surface hydroxyls, as was first inferred by comparing calculated and experimental basal spacings, and later proven from infrared spectroscopy [see e.g. 6–12]. Basal hydroxyls are very poor proton donors and may form hydrogen bonds only with very strong bases such as the NH_2 group of hydrazine, the $C=O$ group (and to some extent also the NH_2) of urea or of several amides, the NO group of pyridine-N-oxide (PNO) and the $S=O$ group of dimethylsulfoxide (DMSO).

The latter group can bond to the kaolin inner-surface hydroxyls through either the sulphur or the oxygen. In all these cases the proton acceptor functional group

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points to the hydroxyl surface and hydrogen bonds are obtained when this group accepts the proton from the hydroxyl group.

On the basis of their mode of intercalation three main groups of polar organic compounds may be distinguished [13, 14]: Group A includes those species that are directly intercalated from either the liquid, the melt, or concentrated aqueous solution; group B includes those species which can enter the interlayer space by means of an "entraining agent"; and group C includes those species that can be intercalated only by displacement of a previously intercalated compound.

Only a few compounds are directly intercalated by kaolinite. Small molecules with a large dipole moment (3.71–5.37 Debye) may serve as group A species and are intercalated directly by batch treatment, without any pretreatment of the kaolinite [5]. This includes compounds which act simultaneously as proton donors and proton acceptors, such as urea [2], hydrazine [13], hydroxylamine, imidazole, formamide [15], acetamide (and mono- or dimethyl derivatives of the amides) [8, 10, 12, 16], small molecules with a betaine-like mesomeric structure which serve as proton acceptors, such as DMSO, dimethyl selenoxide and PNO [14, 17–23] and salts of short-chain fatty acids with large monovalent cations, such as K^+, Rb^+, Cs^+ and NH_4^+ [1, 14].

Several group A compounds, and particularly hydrazine, were proved to act as entraining agents. Hydrazine can entrain any neutral molecule or salt (group B), the only requirement being that the entrained species is soluble in aqueous hydrazine solution. The complex with the approriate entrained compound may then be obtained by selectively removing the hydrazine by evaporation, exposure to air or heat treatment. Some compounds studied by Weiss *et al.* [14] in this manner are benzidine, *n*-octylamine, glycerol, a number of organic salts (sodium acetate, potassium salts of glycine, alanine, lysine, oxalate and lactate), and the inorganic alkali halide salts. Recently, intercalation of sodium and potassium salts of lauric, palmitic, elaidic, oleic and 12-hydroxystearic acids via hydrazine was carried out [24, 25].

Compounds such as nitrobenzene, acetonitrile, glycol and long chain alkylamines (group C) may penetrate the mineral interlayers by replacing other intercalated compounds, such as ammonium acetate [13, 14] or DMSO [18].

In the present paper we describe a solid state intercalation of several alkali halides by kaolinite. A kaolinite-DMSO intercalation complex and alkali halides are used as the reacting materials. Mixtures containing both components are ground and then pressed into disks. The disks are gradually heated and basal spacings are determined by X-ray diffraction. Changes in the basal spacings as a result of thermal treatment suggest that the alkali halides form intercalation complexes with kaolinite. Two factors that affect intercalation were investigated and will be described: (1) the effect of time, and (2) the effect of temperature.

Experimental

Well crystallized Georgia kaolinite (KGa-1), supplied by Wards, was used in the present study. Alkali halides (analytical reagents) were obtained from Merck, BDH and Sigma.

Intercalation of dimethylsulfoxide (DMSO)

5 g kaolinite was stirred with a solution containing 150 ml DMSO and 50 ml H_2O for one week, in a closed bottle. After this treatment, the mixture was centrifuged and the separated slurry was aged at 60°C for one week. The intercalation complex of DMSO in kaolinite was identified from a basal spacing of 1.11 nm in X-ray diffraction.

Intercalation of alkali halides

200 mg kaolinite-DMSO intercalation complex was manually ground in an agate mortar for about half an hour with 200 mg of each alkali halide. The ground mixture was pressed under vacuum into a 12.5 mm diameter disk using a weight of 10 tons for 10 min. Each disk was reground and repressed before it was thermally treated and examined by X-ray.

The disks were gradually heated in air at 50–250°C for different durations as stated in the Results section, after which X-ray diffractograms were recorded. The disks were repressed each time before they were returned to the furnace in order to avoid fast evolution of the DMSO released during thermal treatment.

X-ray diffraction

X-ray diffraction patterns were recorded while the kaolinite/alkali halide mixtures were in disk form. After the last thermal treatment the disks were ground to fine powder and the final diffractograms were recorded. Although peaks can be clearly observed in the diffractograms of the disks, exact locations of the peaks were determined from powder diffractograms.

