INTERCALATION OF BENZAMIDE INTO EXPANDED KAOLINITE UNDER AMBIENT ENVIRONMENTAL CONDITIONS

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Abstract—Waste kaolinite from a fertilizer industry was intercalated with *n*-methylformamide (NMF) under ambient conditions. The complex was washed, characterized and then reacted with benzamide (dissolved in ethanol) under similar conditions. Using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and differential thermal analysis (DTA), clear evidence of benzamide intercalation was observed after a reaction time of 48 h. The FTIR and DTA analysis also confirmed that the ethanol was not involved in the intercalation and that both NMF and benzamide are present in the interlayer region.

Key Words—Benzamide, Ethanol, Intercalation, Kaolinite, *n*-methylformamide.

INTRODUCTION

Kaolinite [$Al_2Si_2O_5(OH)_4$] is a layered aluminosilicate with almost perfect 1:1 layer structures constituted by two different surfaces (Young and Hewat, 1988). One side of the lamella consists of a silica sheet in which Si atoms are co-ordinated tetrahedrally by O atoms. The other side consists of a gibbsite-type sheet where Al atoms are co-ordinated octahedrally by O atoms and OH groups. Quantitative estimates indicate that the cohesive energy between kaolinite layers is primarily electrostatic (Cruz *et al.*, 1972). There is also a certain degree of van der Waals attraction and hydrogen bonding between the OH groups of the gibbsite sheet and the oxygen atoms of the adjoining silica sheet (Wolfe and Giese, 1974).

The ability to modify phyllosilicates by insertion of an inorganic and/or organic guest species into the interlamellar region opens up a range of potential uses for these materials. The smectite minerals possess exchangeable cations within their interlayers that facilitate the encapsulation of polar organic molecules. Kaolinite does not have this property as there are no exchangeable cations between its layers. However, the kaolinite interlayer region can react (intercalation) with a small group of organic and/or inorganic materials. The successful intercalation agents decrease the electrostatic attraction between the lamellae by causing an increase in the dielectric constant when the compounds penetrate between the layers (van Olphen, 1977). Intercalating compounds also have a certain hydrogen bonding capacity. Formamide, dimethylsulfoxide and *n*-methylformamide (NMF) are known to intercalate directly, resulting in an increase of the interlayer spacing within the kaolinite (Olejnik *et al.*, 1968). This increase depends on the size and arrangement of the guest species.

Although not many compounds have the ability to intercalate, the number may be extended by the so-called 'displacement method' (Guimaraes *et al.*, 1998). Displacement involves the substitution of a directly intercalated species (*e.g.* NMF or potassium acetate) by a second organic molecule. The use of a directly intercalating compound as an intermediate for the intercalation of other polar organic compounds opens up new areas for basic, strategic and applied research. The resultant hybrid materials combine the features of the clay and of the guest species. These complexes have the potential to be used as adsorbents, catalyst supports, in chromatographic columns and ion exchangers (Gardolinski *et al*, 1999).

The present study was undertaken to investigate the intercalation of benzamide, under ambient environmental conditions, in a previously expanded kaolinite-NMF material. The intercalation of aromatic compounds has been reported previously (Camazano and Garcia, 1966; Weiss *et al.*, 1968). The materials were characterized by powder XRD, IR spectroscopy and DTA.

MATERIALS AND METHODS

The kaolinite chosen was a waste product from a fertilizer industry, currently being landfilled. It originated from English China Clays International in Cornwall, UK (referred to as sample SO) and the white sample had a chemical composition given as: SiO_2 46.0%, Al_2O_3 38.70%, Fe_2O_3 0.56%, TiO_2 0.09%, CaO 0.20%, MgO 0.20%, K_2O 1.01%, Na_2O 0.07%. The XRD pattern of the kaolinite used shows no impurities and consists of sharp peaks, typical of a well-ordered structure. No purification steps were taken. Analytical grade NMF, benzamide and ethanol were used without further purification.

Intercalation of NMF

The intercalation process was carried out under ambient environmental conditions (room temperature and atmospheric pressure) where 1 g of kaolinite was mixed with 10 ml of NMF, using a magnetic stirrer, for

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48 h. The suspension was then filtered through Whatman no. 42 filter paper. Methanol was used to wash the residue to remove excess NMF. The clay was air dried for 24 h. Dried samples were ground with a mortar and pestle and placed in glass vials.

Intercalation of benzamide

The K-NMF material (1 g) was added to benzamide dissolved in ethanol (10 M). The mixture was agitated by magnetic stirrer for 48 h. The suspension was then filtered with Whatman no. 42 filter paper. Methanol was used to wash the external residue. The material was air dried for 24 h. Dried samples were ground with a mortar and pestle and placed in glass vials for characterization.

