KAOLINITE-PYRIDINE INTERCALATION COMPOUND DERIVED FROM HYDRATED KAOLINITE

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Abstract—A kaolinite-pyridine intercalation compound was prepared using hydrated kaolinite as an intermediate. Hydrated kaolinite having a basal spacing of 10 Å was treated with pyridine to form a well-ordered intercalation compound having a basal spacing of 12.0 Å. Infrared spectroscopy indicated the presence of hydrogen bonding between the hydroxyls of the kaolinite and the pyridine. ^{29}Si nuclear magnetic resonance spectroscopy with cross polarization and magic-angle spinning revealed that intercalated pyridine affected the environment of silicon. The mono-substituted pyridine derivatives were also intercalated with hydrated kaolinite. On the basis of the basal spacings of the intercalation compounds and the stabilities of the derivatives between the layers, the pyridine appeared to be in an approximately perpendicular position, with the nitrogen facing the gibbsitic sheets.

要旨－カオリナイト水和物を中間体として用い、カオリナイト－ピリジン層間化合物を合成した。１０Åの基本面間隔を持つカオリナイト水和物をピリジンで処理することにより、基本面間隔が１２．０Åの層間化合物が得られた。赤外吸光分析によりカオリナイトの水酸基とピリジンの間の水素結合の存在が示された。マジック角回転及び交差分極法を用いた ^{29}Si核磁気共鳴分析により、ピリジンはケイ素の環境に影響を与えていることが明らかとなった。いくつかの１置換ピリジン誘導体もカオリナイト水和物にインターカレートした。これらの層間化合物の基本面間隔と誘導体の層間での安定性から、ピリジンは窒素原子をギブサイト層に向けほぼ垂直に配向しているものと推定された。

INTRODUCTION

Kaolinite is well known to take up neutral polar organic molecules between the layers to form "intercalation compounds", which have attracted much attention recently (Lipsicas *et al.,* 1986; Thompson and Barron, 1987; Raupach *et al.,* 1987). Inasmuch as guest molecules are mainly stabilized by hydrogen bond formation with hydroxyl groups of kaolinite, only specific molecules, such as amides, can be directly intercalated. Some of the molecules which cannot be incorporated by direct reaction, however, can be introduced by displacing the previously intercalated molecules (the so-called "displacement method"). Also, the presence of other molecules (the so-called "entraining agents") enables guest molecules to be intercalated (Theng, 1974).

Hydrated kaolinite has only recently been reported. Range *et al.* (1968) reported its existence, and, more recently, Costanzo *et al.* (1984a) investigated its preparation and properties. In their initial report, 10-Å hydrated kaolinite was obtained by the substitution of fluorine for hydroxyl at the edge of the silicate layers of kaolinite (Costanzo *et al.,* 1980, 1984a). Three related phases were also proposed; an 8.4-Å hydrate, an 8.6-Å hydrate, and a 10-Å quasi-stable hydrate (Costanzo *et al.,* 1982, 1984b). Later, Raythatha and Lipsicas (1985) reported the preparation of the 10-Å and 8.6-Å phases without the fluorination reaction.

From the analogy of the intercalation behavior of hydrated halloysite (MacEwan, 1948; Carr and Chih, 1971), hydrated kaolinite should incorporate a variety of molecules. Thus, it has the potential to act as an intermediate in the "displacement method". The first attempt was recently reported by Wada *et al.* (1987) using the 8.6-Å hydrate. They obtained intercalation compounds of kaolinite with acetone and methanol under a pressure of 1 kbar, and with water and ethanol under pressures as high as 30 kbar.

On the other hand, pyridine and pyridinium ion are known to be typical guest molecules in intercalation chemistry. In terms of clay minerals, pyridine was in-

tercalated in the interlayer space of montmorillonite (Greene-Kelly, 1955) and halloysite (MacEwan, 1948), and pyridinium ion was incorporated by montmorillonite and vermiculite (Serratosa, 1966). The orientation of pyridine and pyridinium ion was different among the intercalation compounds. In the interlayer space of Na^+-montmorillonite, pyridine was in a perpendicular position, and nitrogen was facing sodium ions (Greene-Kelly, 1955). When pyridinium ions were intercalated in the interlayer space of montmorillonite, pyridinium ions showed flat conformation (Serratosa, 1966). In the interlayer space of vermiculite, pyridinium ions were present in a perpendicular orientation in which nitrogen faced the silicate layer (Serratosa, 1966).

Although Weiss (1969) mentioned the formation of a kaolinite-pyridine intercalation compound, its preparation has not been reported in detail. So far, pyridine-N-oxide (Weiss *et al.*, 1966), and 2-, 3-, and 4-methylpyridine-N-oxide (Weiss and Orth, 1973) have been intercalated with kaolinite. Their intercalation compounds showed the basal spacings in the range 12.5–13.3 Å. The aromatic ring was tilted and the NO group faced the gibbsitic sheets between the layers of all the intercalation compounds.