Results

X-ray diffractograms of all the disks recorded before any thermal treatment and after heating them overnight at 50°C showed a single sharp peak which is characteristic for the kaolinite-DMSO intercalation complex. In the powder diffractogram this peak appears at 1.11 nm, whereas in the diffractograms of the disks the peak maximum is sometimes shifted to the range 1.11–1.13 nm.

Intercalation of alkali chlorides

Figure 1 shows the diffractograms which were obtained after heating disks of kaolinite-DMSO ground with different alkali chlorides at 100, 155 and 250°C, overnight at each temperature. The disks were also heated at 205°C, but the corresponding diffractograms are not shown in Fig. 1. In addition to the peak at 1.11–1.13 nm which characterizes kaolinite intercalated with DMSO, two new peaks appear at 0.72 and 1.0–1.10 nm. These arise from non-intercalated kaolinite and kaolinite intercalated with alkali halide, respectively. In the presence of NaCl only traces of non-intercalated kaolinite were observed after heating the disk at

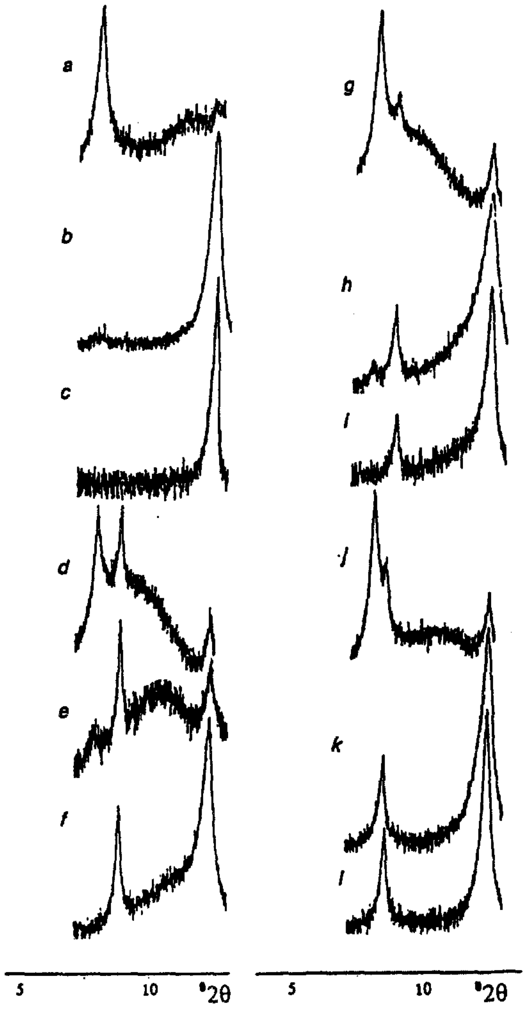

Fig. 1 X-ray diffractograms of disks prepared from mixtures of 200 mg kaolinite-DMSO and 200 mg alkali chloride and gradually heated for one night at each temperature, a–c) NaCl, d–f) KCl, g–i) RbCl, j–l) CsCl; a), d), q) and j) 100°C; b), e), h) and k) 155°C; c), f), i) and l) 250°C

100°C. After heating the disk at 155°C the 1.12 nm peak almost disappeared and the 0.72 nm peak became very strong. This indicates that most of the kaolinite lost the DMSO and became non-intercalated. Only a very small peak was observed at 1.00 nm, indicating the presence of trace amounts of an intercalation complex of NaCl in kaolinite. These small amounts of the kaolinite-NaCl intercalation complex persisted at 205°C but disappeared at higher temperatures. The other alkali chlorides readily showed the presence of considerable amounts of intercalation complexes of KCl, RbCl and CsCl in kaolinite after heating the disks at 100°C. The most intense peak was obtained with KCl. The peak at 1.12 nm became weak at 155°C and disappeared at 250°C. The 0.72 nm peak, on the other hand, intensified. This was due to the thermal evolution of DMSO. At the same time the peak at 1.00–1.05 nm also intensified. This is an indication that some of the intercalated DMSO was replaced by the alkali chloride. At 250°C the peak from the kaolinite-

Fig. 2 X-ray diffractograms of a disk mixture of 200 mg kaolinite-DMSO and 200 mg NaBr, heated as a disk for one night at a) 100°C, b) 155°C, c) 250°C, d) sample c ground down to fine powder, e) the disk was heated during 96 h at 100°C, the recorded diffractogram is that of the disk, f) the disk was heated during 180 h at 100°C and ground. The recorded diffractogram is that of powder