X-ray diffraction

For powder XRD analysis the sample was placed evenly into a circular hollow aluminum holder. The analysis was carried out on a Philips X'Pert diffractometer using CuKα radiation. The samples were measured in the step-scan mode with steps of $0.04°2\theta$ and a counting time of 1 s per step.

Differential thermal analysis

Combined DTA/TGA was used to study the weight changes accompanying crystallization, decomposition, combustion and desorption processes. A Stanton Redcroft DTA/TGA 1600 (Rheometric Scientific, Epson UK) was used with a heating rate of $10°C$ min^{-1}. The crucibles used were matched pairs made of Pt-Rh alloy. Alumina was used as a reference material.

Fourier Transform Infrared Analysis

Infrared spectra of the powdered samples were recorded using a Bomem Michelson MB 100 FTIR spectrometer. After mixing 1 mg of the sample with 100 mg of FTIR-grade KBr, the mixture was poured into a hollow steel holder. The samples were scanned 50 times at 2 cm^{-1} resolution, between 4000−600 cm^{-1}.

RESULTS AND DISCUSSION

XRD analysis

Initially an attempt was made to intercalate benzamide directly into the kaolinite. This proved unsuccessful. As a result, it was decided to use an NMF-intercalated kaolinite compound as an intermediate. In previous displacement studies (Komari and Sugahara, 1998), successful treatment of an intermediate complex (such as NMF-intercalated kaolinite) with a secondary compound resulted in a slight increase or decrease in the basal spacing of the NMF-rich kaolinite intercalate. This is an indication of complete exchange within the kaolinite between the primary and secondary intercalating species. The NMF-rich kaolinite intermediate treated with benzamide, did not, however, produce this result. Figure 1 shows that after a reaction time of 48 h, three

peaks were observed on the XRD pattern. The peak at 0.7 nm suggests the presence of unmodified kaolinite, while the peak at 1.0 nm indicates the presence of NMF-intercalated kaolinite. The presence of a third peak at 1.4 nm may be due to intercalated ethanol (solvent used with benzamide) or intercalated benzamide.

Influence of ethanol

To investigate the influence of ethanol, an attempt was made firstly to intercalate ethanol directly into the unmodified kaolinite and secondly into the NMF-rich kaolinite compound. The XRD patterns in Figure 1(b,d) clearly show no change in the basal spacings as a result of both attempts at intercalation of ethanol.

Figure 2 represents the FTIR spectra for the unmodified kaolinite, the ethanol-treated kaolinite, the NMF-rich kaolinite intercalate and the ethanol-treated NMF-rich kaolinite. The spectra of unmodified and ethanol-treated kaolinite are illustrated in parts a and b, respectively, of Figure 2. There is clearly no difference between the two spectra, indicating that ethanol was unable to intercalate directly in the unmodified kaolinite. Upon intercalation with NMF (Figure 2c), the inner surface OH bands of the pure kaolinite at 3696 cm^{-1} and 3653 cm^{-1} are perturbed. This is due to hydrogen bonding between the OH groups of the mineral and the NMF (Guimaraes *et al.,* 1998). The band at 3619 cm^{-1} can be assigned to inner OH groups inaccessible to the NMF. Therefore, this band remains unchanged. Other bands confirming the presence of NMF include the N−H and carbonyl-stretching bands at 3419 cm^{-1} and 1681 cm^{-1}, respectively. A summary of these bands and others is presented in Table 1. The IR spectrum of the attempted intercalation of NMF-rich kaolinite with ethanol (Figure 2d) is similar to that of the NMF-rich kaolinite intercalate starting material, indicating that
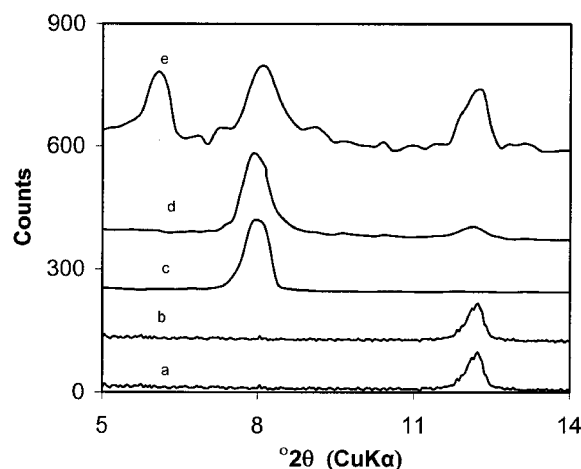

