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Antimicrobial and antifungal agents derived from clay minerals

Part VIII *Thermostability of montmorillonite intercalated by silver chelate of 2-(4-thiazolyl)-benzimidazole or quaternary ammonium cations*

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A silver chelate of 2-(4-thiazolyl)-benzimidazole, dodecyltrimethylammonium cation and hexadecylpyridinium cation have been intercalated between montmorillonite, and the resulting samples were subjected to examination of their thermostabilities by thermogravimetry and carbon dioxide evolution analysis up to 500 °C in air. The degradation behaviour of the intercalant was significantly changed by intercalating between the montmorillonite layers. Two quaternary ammonium cations were released from the montmorillonite both at the same temperature, which was higher than those for the quaternary ammonium cations themselves. This relation was also observed in the case of 2-(4-thiazolyl)-benzimidazole. The improvement of the thermostability after intercalation can be attributed to the bonding between the intercalant and the host montmorillonite layers.

1. Introduction

Montmorillonite (Mont) intercalated by silver cations, has strong antibacterial activity. However, when the aqueous sol is allowed to stand under sunshine, the silver cations between the Mont layers are easily reduced to metallic silver particles, leading to a lowering of the antibacterial activity and a change in colour from pale blue to black [1]. This reduction has been successfully suppressed by the use of the silver chelate instead of the silver cation [2, 3]. This technique was further extended to prepare an agent with both strong antibacterial and antifungal activities. For example, Mont intercalated by (i) silver chelate of 2-(4-thiazolyl)-benzimidazole which has strong antifungal activity, and (ii) the quaternary ammonium cation which has strong antibacterial activity, has been prepared and described in elsewhere [4]. There is the possibility that this intercalation technique using Mont as a host material can be employed to prepare an antimicrobial agent with high thermostability.

In this work, Mont was intercalated by a silver chelate of 2-(4-thiazolyl)-benzimidazole (TBZ), dodecyltrimethyl-ammonium cation and hexadecylpyridinium cation, respectively, and their thermostabilities were examined. Thermostability was examined by analysis of evolved carbon dioxide gas. Thermogravimetric analysis up to 500 °C in air was also carried out.

2. Experimental procedure

2.1. Materials

The purified Mont (trade name Kunipia-F, Kunimine Industries Co. Ltd) was used as a host material. The theoretical chemical formula is $Na^{0.66+}[(Al_{3.34}Mg_{0.66})Si_8O_{20}(OH)_4]^{0.66-}$. The cation exchange capacity (CEC) of this Mont is 115 meq/100 g, and the particle size is smaller than 2 μm [5].

The chelating agent was, 2-(4-thiazolyl)-benzimidazole (TBZ; $C_{10}H_7N_3S$, m.p. 296–303 °C, decomposition temperature 700 °C, Tokyo Chemical Industry Co. Ltd) and silver nitrate ($AgNO_3$, 99.8% purity, Wako Pure Chemical Industry Co. Ltd). Two quaternary ammonium salts, *n*-dodecyltrimethyl-ammonium chloride (Dode; $C_{12}H_{25}N(CH_3)_3Cl$, m.p. 246 °C, Tokyo Chemical Industry Co. Ltd. and another hexadecylpyridinium chloride monohydrate (Hexa; $C_5H_5NC_{16}H_{33}Cl \cdot H_2O$, m.p. 77–83 °C, Tokyo Chemical Industry Co. Ltd) were used. All reagents were of laboratory reagent grade.

2.2. Preparation

An aqueous dispersion of Mont sol (content 3 wt %) was prepared in a 2000 ml three-necked round-bottomed flask equipped with a stirring rod. The two

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quaternary ammonium salts were dissolved in deionized water by an equivalent molar quantity of the CEC of the prepared Mont sol. These organic solutions were added to a 3 wt % Mont aqueous sol and stirred at 80 °C for 48 h. After cation exchange reaction, samples were washed with deionized water until chloride ions were no longer detected. Next, these agents were dried by the freeze drying method using an FRD-50M freeze dryer produced by Iwaki Glass Co. Ltd. The resulting powder, Mont intercalated by Dode or Hexa, is abbreviated as DoM or HeM, respectively.

Mont-containing silver TBZ chelate was prepared as follows: the weight of 3 wt % Mont aqueous sol was measured. Then TBZ of double the molar quantity of Mont CEC was dissolved in methanol. Silver nitrate was dissolved in deionized water by an equal molar quantity of Mont CEC. Both solutions were mixed together and stirred, resulting in a white suspension of silver chelate of TBZ. The resulting chelate suspension was added to the Mont sol and stirred at 80 °C for 48 h in order to synthesize the sol of silver TBZ chelate/Mont. Afterwards, the sample was washed thoroughly with deionized water to remove free silver cations and/or free silver TBZ chelate. The resulting sol was then freeze dried. Mont intercalated by the silver TBZ chelate will be referred to in the text as TAM.