The present study deals with the application of hydrated kaolinite in the preparation of a kaolinite-pyridine intercalation compound. Inasmuch as hydrated halloysite incorporates pyridine, its intercalation to hydrated kaolinite is expected. Its mono-substituted derivatives were also intercalated to study the orientation of pyridine between the layers.

MATERIALS AND METHODS

Materials

The kaolinite used in the present study was API clay minerals standard No. 9 (Mesa Alta, New Mexico). It was used after grinding to pass a 100-mesh sieve. Its X-ray powder diffraction (XRD) pattern showed no crystalline impurities. Pyridine (I), 2-methylpyridine (II), 3-methylpyridine (III), 4-methylpyridine (IV), and 4-ethylpyridine (V) were used as received. Structural formulae of these materials are shown below.

(I)   (II)   (III)

(IV)   (V)
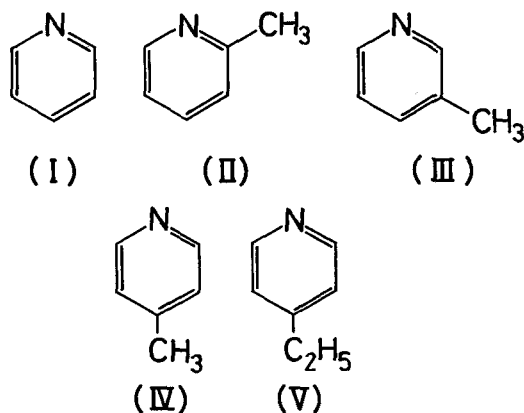
Preparation of hydrated kaolinite

Hydrated kaolinite was synthesized from a kaolinite-dimethylsulfoxide (DMSO) intercalation compound essentially by the method reported by Costanzo *et al.* (1980). The kaolinite-DMSO intercalation compound was prepared by stirring 3 g of kaolinite in 20 ml of DMSO containing 1.8 ml of H_2O at 60°C for 5 hr. After the addition of 1.3 g of NH_4F, the suspension was stirred at 60°C for 1 hr. The supernatant solution was removed by centrifugation, and the crude product was heated at 110°C for 4 hr. After the product was crushed, it was stirred in 20 ml of H_2O for 15 min, and separated by centrifugation. The product was washed with water three times. Finally, the product was again stirred in the same amount of H_2O overnight.

In our procedure, a fluorinated kaolinite-DMSO intercalation compound was heated at 110°C for 4 hr in addition to the procedure reported by Costanzo *et al.* (1980). In their subsequent report (Costanzo *et al.*, 1984b), the heat treatment of the fluorinated kaolinite-DMSO intercalation compound at 110°C led to the collapse to 7.2-Å kaolinite, which was then converted into the 8.4-Å hydrate. In our experiment, however, the fluorinated kaolinite-DMSO intercalation compound did not collapse by the heat treatment at 110°C for 4 hr, and its hydration resulted in a good yield of the 10-Å kaolinite. Hence, this operation was added to the reported procedure.

Preparation of intercalation compounds of kaolinite and pyridine or its derivatives

Pyridine and its derivatives were intercalated by stirring a mixture of hydrated kaolinite and the appropriate organic at room temperature. After the hydrated kaolinite was separated from excess water by centrifugation, it was immediately stirred in pyridine (or its derivatives) (20 ml/g kaolinite) for 15 min. The supernatant pyridine was then removed by centrifugation, and the same amount of pyridine was again added. The resulting suspension was finally stirred overnight.

The preparation of the kaolinite-pyridine intercalation compound from a kaolinite-N-methylformamide (NMF) intercalation compound or the raw kaolinite was also attempted in the same manner. The kaolinite-NMF intercalation compound was prepared by the method of Olejnik *et al.* (1970).

Analyses

Basal XRD spacings of products were obtained using a Rigaku Denki RAD I-B instrument and Ni-filtered $CuK\alpha$ radiation. Because some of the products were unstable in air, the crude products were coated on the glass slide for the measurement immediately after the centrifugation. Also, the XRD patterns of products dried in a desiccator (silica gel was used as a desiccant) were obtained to study the stabilities of the intercalation compounds. The infrared (IR) spectra of the products were recorded on a Shimadzu IR-435 and/or a JASCO FT/IR-5M spectrophotometer. Products dried in a desiccator were pelletized using KBr as a diluent. ^{29}Si nuclear magnetic resonance with cross polarization and magic-angle spinning spectra (^{29}Si CP/MASNMR) of the products were obtained using a JEOL GSX-270 instrument at 53.67 MHz with a slight resolution-enhancement technique (Jeremy *et al.*, 1987). Repetition time was 5 s, and 32–128 free induction decays were accumulated. Chemical shifts were quoted from tetramethylsilane. The amount of fluorine in hydrated kaolinite was investigated using ion chromatography (IC) (Yokokawa, IC-100-5A). For the IC measurement, the thoroughly washed product was fused with Na_2CO_3, and the fusion mixture was dissolved in water.