Figure 1. XRD patterns of: (a) unmodified kaolinite; (b) ethanol-treated kaolinite; (c) NMF-rich kaolinite intercalate; (d) ethanol-treated NMF-rich kaolinite intercalate; and (e) benzamide-treated NMF-rich kaolinite intercalate (48 h).
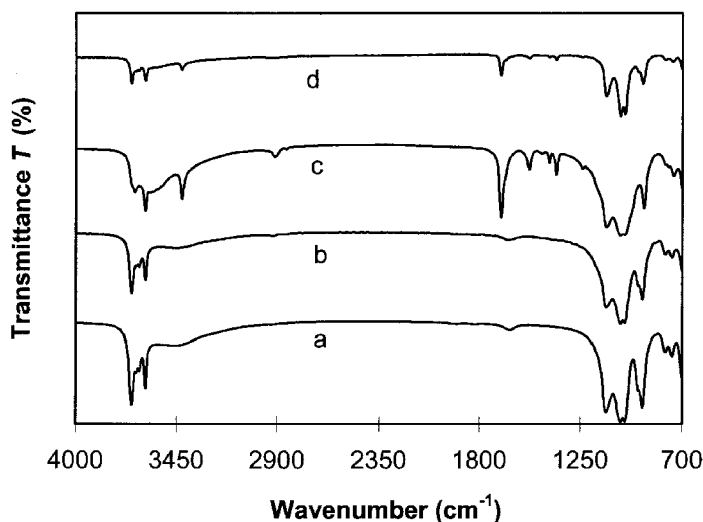
Figure 2. IR spectra of: (a) unmodified kaolinite; (b) ethanol-treated kaolinite; (c) NMF-rich kaolinite intercalate; and (d) ethanol-treated NMF-rich kaolinite intercalate.

ethanol has not intercalated or reacted with the clay. The only differences are in the intensity of the bands (bands in NMF-rich kaolinite are more intense) and the reappearance of the 3696 cm^{-1} band in the ethanol-treated NMF kaolinite complex. As mentioned, a decrease in the intensity of the 3696 cm^{-1} band can be attributed to successful hydrogen bonding between the OH groups of the clay and the guest species. The reappearance of this band can therefore be linked to a partial deintercalation of the NMF. This is due to the attempted intercalation of ethanol, which, while not

itself reacting, was successful in removing some of the NMF from the interlayer region. Otherwise, the similarity of the two spectra confirms that ethanol, despite being used as a solvent in the benzamide treatment of the NMF-intercalated kaolinite intermediate, is not involved in the intercalation process.

Intercalation of benzamide

The second hypothesis is that the presence of the third peak on the XRD pattern may be attributed to an intercalated benzamide compound. The FTIR spectrum

Table 1. Infrared wavelengths (cm^{-1}) and assignments of NMF-rich kaolinite intercalate, pure benzamide and benzamide-treated NMF-rich kaolinite intercalate.

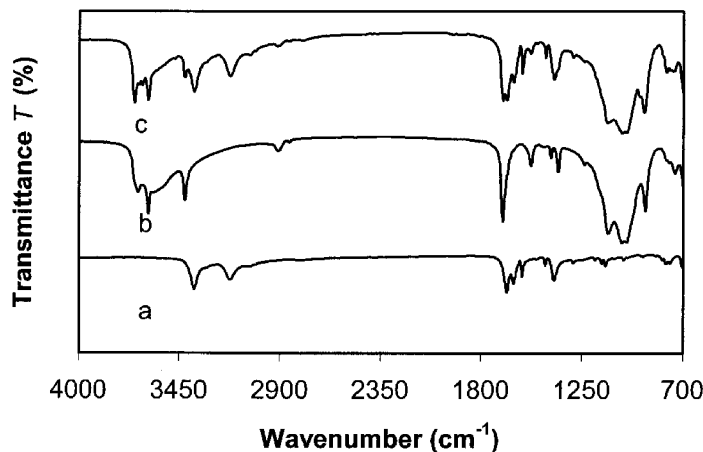| Complex	Bands observed (cm^{-1})	Assignment
NMF-rich kaolinite	3677	Vibration of inner hydroxyl group
	3419	N−H stretching
	1681	C=O stretching
	1528	N−H bending
	1419	C−N stretching
	1379	$\delta_s CH_3$
	1236	Interaction between N−H bending and C−N stretching
Benzamide	3367	Antisymmetric N−H stretching
	3172	Symmetric N−H stretching
	1658	Amide I band, [ν(C=O)]
	1623	Amide II band, [δ(NH)]
	1576	C=C stretching
	1401	C−N stretching
Benzamide-treated NMF-rich kaolinite	3420	N−H stretching
	3368	Antisymmetric N−H stretching
	3172	Symmetric N−H stretching
	1681	C=O stretching
	1576	C=C stretching
	1529	N−H bending
	1402	C−N stretching