2.3. Measurements

Powder X-ray diffraction was carried out using a Geiger Flex CN2155D5 diffractometer RAD-B system (Rigaku Electrical Co. Ltd) with nickel filtered CuK_α radiation. The X-ray tube setting was 15 mA and 35 kV. The measurement conditions were divergence slit 1 °, receiving slit 0.3 mm, and scattering slit 1 °. The scanning angle was from 3 °–20 ° (2θ, CuK_α) with scanning speed 1 ° min^{-1}. The (0 0 1) diffraction peak was used to calculate the basal spacing of the samples. However, because the basal spacing was strongly influenced by atmospheric humidity, after drying at 120 °C for 24 h the sample was covered with paraffin wax to avoid any rehydration before X-ray diffraction measurements.

Infrared spectra (4000–250 cm^{-1}) using the conventional KBr disc method, were acquired using a Hitachi-1270-50 infrared double-beam spectrophotometer. About 1 mg of the powder sample was mixed with ~ 100 mg dried KBr crystals and pressed to make a tablet of 13 mm diameter under 400 kgf cm^{-2} for 2 min.

Carbon and sulphur contents were determined by a carbon–sulphur infrared absorption apparatus EMIA-510 (Horiba Faculty Co. Ltd). This is a combustion method using tin particles as a combustion accelerator. The combustion temperature used in the analysis was 1450 °C under an oxygen atmosphere.

Thermogravimetric (TG) analysis and evolved carbon dioxide gas analysis were conducted using a thermogravimeter TAS-200 TG8110D (Rigaku Electrical Co. Ltd). The sample of 40 mg was heated to 500 °C at a rate of 5 °C min^{-1} in a stream of air (60 ml/min^{-1}). The evolution rate of carbon dioxide was measured at intervals of 25 °C using a gas chromatography mass spectrometre (GC-3BT, Shimadzu Faculty Co. Ltd), further details of which were described elsewhere [6].

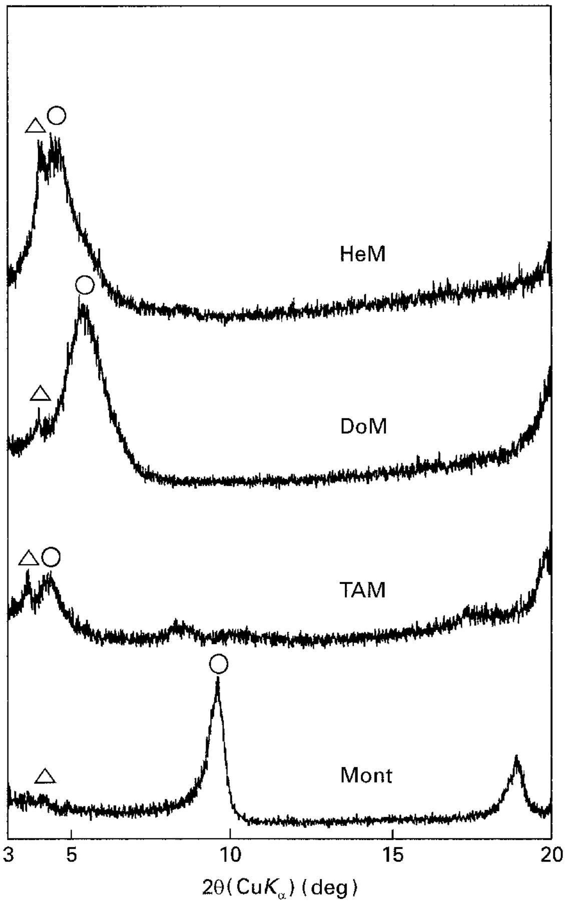

Figure 1 X-ray diffraction profiles of the raw Mont and the synthesized samples: (○) (0 0 1), (△) paraffin.

3. Results

3.1. X-ray diffraction

X-ray diffraction profiles of the Mont, TAM, DoM and HeM before heating are shown in Fig. 1. The Mont after drying gave a sharper (0 0 1) diffraction profile corresponding to an interlayer distance of 0.96 nm, smaller than those of the other samples. The interlayer distance of TAM was 2.04 nm. The spacings 1.64 nm for DoM and 1.92 nm for HeM also show the intercalation of Dode and Hexa between the Mont layers.

3.2. Infrared spectra

Fig. 2 shows the infrared spectra of TAM, DoM, HeM together with the original Mont with no heating. The two absorptions around 3500 cm^{-1} and around 1600 cm^{-1} in the Mont were assigned to the hydroxyl group, –OH. An absorption from Si–O was observed around 1000 cm^{-1}. Two absorptions around 500 cm^{-1} were assigned to Si–O and/or Si–O–Al in the Mont layer. TAM showed characteristic absorptions from TBZ at 1454, 1436, 1326, 1296 and 1280 cm^{-1} assigned to heterocyclic or aromatic C=C, C=N stretching vibrations.