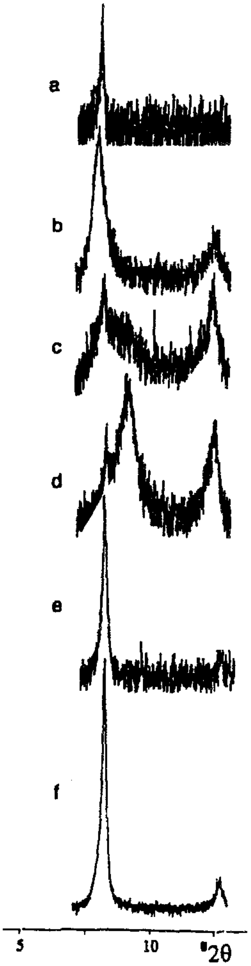

Fig. 3 X-ray diffractograms of disks prepared from mixtures of 200 mg kaolinite-DMSO and 200 mg alkali bromides and gradually heated for one night at each temperature. a–c) KBr, d–e) CsBr; a) and d) 100°C; b) 150°C; c) and e) 250°C

alkali chloride complex decreased and that of non-intercalated kaolinite increased, implying that at this high temperature considerable amounts of the intercalation complexes were decomposed to non-intercalated kaolinite. In another series of experiments a NaCl disk of kaolinite-DMSO was heated at 100°C for 180 h and then at 120 and 145°C. At the latter temperature the kaolinite-DMSO complex lost DMSO, the 1.12 nm peak decreased and the 0.72 nm peak increased with time of heating. No kaolinite-NaCl intercalation complex was obtained by this treatment.

Intercalation of alkali bromides

Figure 2 shows X-ray diffractograms which were obtained after gradually heating a disk of kaolinite-DMSO ground with NaBr. At 100°C only the kaolinite-DMSO intercalation complex was present. A small peak at 0.72 nm from non-intercalated kaolinite was detected after heating the disk at 155°C. Further heating at 250°C caused the kaolinite-DMSO complex to disappear and a new peak to appear at 1.09 nm. This peak characterizes the kaolinte-NaBr intercalation complex which was obtained concomitantly with the thermal evolution of DMSO. Moreover the 0.72 nm peak of non-intercalated kaolinite intensified during the treatment.

In another series of experiments a NaBr disk of the kaolinite-DMSO complex was heated at 100°C for 180 h. DMSO was lost and a 1.08 nm peak appeared due to the kaolinite-NaBr intercalation complex. Figure 3 shows the diffractograms obtained during gradual heating of kaolinite-DMSO disks ground with KBr and CsBr overnight at each temperature. The figure shows that thermal evolution of DMSO from the kaolinite is associated with the formation of kaolinite-alkali bromide intercalation complexes. At 100°C kaolinite-KBr and kaolinite-CsBr intercalation complexes were present together with the kaolinite-DMSO complex. At 155°C kaolinite-alkali bromide was the principal phase, but at higher temperatures it decomposed into non-intercalated kaolinite.

Intercalation of alkali iodides

No reaction product was identified in the interaction between NaI and kaolinite-DMSO. The disk became dark, the X-ray diffractograms were very noisy and no peaks were observed. In the case of KI the disk also became dark during thermal treatment and the X-ray diffractograms were not clear. However, after grinding a disk which was heated at 250°C, a clear diffractogram was obtained (Fig. 4a) with peaks at 1.09 and 0.72 nm arising from KI-intercalated and non-intercalated kaolinites, respectively. Figure 4 b–e shows X-ray diffractograms which were recorded after heating a RbI disk of kaolinite-DMSO one night at each temperature. A peak at 1.15 nm is observed in the diffractogram of the powder obtained by grinding the disk which had been heated to 250°C.

This peak is due to RbI-intercalated kaolinite. It already appeared at 155°C together with a peak at 1.04–1.07 nm. The latter feature, which represents an additional intercalation complex, disappeared at 250°C. The occurrence of this

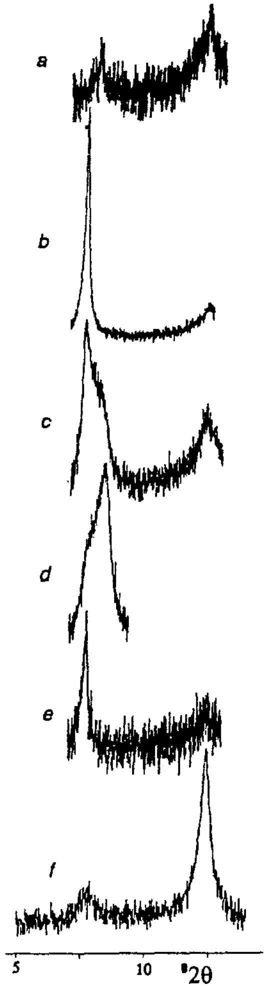

Fig. 4 X-ray diffractograms of disks or powders prepared from mixtures of 200 mg kaolinite-DMSO and 200 mg alkali iodides and gradually heated for one night at each temperature. a) KI, the disk was gradually heated to 250°C and ground down to fine powder. b–e) RbI, heated as a disk for one night at b) 100°C, c) 155°C, d) 205°C, e) heated at 250°C as a disk for one night and ground down to fine powder. f) CsI, the disk was heated at 145°C for 120 h and ground down to fine powder

1.04–1.07 nm peak requires further investigation. The formation of the CsI intercalation complex is complicated. Only traces were detected after gradual heating to 250°C. In another series of experiments a CsI disk of kaolinite-DMSO was heated 120 h at 145°C and later ground to fine powder. A small broad peak at 1.15 nm appeared in the X-ray diffractogram representing the presence of a kaolinite-CsI intercalation complex (Fig. 4f).

