Bull. Chem. Soc. Jpn., 59, 2607—2610 (1986)

Synthesis of Kaolinite-Lactam Intercalation Compounds

Yoshiyuki SUGAHARA, Shuichi KITANO, Shigeo SATOKAWA, Kazuyuki KURODA, and Chuzo KATO*
Department of Applied Chemistry, School of Science and Engineering, Waseda University,
Ohkubo, Shinjuku-ku, Tokyo 160

(Received February 21, 1986)

Intercalation compounds of kaolinite with 2-pyrrolidone and 2-piperidone have been prepared for the first time by displacing other intercalates. 2-Pyrrolidone expanded the lattice of kaolinite to 11.9 Å, while d_{001} of 12.7 Å was observed with the kaolinite-2-piperidone intercalation compound. Their IR spectra indicated the formation of a hydrogen bond between the C=O of the lactams and the OH of kaolinite. Nevertheless, their interactions were different between these two intercalation compounds. By a comparison of their behaviors, it has been concluded that the kaolinite-2-pyrrolidone intercalation compound is thermally more stable than the kaolinite-2-piperidone intercalation compound.

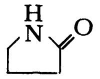
It is well-known that some clay minerals with a layer structure form intercalation compounds. Kaolinite can form intercalation compounds only with a limited number of polar molecules, whereas smectite reacts with a variety of molecules. Though some of them can react with kaolinite directly, others form intercalation compounds only in the presence of an "entraining agent" or by displacement of other intercalates.1)

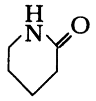
Intercalated polar molecules form hydrogen bonds with hydroxyl groups of kaolinite on the surface of the sheet. The hydroxyl groups of kaolinite show four sharp IR absorption bands at approximately 3690, 3670, 3650, and 3620 cm^{-1}. With the formation of a hydrogen bond, only the absorption bands at 3690, 3670, and 3650 cm^{-1} are perturbed, since these bands are ascribed to the vibration of the hydroxyls on the surface of the sheet and the 3620 cm^{-1} band is assigned to the inner-sheet hydroxyl.1)

Amides are typical polar organic molecules, and some of them can be intercalated into the interlayer space of kaolinite. Many investigations were reported on the intercalation compounds with formamide (FA),2—8) *N*-methylformamide (NMF),4,5,8—10) *N,N*-dimethylformamide (DMF),4,5,8) acetamide,5,8,11) *N*-methylacetamide (NMA),5,8,11) and *N,N*-dimethylacetamide (DMA).5,8,11)

In their IR spectra, Ledoux and White3) and Cruz et al.4) observed the intensity decrease of the bands at 3690, 3670, and 3650 cm^{-1} for the hydroxyls in the intercalation compounds with FA, NMF, and DMF, while Oljenik et al.6,11) reported that all of six amides perturbed a pair of hydroxyl bands; those at 3690 and 3670 cm^{-1} or those at 3690 and 3650 cm^{-1}. In other regions, the results showed a similar tendency; that is, an amide I band was observed at the same or a slightly higher wavenumber than liquid, and the NH stretching band was shifted to a higher wavenumber.

Lactams have NHCO group in their structures, so they can be regarded as "cyclic amides." Therefore, it is expected that an investigation of kaolinite-lactam intercalation compounds contributes to a series of studies on intercalation chemistry between kaolinite and organic molecules. In this study, 2-pyrrolidone and 2-piperidone were selected as lactams to synthesize the kaolinite-lactam intercalation compounds by a direct reaction or displacement method.


2-pyrrolidone


2-piperidone

Experimental

The kaolinite used was the API standard clay mineral No. 9 (Nesa Alta, New Mexico). The X-ray diffraction (XRD) pattern of kaolinite showed no obvious peaks due to impurities.

(1) **Direct Reaction.** A lactam was added to kaolinite at a ratio of 20 ml/1 g kaolinite. The suspension was then stirred for 72 h. The reaction was performed at two different temperatures to study the effect of the increase in the reaction temperature. One was just above the melting points of the lactams, that is, 30 °C for 2-pyrrolidone and 50 °C for 2-piperidone; the other temperature was 70 °C.