Characterization of hydrated kaolinite

Hydrated kaolinite was characterized by XRD and IC. The XRD pattern showed the presence of an intense peak at 10.2 Å and a weak peak at 7.2 Å. The IC results indicated that the product contained 0.5 wt. % F. This value corresponded to the replacement of about 1.7% of hydroxyl of kaolinite.

An IR spectrum of hydrated kaolinite even after complete dehydration was slightly different from that of the raw kaolinite (KBr method). The IR spectrum of hydrated kaolinite could not be obtained probably due to its dehydration during the sample preparation. Although the amount of fluorine was small, relative intensities of hydroxyl bands drastically decreased. Correspondingly, two broad bands were present at about 3450–3550 cm^{-1}. Nevertheless, the profile of the original OH-stretching bands was similar to that of the raw kaolinite.

A ^{29}Si CP/MASNMR spectrum of hydrated kaolinite was obtained only after dehydration because the wet sample could not be measured. The profile of the peaks was similar to that of the raw kaolinite. Therefore, the substitution of a trace of fluorine for hydroxyl did not significantly affect the profile of ^{29}Si NMR peaks.

In terms of the stability, 10-Å hydrated kaolinite was unstable in air. After it was exposed in air for several days, it collapsed to a 7.2-Å kaolinite via an 8.4-Å hydrate.

RESULTS

Kaolinite-pyridine intercalation compound

Figure 1 shows the XRD patterns of the raw kaolinite, hydrated kaolinite, and the product dried in the desiccator. The treatment of hydrated kaolinite with pyridine led to the formation of an intercalation compound having the basal spacing of 12.0 Å. The XRD pattern of the kaolinite-pyridine intercalation compound dried in the desiccator even for a month was very similar. The XRD pattern of the product showed the presence of an intense 001 peak at 7.36°2θ (12.0 Å). The appearance of the 12-Å peak was accompanied by the disappearance of the peak due to 10-Å hydrated kaolinite, indicating the completion of the reaction. In addition to the 001 peak, three higher orders were detected at 6.0, 4.0, and 3.0 Å.

Figure 2 shows the IR spectrum of the raw kaolinite, pyridine dissolved in CCl$_4$, and the dried product. The spectrum of the product clearly shows bands of pyridine. In addition to the bands due to kaolinite (Figure 2a), those assigned to pyridine (Figure 2b) were observed in the spectrum of the product (Figure 2c). The bands ascribed to pyridine at 1400–1650 cm^{-1}, especially those at 1583 and 1601 cm^{-1}, shifted to higher frequencies in the spectrum of the intercalation compound (1440 → 1442, 1483 → 1487, 1583 → 1593, and 1601 → 1612 cm^{-1}).

The effect of the intercalation of pyridine on the vibration modes of the kaolinite was clearly observed in the OH-stretching region. Figure 3 shows the IR patterns of the raw kaolinite and the product in the OH-stretching region. The profile of the product (Figure 3b) is different from that of the raw kaolinite (Figure 3a). Compared with the pattern of the raw kaolinite, a
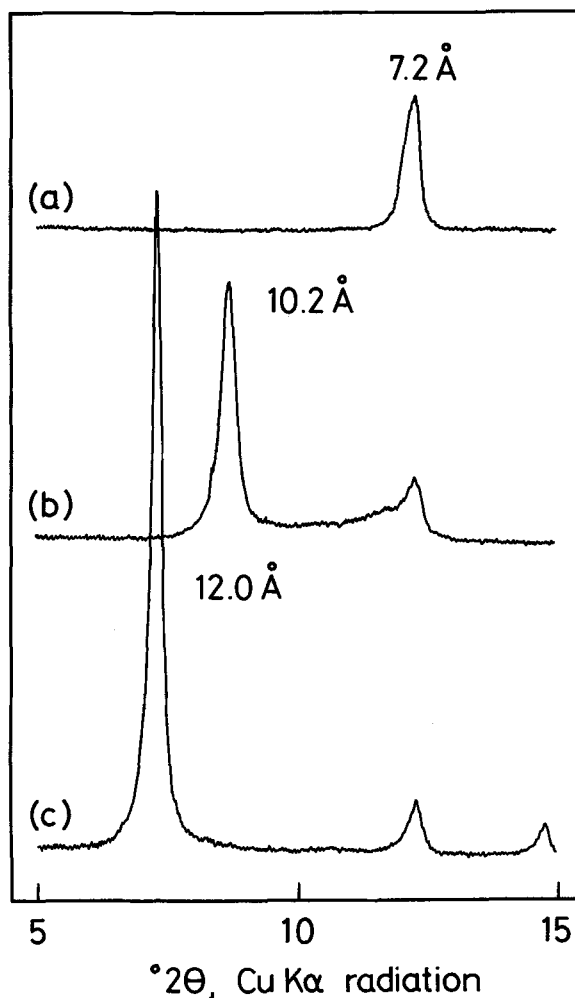

Figure 1.   X-ray powder diffraction patterns of (a) raw kaolinite, (b) hydrated kaolinite, and (c) kaolinite-pyridine intercalation compound dried in a desiccator.

new band is present at 3637 cm^{-1}; however, the intensity ratio between the 3693-cm^{-1} band and the 3621-cm^{-1} band is similar.