Discussion

In the present study we showed that intercalation complexes of alkali halides in kaolinite can be obtained in a solid state reaction from a kaolinite-DMSO intercalation complex. During the thermal treatment alkali halide ions diffuse into the swollen mineral interlayers and replace the intercalated DMSO molecules. Such a replacement may take place only if the thermal diffusion of the penetrating species is faster than the evolution of the intercalated DMSO. This is obtained by pressing the mixed material into a disk and repeated pressing after each thermal treatment, thereby decreasing the rate of evolution of DMSO. All experiments to replace DMSO by any of the alkali halides without pressing the mixtures into disks failed. Furthermore, we did not succeed in finding appropriate conditions for obtaining an intercalation complex of NaI, and only a small amount of NaCl was intercalated. Lithium and fluoride salts could not be studied because these salt-clay mixtures are hygroscopic and in our conditions it was impossible to press them into disks with kaolinite.

Weiss *et al.* obtained kaolinite-alkali halide intercalation complexes from aqueous salt solutions through the use of kaolinite intercalated by ammonium acetate or hydrazine [14]. The basal spacings which were observed in that work are similar to those that were detected in our study (Table 1). It may be concluded that similar intercalation complexes were obtained by both techniques, although the complexes of Weiss *et al.* were obtained in the presence of water, whereas our complexes were obtained in the solid state.

Table 1 The 001 spacings of kaolinite-alkali halide intercalation complexes obtained from powder diffractograms of ground thermal treated disks, (a) and of complexes obtained from aqueous salt solutions (b)

Alkali halide	001 spacings (nm)	
	a	b
NaCl	1.00	1.01
KCl	1.05	1.00
RbCl	1.01	1.01
CsCl	1.05	1.03
NaBr	1.07	1.07
KBr	1.03	1.04
CsBr	1.09	1.08
KI	1.09	1.08
RbI	1.15	1.14
CsI	1.17	–

a – Present study
b – from Weiss, Thielepape and Orth [14].

The thermal stability of the kaolinite-alkali halide intercalation complexes is limited and at elevated temperatures (e.g. 250°C) a basal spacing of 0.72 nm is obtained with all alkali halides in additon to the 1.00–1.15 nm basal spacing, for which the corresponding peak becomes weak. The 0.72 nm spacing represents non-intercalated kaolinite. From this study it is not clear whether the alkali halide ions diffuse from the interlayer or whether hydrogen halide is evolved due to a thermal hydrolysis of the alkali halide, as suggested to occur by Heller-Kallai [26] and Gabor *et al.* [27] during thermal dehydroxylation of the kaolinite in a mixture containing this clay and the salt.

Recently Thompson *et al.* claimed that they obtained intercalation of alkali halides in kaolinite by dry grinding mixtures of kaolinite with the appropriate alkali halides [28]. Their claim was based on the disappearance of the sharp and strong 0.72 nm peak and the appearance of extremely weak and broad peaks at smaller angles. If those X-ray diffractograms are compared with our data, in which peaks due to the intercalation complexes are sharp and strong, it seems that the peaks shown by Thompson *et al.* are artifactual. It should also be noted that Yariv studied the dry grinding of the same mixtures by infrared spectroscopy, and showed that under dry conditions only CsCl formed an intercalation complex with kaolinite [29]. None of the other alkali halides formed intercalation complexes with kaolinite. Thus the disappearance of the 0.72 nm peak with increased time of grinding must be due to the gradual amorphization of the clay. The spacings of the intercalation complexes reported by Thompson *et al.* [28] are completety different from those of Weiss *et al.* [14] and from those found in the present study.

In conclusion, solid state intercalation of alkali halides into kaolinite is obtained by heating a pressed disk made of an alkali halide salt and kaolinite-DMSO complex. In this system the alkali halide replaces the intercalated DMSO. The mechanism of the reaction involves the diffusion of the alkali halide ions into the interlayer space and the diffusion of DMSO outside this space. At higher temperatures, the amounts of the intercalation complexes decrease, and non-intercalated kaolinite is obtained. This may be due to the diffusion of the alkali halide ions outside the interlayer space or to thermal hydrolysis of the salt leading to evolution of hydrogen halide.

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