(2) **Displacement Method.** Intercalation compounds with FA, NMF, or dimethyl sulfoxide (DMSO) were used as starting materials. The lactam was added to a preformed complex with the same ratio as that in the direct reaction. The suspension was stirred for 10 min, and centrifuged. Then, the lactam was added again with the same ratio and the suspension was stirred between 0 and 96 h. The reaction temperatures were varied from 30 to 90 °C for 2-pyrrolidone and from 50 to 90 °C for 2-piperidone.

Products were analyzed by XRD (Shimadzu VD-11). The yield was calculated approximately from the proportion of the (001) peak heights of the intercalation compound, the preformed complex and the nonexpanded kaolinite.1) The IR spectra of the products were also measured with a Shimadzu IR-435 (wavenumbers were calibrated using indene and polystyrene) using the KBr method (ca. 0.5%) after drying the products at 110 °C. Also, the IR spectra of the lactams were measured in CCl$_4$ (0.05 mol dm^{-3}).

Results and Discussion

In syntheses of the intercalation compounds with a direct reaction, no peaks due to intercalation compounds were observed in their XRD patterns. This indicated that lactams could not form intercalation

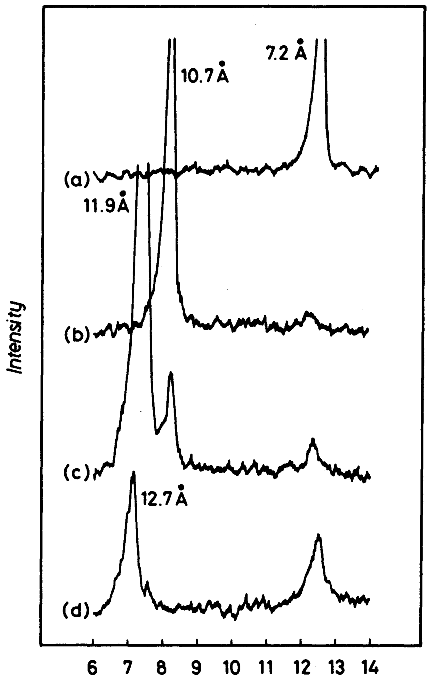


Fig. 1. X-ray diffraction patterns of (a) kaolinite, (b) kaolinite–NMF complex, (c) kaolinite–NMF complex treated with 2-pyrrolidone for 72 h, and (d) kaolinite–NMF complex treated with 2-piperidone for 72 h.

compounds under these conditions. However, the possibility of intercalation with a direct reaction could not be excluded, since a relatively large molecule like DMF was intercalated directly after a long reaction period.[5]

On the other hand, intercalation compounds with 2-pyrrolidone and 2-piperidone were easily formed by a displacement reaction. The reaction temperatures were 30 °C for 2-pyrrolidone and 50 °C for 2-piperidone, and the reaction time was 72 h. Figure 1 shows the XRD patterns of products prepared from a kaolinite–NMF complex. In the case of 2-pyrrolidone, a new peak due to a (001) diffraction line appeared at d=11.9 Å, whereas 2-piperidone expanded the lattice of kaolinite to 12.7 Å.

It was hard to assume the orientation of lactams from their basal spacings since the conformations of their monomeric species could not be determined; 2-pyrrolidone can not be in a planner conformation, and 2-piperidone can show a few structures without strain.[12] Pyridine *N*-oxide had a six-membered ring in its structure and could be intercalated into a kaolinite lattice with a basal spacing of 12.5 Å.[5] Its orientation was assumed to be perpendicular to the plane of kaolinite. Therefore, the similar basal spacing of a kaolinite–2-piperidone intercalation compound (12.9 Å) might imply the possibility of a perpendicular orientation of lactams in the interlayer space of kaolinite. However, further work, such as neutron diffraction, is needed for a precise discussion.

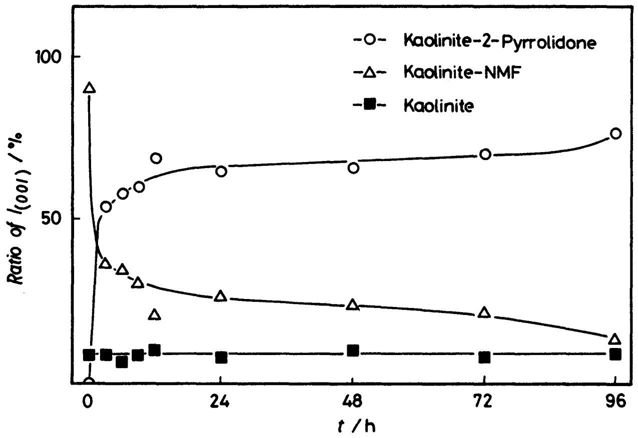


Fig. 2. The variation of the composition of the products with reaction time (t) at 30 °C (kaolinite–NMF complex reacted with 2-pyrrolidone).