Figure 3. IR spectra of (a) benzamide; (b) NMF-rich kaolinite intercalate; and (c) benzamide-treated NMF-rich kaolinite intercalate (48 h).

for the benzamide-treated NMF-intercalated kaolinite after 48 h is shown in Figure 3c while the spectrum for benzamide (Figure 3a) and the NMF-intercalated kaolinite are also present. Compared with the FTIR spectra for kaolinite and the NMF-intercalated kaolinite compounds, the benzamide-treated NMF-intercalated kaolinite show new bands at 3368 and 3172 cm^{-1} which can be attributed to asymmetric and symmetric N—H stretching, respectively. The two bands are also clearly present in the pure benzamide spectrum. There is, however, a third band at 3419 cm^{-1} that can be attributed to N—H stretching in the NMF compound. The appearance of bands in the 1620 to 1529 cm^{-1} region provides evidence of aromaticity in the intercalated product, which also suggests that benzamide has intercalated the interlamellar region of the kaolinite. These bands are also seen in the pure benzamide spectrum. The original fingerprint peaks for the NMF-intercalated kaolinite are present in the benzamide-treated NMF-intercalated kaolinite product. The FTIR analysis, coupled with the presence of a third peak at 1.4 nm in the XRD pattern provides confirmation of the presence of both benzamide and NMF in the interlamellar spacings of the kaolinite.

Thermal analysis

Further evidence of the presence of benzamide in the interlamellar spacings in the kaolinite was observed in the DTA curves as depicted in Figure 4. The unmodified waste kaolinite shows two endothermic peaks at 51 and 540°C. These can be attributed to the elimination of sorbed water and to a dehydroxylation process to metakaolinite, respectively (Frost and Vassallo, 1996). An exotherm at 995°C is due to a phase transition or complete breakdown of crystalline structures. These peaks are also visible in the NMF-intercalated kaolinite DTA curve along with an endotherm at ~214°C corresponding to the elimination of NMF from the complex (boiling point is 195.5°C), and a slight exotherm at 310°C due to the combustion of residual

NMF. The benzamide-treated NMF-intercalated kaolinite plot provides further evidence for the co-existence of both compounds within the interlayer region. Again there is elimination of NMF and an endotherm at 350°C suggesting the elimination of benzamide (boiling point 290°C). The exotherms at 370 and 450°C can be attributed to the combustion of NMF and benzamide residue, respectively. Slightly higher temperatures for elimination and combustion of NMF can be explained by the fact that the NMF remaining after treatment with benzamide is more strongly bonded and requires more energy to decompose.

CONCLUSIONS

The results reported here show that benzamide will not intercalate directly into kaolinite but will do so when an intermediate, in this case NMF, is used to expand the kaolinite layers. The intercalation of benzamide does not
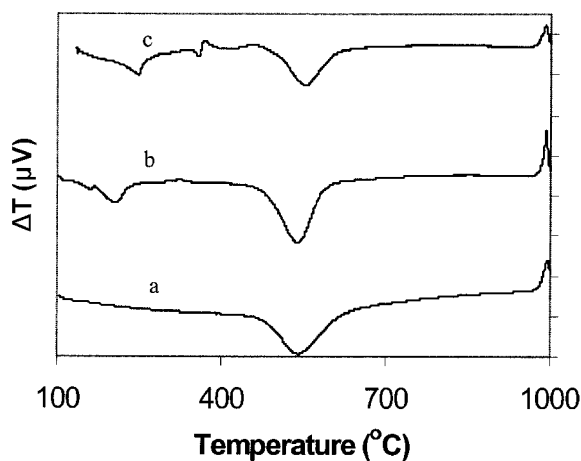

Figure 4. DTA curves of: (a) unmodified kaolinite; (b) NMF-rich kaolinite intercalate; and (c) benzamide-treated NMF-rich kaolinite intercalate (48 h).

replace all the NMF, as they appear to co-exist. This is indicated by the extra peak in the XRD pattern which can be attributed to the presence of benzamide. The IR spectrum of benzamide-treated NMF-rich kaolinite confirms that both molecules are involved in intercalation due to bands that can be specifically attributed to both. Differential thermal analysis provides further evidence of their co-existence within the interlayer region. Temperature changes accompanying decomposition and combustion processes are in agreement with the physical properties of both compounds and are represented in the DTA curve of the benzamide and NMF-rich kaolinite. Ethanol, which is used to dissolve the benzamide, is not involved in the intercalation.

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