The change in the Si environment was studied by ^{29}Si NMR spectroscopy. The ^{29}Si CP/MASNMR spectra of the raw kaolinite and the product are shown in Figure 4. The raw kaolinite spectrum shows a doublet at −91.0 ppm (Figure 4a), in line with previous work (Barron *et al.*, 1983). The spectrum of the product (Figure 4b) shows a peak at −91.8 ppm and two weak peaks that can be assigned to unexpanded kaolinite.

The advantage of using hydrated kaolinite is shown by the comparison with the preparation of the kaolinite-pyridine intercalation compound from that of a kaolinite-NMF intercalation compound. Treating the kaolinite-NMF intercalation compound with pyridine did not change the XRD pattern, indicating no reaction.
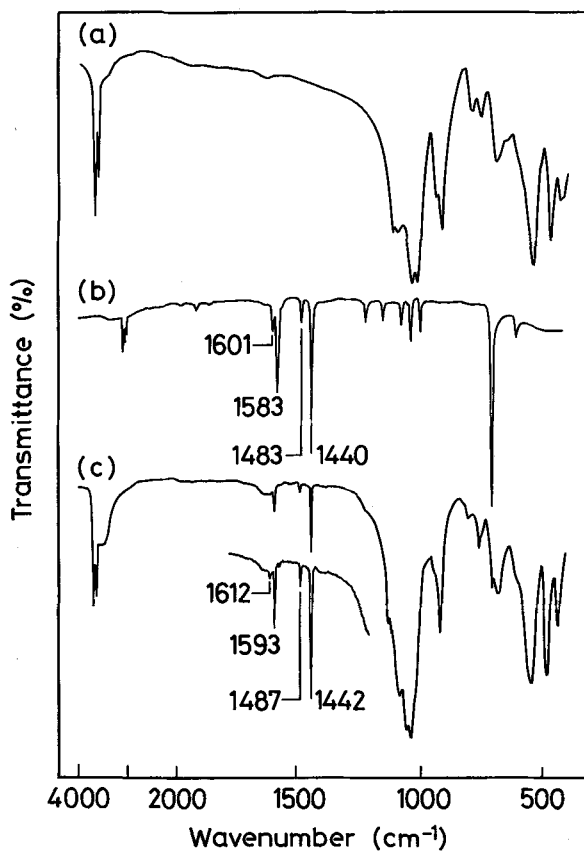
Figure 2. Infrared spectra of (a) raw kaolinite, (b) pyridine (in CCl$_4$), and (c) kaolinite-pyridine intercalation compound dried in a desiccator.

Also, the raw kaolinite did not take up pyridine directly.

Intercalation compounds of kaolinite and pyridine derivatives

Figure 5 shows the XRD patterns of the products without drying. The products gave more or less well-defined peaks in the range 12.2–14.4 Å, proving intercalation had occurred. Correspondingly, the 10-Å peak disappeared; the reaction was completed, so that hydrated kaolinite was converted into intercalation compounds or collapsed. All the basal spacings of the intercalation compounds were larger than that of the kaolinite-pyridine intercalation compound (12.0 Å). The spacings depended on the kind and position of the substituents. The spacings were as follows: for kaolinite-2-methylpyridine, 12.2 Å; for kaolinite-3-methylpyridine, 12.8 Å; for kaolinite-4-methylpyridine, 13.8 Å; for kaolinite-4-ethylpyridine, 14.4 Å. Apparently, the presence of the substituents at the 4-position led to the much larger basal spacings.