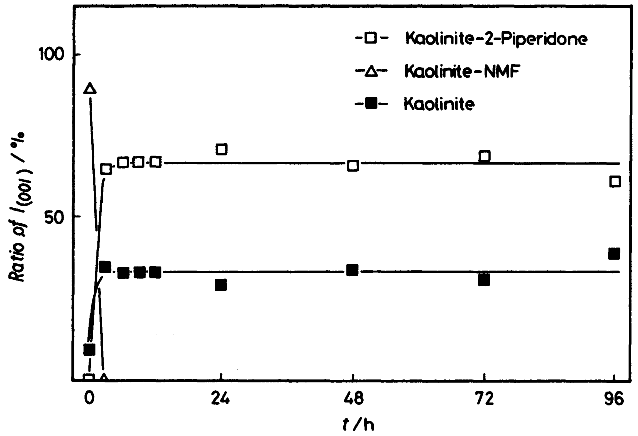


Fig. 3. The variation of the composition of the products with reaction time (t) at 50 °C (kaolinite–NMF complex reacted with 2-piperidone).

Figures 2 and 3 reveal the variation of the approximate composition of the products with the reaction time. In a reaction with 2-pyrrolidone, the yield of the kaolinite–2-pyrrolidone intercalation compound was gradually augmented with an increase in the reaction time. A corresponding decrease in that of the kaolinite–NMF complex was observed during the reaction. The ratio of nonexpanded kaolinite was the same, indicating no collapse from both the preformed complex and the kaolinite–2-pyrrolidone intercalation compound to kaolinite during the reaction.

In the case of 2-piperidone, an increase in the reaction rate was observed; the X-ray diffraction line due to the kaolinite–NMF complex disappeared within 3 h and the yield of the kaolinite–2-piperidone intercalation compound did not change after 3 h. This increase of the reaction rate was ascribed to a high reaction temperature of 50 °C. The ratio of the nonexpanded kaolinite increased at the beginning of the reaction.

Table 1. Effect of Reaction Temperature on the Yield of the Kaolinite-Lactam Intercalation Compounds[a)]

Lactam	Reaction Temperature			
	30 °C	50 °C	70 °C	90 °C
2-Pyrrolidone	70%	90%	93%	92%
2-Piperidone		69%	62%	30%

a) Reaction time was 72 h, and starting complex was kaolinite-NMF complex.

Since the composition was constant after 3 h, the kaolinite-2-piperidone intercalation compound was thermally stable at 50 °C. Therefore, this indicates that the NMF complex partly collapsed to kaolinite during the reaction.

The effect of the reaction temperature is given in Table 1. The yield of the kaolinite-2-pyrrolidone intercalation compound increased when the reaction temperature was increased from 30 to 50 °C. However, similar yields were obtained above 50 °C. Since the yield of the kaolinite-NMF complex was about 90%, the kaolinite-NMF complex was completely converted to the kaolinite-2-pyrrolidone intercalation compound above 50 °C during a reaction for 72 h.

In the case of 2-piperidone, yields of around 65% were obtained at 50 and 70 °C. The yield was 30% at 90 °C, while no differences were observed in the temperature range from 50 to 90 °C with the kaolinite-2-pyrrolidone intercalation compound. A decrease in the yield at 90 °C implied that the kaolinite-2-piperidone intercalation compound was thermally less stable than the kaolinite-2-pyrrolidone intercalation compound.

In addition, preparations from various preformed complexes were attempted. 2-pyrrolidone could form the intercalation compound from all of the starting complexes at 30 °C. However, the formation of the kaolinite-2-piperidone intercalation compound was observed only from the FA and NMF complexes, in spite of a reaction temperature of 50 °C; the DMSO complex was not converted to the intercalation compound and did not collapse to kaolinite. This fact suggested that the kaolinite-DMSO complex was much more stable than the kaolinite-2-piperidone intercalation compound at 50 °C.

For measuring the IR spectra, the excess lactams adsorbed on the external surface of the particles must be removed. It is well known that intercalation compounds of kaolinite are generally unstable against washing. Therefore, the removal of the excess lactams by evaporation seemed to be suitable. Thus, the effect of the drying time on the yields of the kaolinite-lactam intercalation compounds at 110 °C was initially investigated to clarify the thermal behavior of the compounds.

Figure 4 shows the results of drying the intercalation compounds at 110 °C. The kaolinite-2-pyrrolidone intercalation compound used was prepared at 70 °C, while the sample prepared at 50 °C was used for the kaolinite-2-piperidone intercalation compound. In the case of the kaolinite-2-pyrrolidone intercalation compound, the initial yield was retained. After 20 h, the yield of the compound began to decrease gradually.

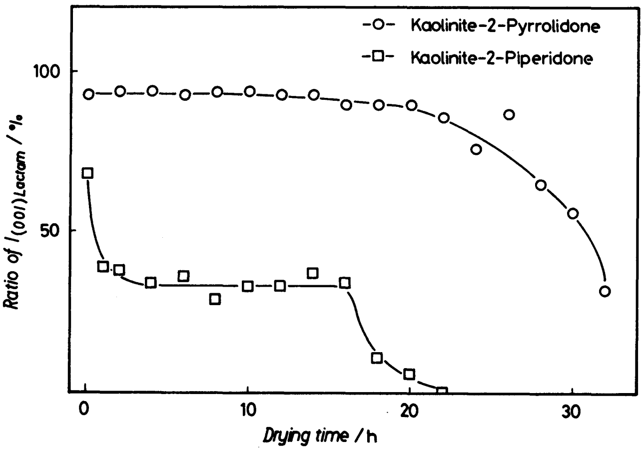


Fig. 4. The variation of the yield of the kaolinite-lactam intercalation compounds with drying time at 110 °C.

On the other hand, the kaolinite-2-piperidone intercalation compound showed a different behavior; the yield decreased to about 30% within 1 h. Then, the compound showed the same yield for 15 h. After 18 h, the compound began to collapse again; the X-ray diffraction line of the compound disappeared after 22 h.

The difference in the initial period suggested that the kaolinite-2-piperidone intercalation compound contained at least two different kinds of arrangements of 2-piperidone in the interlayer space; 2-piperidone was present in different ways with the same d_{001} value. Also, weakly bonded 2-piperidone was unstable at a higher temperature and was deintercalated. This assumption was supported by the fact that the product prepared at 90 °C showed the similar yield of 30%.

In both intercalation compounds, the products changed to a dried state during the periods, with a plateau as shown in Fig. 4. It seems that most of the lactams adsorbed on the external surface vaporize before those in interlayer spaces were deintercalated. Thus, the samples just after the plateau periods were used for IR measurements; the kaolinite-2-pyrrolidone intercalation compound was dried for 26 h (yield=87%) and the kaolinite-2-piperidone intercalation compound was dried for 16 h (yield=34%).

Figure 5 shows the IR spectra of the products. In the case of the kaolinite-2-pyrrolidone intercalation compound (Fig. 5-c), amide I bands were observed at 1698 and 1666 cm^{-1}. The position of the 1666 cm^{-1} band was at a lower wavenumber than that of 2-pyrrolidone (Fig. 5-b). This indicated that a part of the C=O groups formed hydrogen bonds. Since the other band showed similar wavenumbers to that of 2-pyrrolidone monomer, this band was assigned to the C=O

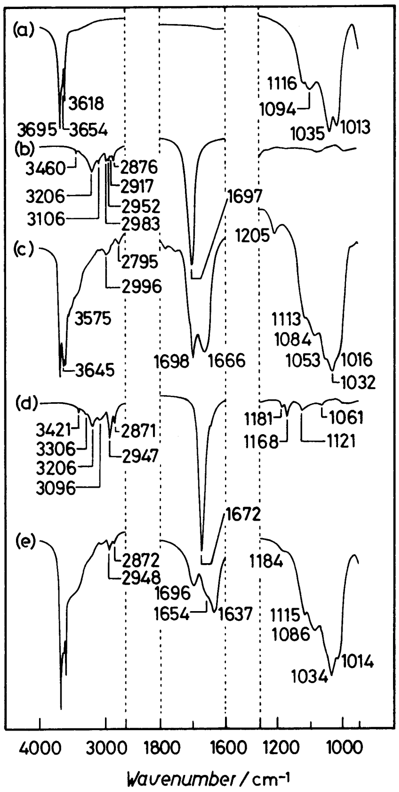


Fig. 5. IR spectra of (a) kaolinite, (b) 2-pyrrolidone (in CCl_4), (c) kaolinite-2-pyrrolidone intercalation compound dried for 26 h, (d) 2-piperidone (in CCl_4), and (e) kaolinite-2-piperidone intercalation compound dried for 16 h.