The intensities of the 001 peaks of the intercalation compounds were also different. Among the intercala-
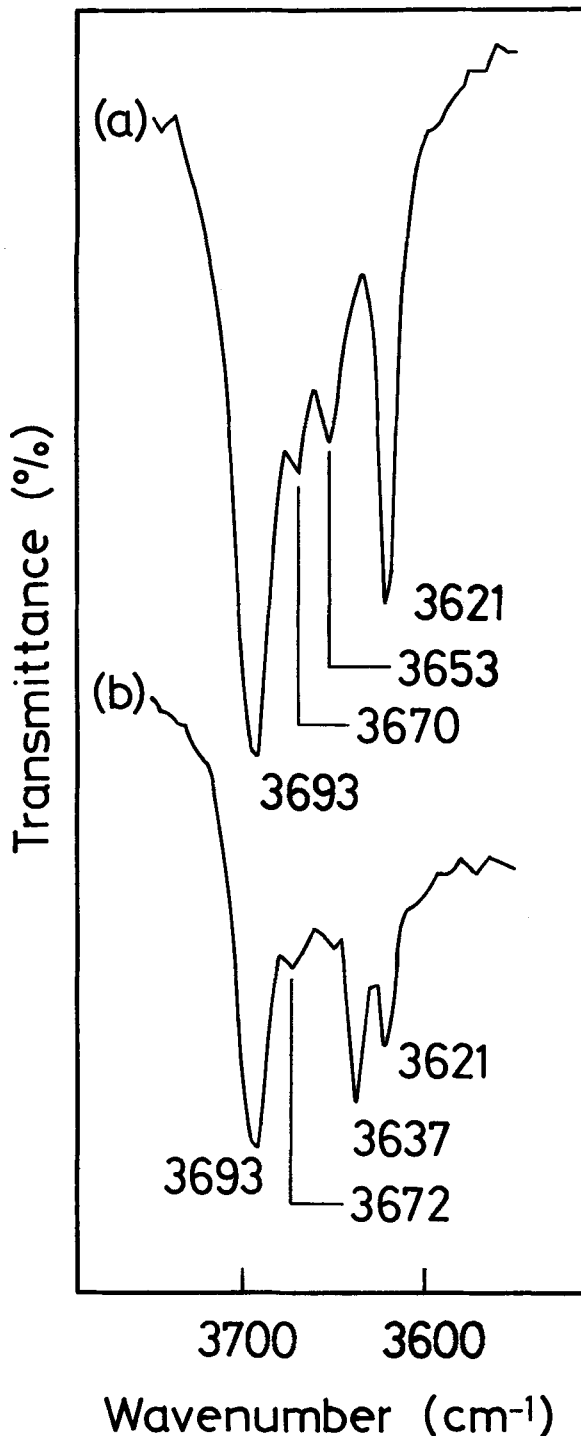

Figure 3. Infrared spectra in the OH-stretching region of (a) raw kaolinite and (b) kaolinite-pyridine intercalation compound dried in a desiccator.

tion compounds containing methylpyridine, the 001 peak intensity of the kaolinite-2-methylpyridine intercalation compound was much weaker than those of the other compounds; the intercalation compounds con-
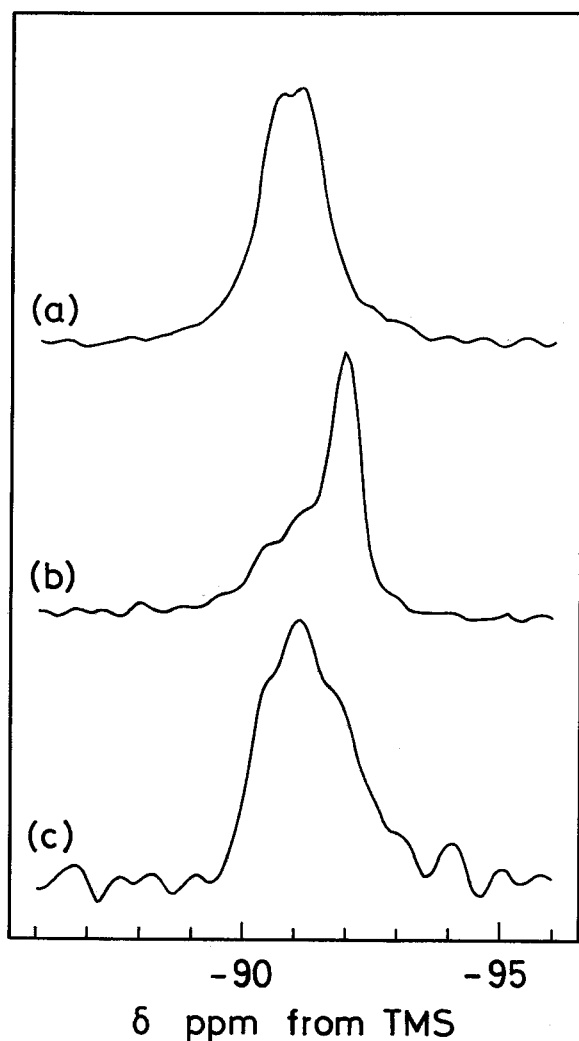
Figure 4. ^{29}Si nuclear magnetic resonance spectra with cross polarization and magic angle spinning of (a) raw kaolinite, (b) kaolinite-pyridine intercalation compound, and (c) kaolinite-4-methylpyridine intercalation compound. Samples (b) and (c) were dried in a desiccator.
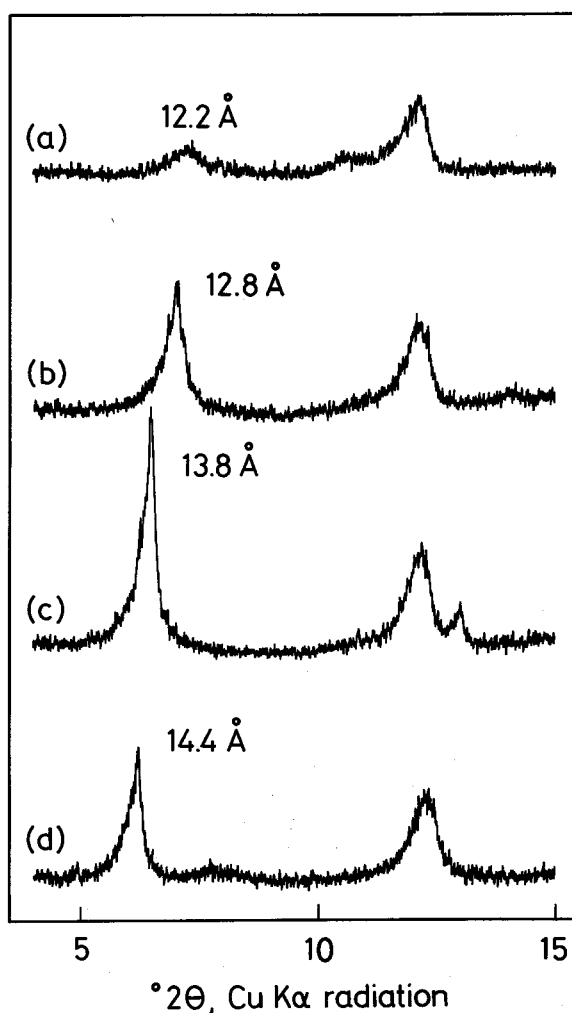
Figure 5. X-ray diffraction patterns of intercalation compounds of kaolinite and pyridine derivatives; (a) kaolinite-2-methylpyridine intercalation compound, (b) kaolinite-3-methylpyridine intercalation compound, (c) kaolinite-4-methylpyridine intercalation compound, and (d) kaolinite-4-ethylpyridine intercalation compound. Patterns were measured for samples coated on a glass slide immediately after centrifugation.