group having no hydrogen bonds with OH groups of kaolinite. In the OH region, new bands were observed at 3645 and 3575 cm^{-1}; these were ascribed to the shifted OH groups involved in the hydrogen bond. Also, a corresponding decrease of the original hydroxyl bands of kaolinite was observed; the 3695 cm^{-1} band was perturbed by 2-pyrrolidone (Fig. 5-a, c).

In terms of an Si–O stretching vibration, the spectrum (Fig. 5-c) showed a different profile from that of nonexpanded kaolinite; an intensity decrease of the 1013 cm^{-1} band and some additional shoulder bands (at 1084 and 1053 cm^{-1}) were observed. This suggested the presence of an interaction between 2-pyrrolidone and the SiO_2 surface of kaolinite.

For a measurement of the kaolinite–2-piperidone intercalation compound, a sample with a relatively lower yield (34%) was used. It should be noted that the weakly bonded 2-piperidone which was present before drying had already been deintercalated from the sample and the spectrum must have been different from that of a sample with the higher yield before drying.

The IR spectrum of a kaolinite–2-piperidone intercalation compound differed from that of a kaolinite–2-pyrrolidone intercalation compound (Fig. 5-e). The amide I band became more complicated; they split into three bands, two of which were shifted to lower frequencies than that of 2-piperidone in CCl_4 (Fig. 5-d). This implied the presence of different kinds of hydrogen bonds in the intercalation compound. In the OH region, no bands due to hydrogen-bonded OH were observed. Also, no original OH bands were clearly perturbed. This was ascribed to the low yield of the compound.

The Si–O stretching mode was slightly different from that of the kaolinite–2-pyrrolidone intercalation compound; a new band at about 1050 cm^{-1} was not clearly observed. This implied that the effect of intercalation of 2-piperidone on the Si–O stretching was similar to that of 2-pyrrolidone.

Though some similarities were observed in their IR spectra, the profiles of the bands due to C=O stretching, the yields of the compounds and their thermal stabilities were quite different between these two intercalation compounds. These facts suggest that structural differences in the lactams considerably influence the hydrogen bonds. Between two lactams, 2-pyrrolidone seems more preferable for forming an intercalation compound.

This work was supported by the Grant-in-Aid for Special Project Research on the Properties of Molecular Assemblies (No. 58218033, 60104004) from the Ministry of Education, Science and Culture.

References

1) B. K. G. Theng, "The Chemistry of Clay-Organic Reactions," Adam Hilger, London (1974), p. 243.

2) A. Weiss, W. Thielepare, G. Gornig, W. Ritter, and H. Schafer, *Proc. Inter. Clay Conf., Stockholm*, **1**, 287 (1963).

3) R. L. Ledoux and J. L. White, *J. Colloid Interface Sci.*, **21**, 127 (1966).

4) M. Cruz, A. Laycock, and J. L. White, *Proc. Inter. Clay Conf., Tokyo*, **1**, 775 (1969).

5) S. Olejnik, A. M. Posner, and J. P. Quirk, *Clay Minerals*, **8**, 421 (1970).

6) S. Olejnik, A. M. Posner, and J. P. Quirk, *Clays Clay Miner.*, **19**, 83 (1971).

7) J. M. Adams, P. I. Ried, J. M. Thomas, and M. J. Walters, *Clays Clay Miner.*, **24**, 267 (1976).

8) J.M. Adams, *Clays Clay Miner.*, **26**, 291 (1978).

9) A. Weiss, W. Thielepape, and H. Ohth, *Proc. Inter. Clay Conf., Jerusalem*, **1**, 277 (1966).

10) J. M. Adams, *Clays Clay Miner.*, **26**, 169 (1978).

11) S. Olejnik, A. M. Posner, and J. P. Quirk, *J, Colloid Interface Sci.*, **37**, 536 (1971).

12) H. E. Hallam and C. M. Jones, *J. Mol. Struc.*, **1**, 413 (1967-68).