taining 3- or 4-methylpyridine showed well-defined 001 reflections. Especially, the kaolinite-4-methylpyridine intercalation compound showed intense 001 peak and higher orders.

Pyridine derivatives were highly unstable between the layers of kaolinite than was unsubstituted pyridine. If the crude products were dried in the desiccator, the peaks of all the intercalation compounds became remarkably weaker. On the other hand, the kaolinite-pyridine intercalation compound was extremely stable, as mentioned above.

The stabilities of the derivatives depended on the position of the substituents. After the intercalation compounds containing 2- or 3-methylpyridine were dried, only weak peaks due to expanded phases were observed, and the 001 peaks of two compounds containing the 4-substituted species were remarkably weaker. Part of the layers, however, still expanded, if the intercalation compounds containing the 4-substituted species were dried. Hence, the 4-substituted species were more stable than the other derivatives.

The IR spectrum was recorded for the relatively stable kaolinite-4-methylpyridine intercalation compound. The yield based on its XRD pattern was about 50%. The IR spectra of the other intercalation compounds were not measured, because they showed much lower yields after drying. Bands due to 4-methylpyridine were clearly observed. By analogy with the kaolinite-pyridine intercalation compound, three bands

assigned to pyridine ring vibration shifted to higher frequencies. In terms of the OH-stretching region, the profile was similar to that of the raw kaolinite.

The ^{29}Si CP/MASNMR spectrum of the kaolinite-4-methylpyridine intercalation compound dried in the desiccator is shown in Figure 4c. In addition to the NMR peaks due to unexpanded kaolinite at about −91 ppm, a shoulder was observed at about −91.6 to −91.8 ppm, which was probably due to silicon in the kaolinite-4-methylpyridine intercalation compound. The chemical shift was similar to that of the kaolinite-pyridine intercalation compound (−91.8 ppm).

DISCUSSION

Kaolinite-pyridine intercalation compound

The reaction between hydrated kaolinite and pyridine led to the formation of a highly-ordered intercalation compound. In addition to XRD, IR and NMR results support the intercalation of pyridine between the layers of kaolinite.

The IR spectroscopy generally gives information on hydrogen bonding. The stretching mode of the hydroxyls of kaolinite are known to split into four bands at 3693, 3670, 3653, and 3621 cm^{-1}. The guest molecules can perturb the 3693-, 3670-, and 3653-cm^{-1} bands, which are ascribed to the "inner-surface hydroxyls". The 3621-cm^{-1} band is not affected generally, because it results from the "inner-sheet hydroxyls" (Theng, 1974). The perturbation of the 3621-cm^{-1} band, however, was recently reported for a kaolinite-dimethylselenoxide intercalation compound (Raupach *et al.*, 1987).

The IR spectrum of the kaolinite-pyridine intercalation compound in the OH-stretching region proves the presence of hydrogen bonding between the hydroxyls of the kaolinite and the pyridine. The new band at 3637 cm^{-1} in the product cannot be ascribed to the hydroxyls interacting with H$_2$O, because H$_2$O was unstable between the layers. The fluorination reaction also did not lead to the 3637-cm^{-1} band formation (see experimental section). Hence, the 3637-cm^{-1} band must be assigned to the hydroxyls interacted with pyridine.

In terms of the original hydroxyl bands, the intensity ratio of the 3693-cm^{-1} band over the 3621-cm^{-1} band was similar to that of the raw kaolinite, although the ratio decreased in most of the previously reported intercalation compounds (Theng, 1974). As mentioned in the experimental section, the intensities of the original hydroxyl bands decreased in hydrated kaolinite. The original hydroxyls, however, must have been perturbed, because the 3637-cm^{-1} band was present; the profile must be changed in addition to the presence of the 3637-cm^{-1} band. One possible interpretation is the perturbation of both the 3693-cm^{-1} and 3621-cm^{-1} bands.

The shifted bands assigned to pyridine also support hydrogen bonding between the hydroxyls of kaolinite and pyridine. Four bands shifted to higher frequencies were attributed to the ring-vibration modes (Kline and Turkevich, 1944). They correspond to the following vibration modes of benzene: 1442 cm^{-1}, 19b; 1487 cm^{-1}, 19a; 1593 cm^{-1}, 8b; 1612 cm^{-1}, 8a (Langseth and Load, 1938). Their positions shift if pyridine is adsorbed and interacts with the surface of oxides. The magnitude of shifts depends on the strength of interaction. The observed values for the 19b and 8a bands correspond to those for hydrogen-bonded pyridine (1440–1447 cm^{-1}, 19b; 1580–1600 cm^{-1}, 8b) (Knözinger, 1976).

^{29}Si NMR spectroscopy is also effective in studying the interaction between kaolinite and the guest molecules. Thompson (1985) investigated four kinds of kaolinite-organic intercalation compounds using ^{29}Si CP/MASNMR spectroscopy and observed a single peak with a chemical shift at higher field than those of the raw kaolinite. The shift of the ^{29}Si peak to higher field was ascribed to additional shielding by the intercalated molecule.

The NMR results provide additional evidence for the intercalation of pyridine. On the basis of Thompson's results (1985), the singlet peak at slightly higher field may be attributed to additional shielding by intercalated pyridine. The magnitude of the shift is comparable to those of the other intercalation compounds reported by Thompson (1985).

The kaolinite-pyridine intercalation compound was more stable than the halloysite-pyridine intercalation compound. Carr and Chih (1971) reported that the halloysite-pyridine intercalation compound shows a Δd value of 5.0 Å and higher orders. The halloysite-pyridine intercalation compound collapsed when it was exposed to air for 20 hr (Carr and Chih, 1971). On the contrary, the kaolinite-pyridine intercalation compound was stable even after a month. This stability can be attributed to the possible difference in the a/b stacking order between halloysite and kaolinite.

Hydrated kaolinite seemed to be a good intermediate for the displacement method. As well as pyridine, various guests seem to be intercalated between the layers of hydrated kaolinite. The advantage of hydrated kaolinite over the kaolinite-NMF intercalation compound may be due to the instability of H$_2$O between the layers.

Intercalation compounds of kaolinite and pyridine derivatives

On the basis of the results, the stabilities of the pyridine derivatives can be discussed. The behavior on drying indicates the order of the deintercalation rate. The variation in the yields of the intercalation compounds immediately after the centrifugation are possibly due to: (1) the amount of the intercalation compound formed during the reaction, (2) the degree of the stacking order, and (3) the rate of the deintercalation.

Hence, the yields could also reflect the stabilities of the derivatives partially. The presence of the 7.2-Å peak of the unexpanded kaolinite, with similar intensities for all samples, was probably due to the disorder after the collapse. Such disorder was also observed, if the kaolinite-DMSO intercalation compound was repeatedly washed with water (Raythatha and Lipsicas, 1985).

The instabilities of pyridine derivatives indicates that the steric factor strongly affected the stabilities. If the I-effect of a methyl group is considered, a methyl group especially at the 2- or 4-position can increase the electron donating ability of pyridine; the ability of hydrogen bonding in methylpyridine can be larger. Nevertheless, the pyridine derivatives were less stable than the unsubstituted pyridine. Thus, no influence of the I-effect was observed in the present system.

The stabilities of methylpyridines were in the following order: 4-methylpyridine > 3-methylpyridine ≫ 2-methylpyridine. The results of the stabilities showed that the 4-substituted species deintercalated at lower rates than 3-methylpyridine. The extremely lower yield of the kaolinite-2-methylpyridine intercalation compound suggests the instability of 2-methylpyridine between the layers.

The IR spectrum of the kaolinite-4-methylpyridine intercalation compound did not provide enough information on the interaction. The shifts of the ring vibration bands to higher frequencies imply that the interaction between the kaolinite and the 4-methylpyridine was similar to that between the kaolinite and the pyridine. The profile in the OH-stretching region, which did not show clear perturbation, is probably due to the relatively lower yield of the compound after drying (about 50%). The actual yield was probably <50%, because of the disorder of the collapsed 7.2-Å phase.

The NMR data for the kaolinite-4-methylpyridine intercalation compound and the basal spacings of the intercalation compounds containing pyridine derivatives suggest that the orientation of the aromatic ring was similar in the kaolinite-pyridine intercalation compound and all of the intercalation compounds of kaolinite and pyridine derivatives. The similar effects on the Si environment indicate that the larger basal spacing of the kaolinite-4-methylpyridine intercalation compound cannot be ascribed to a completely different orientation between the layers. Therefore, the orientation of 4-ethylpyridine must also have been similar. Moreover, the orientation of 2- and 3-methylpyridine appeared to be similar to that of pyridine, inasmuch as the basal spacings of their intercalation compounds were only slightly larger than that of the kaolinite-pyridine intercalation compound.

Orientation of pyridine between the layers

The orientation of the aromatic ring can be estimated from the observed basal spacing of the kaolinite-pyr-
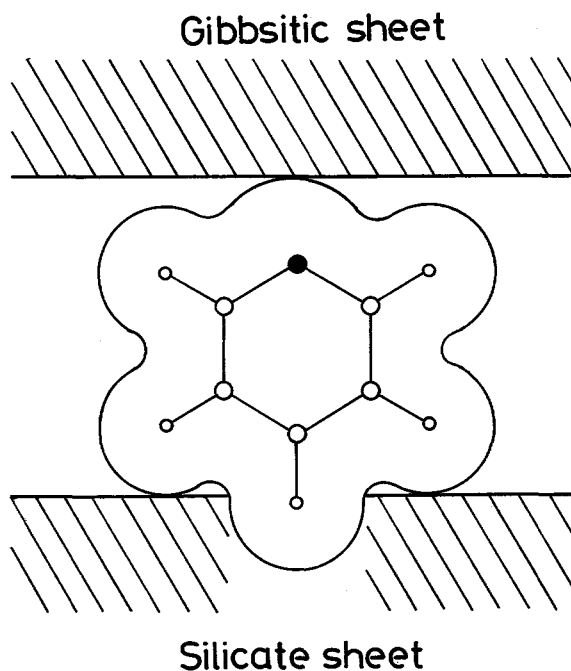

Figure 6. Schematic illustration of proposed orientation of pyridine molecule between layers of kaolinite.

idine intercalation compound. The layers were expanded by 4.8 Å after the intercalation of pyridine. Pyridine in a perpendicular position has a thickness of about 6–7 Å (Cumper, 1958); however, its size is slightly smaller in the interlayer space because of contraction (~1 Å) (Greene-Kelly, 1955). For example, the Na+-montmorillonite-pyridine intercalation compound showing a perpendicular orientation had a Δd value of 5.3 Å (Greene-Kelly, 1955). Therefore, the Δd value of 4.8 Å is slightly small for such an ideal perpendicular orientation.

To achieve a separation of 4.8 Å, two different orientations are possible. One is a tilted orientation; the other is a perpendicular orientation in which the aromatic ring keys into the layers. For the latter orientation, a Δd value of 4.6 Å was observed, if pyridinium ions were present in the interlayer space of vermiculite in the perpendicular position (Serratosa, 1966).

The orientation of the aromatic ring can also be discussed on the basis of the effect of the substituents on the basal spacings. This effect supports the perpendicular orientation. Of the several intercalation compounds containing methylpyridines, the spacing of that containing 4-methylpyridine was much larger than the spacings of those containing the 2- and 3-substituted species. If a methyl group was introduced to the 4-position, the basal spacing was larger than that of the kaolinite-pyridine intercalation compound by 1.8 Å. Because the van der Waals radius of the methyl group is ~2 Å, only a methyl group at the 4-position could have produced such an expansion. This observation

cannot be explained on the basis of the tilted orientation, and therefore suggests that nitrogen and the 4-position were facing the opposite layers.

The position of nitrogen has been assumed from the effect of the substituents on the stabilities between the layers. Nitrogen is assumed to have been involved in hydrogen bonding, because it normally interacts with hydroxyls because of its slight negative charge. The shifts of the IR bands due to pyridine ring vibration also suggest the presence of hydrogen bonding via nitrogen. Therefore, nitrogen must face the gibbsitic sheets.

This assumption is strongly supported by the effect of the substituents. The greater stabilities of the 4-substituted species can be ascribed to the fact that the presence of the substituents at the 4-position did not seem to affect significantly the position of nitrogen against the layers. On the contrary, the methyl groups at the 2- and 3-positions appear to have tilted the aromatic ring without changing the perpendicular orientation. The tilt seems to have weakened the hydrogen bonding, so that the stabilities decreased. The remarkable instability of 2-methylpyridine is reasonable, inasmuch as the introduction of a methyl group to the 2-position must significantly disturb the interaction between nitrogen and the hydroxyls.

On the basis of these discussions, the orientation of pyridine shown in Figure 6 is proposed. Pyridine is probably oriented more or less perpendicular to the layers. Nitrogen faces the gibbsitic sheets to interact with the inner-surface hydroxyls.

ACKNOWLEDGMENT

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