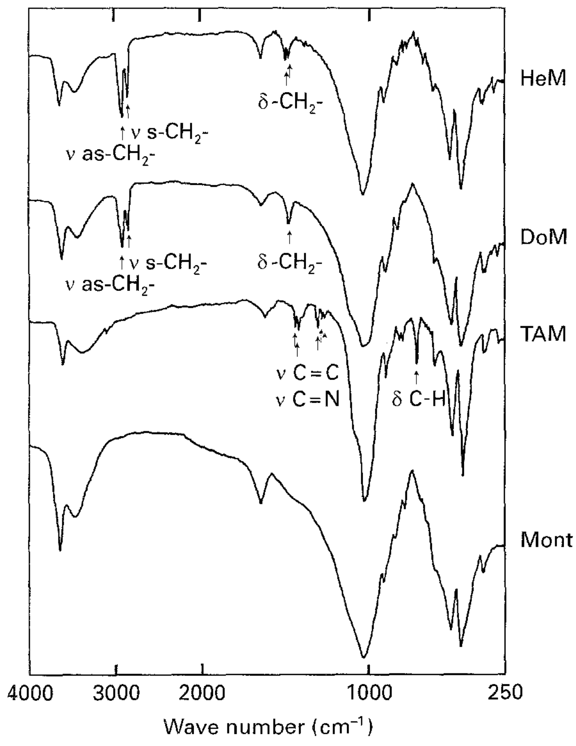

Figure 2 Infrared spectra of the raw Mont and the synthesized samples.

TABLE I. Carbon content of the synthesized samples

Agent	Carbon content (wt %)		Exchange ratio (%)
	Observed	Calculated[a]	
TAM	16.1	17.0	94.7
DoM	15.2	16.8	91.7
HeM	22.2	22.3	99.6

[a] TAM, calculated as Mont intercalated by $Ag(TBZ)_2$ the molar quantity of the CEC. DoM and HeM, calculated as Mont intercalated by quaternary ammoniumcation of the molar quantity of the CEC.

DoM exhibited absorptions at 2928 and 2852 cm^{-1} assigned to the vibration of aliphatic $-CH_2-$ antisymmetrical and symmetrical stretching and 1480 cm^{-1} assigned to aliphatic $-CH_2-$ bending vibration. HeM showed the absorptions at 2924 and 2852 cm^{-1} from aliphatic $-CH_2-$ antisymmetrical and symmetrical stretching vibration and at 1490 and 1480 cm^{-1} assigned to aliphatic $-CH_2-$ bending vibration, which suggests the presence of Hexa.

3.3. Carbon content

Table I shows the observed and the calculated carbon contents and the cation exchange ratio for TAM, DoM and HeM. According to the carbon contents, silver-TBZ chelate, Dode and Hexa were intercalated between the Mont layers in amounts of 94.7%, 91.7% and 99.6%, respectively.

3.4. Thermogravimetric (TG) analysis

Fig. 3 shows TG curves for TBZ, silver-TBZ chelate and TAM in air. TBZ showed a weight loss at 265 °C in contrast to 238 °C for silver-TBZ chelate. The latter sample showed four weight-loss steps at higher temperature. The weight loss of TAM was observed at 353 °C and proceeded gradually to reach to 24% at 500 °C.

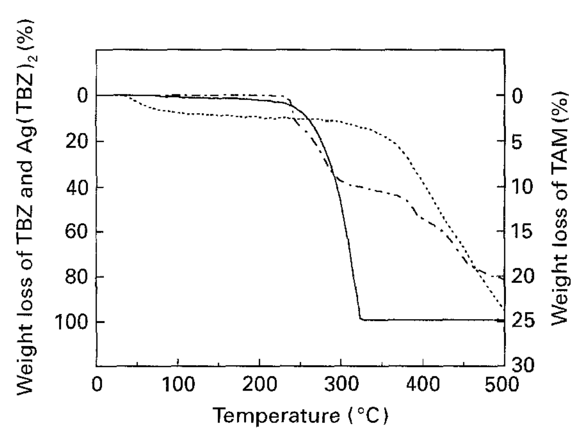

Figure 3 TG curves for (——) TBZ, (— — —) $Ag(TBZ)_2$ and (- - -) TAM.

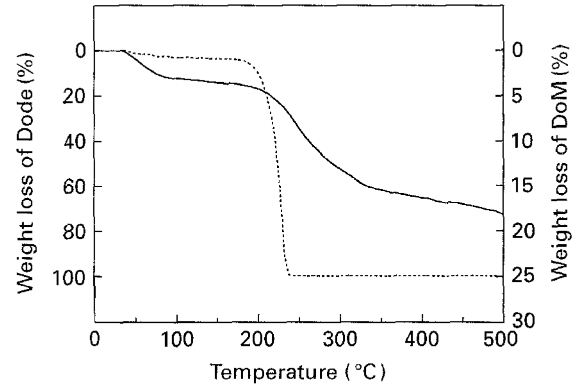

Figure 4 TG curves for (- - -) Dode and (——) DoM.

Fig. 4 shows TG curves for Dode and DoM. The weight of Dode started to decrease at 200 °C, but DoM indicates a weight loss at 217 °C. The weight losses for Dode and DoM at 500 °C were 100% and 18%, respectively. Fig. 5 shows TG curves for Hexa and HeM. Hexa showed a weight loss at 200 °C in contrast to a gradual weight loss from 225 °C for HeM.

3.5. Evolution rate of carbon dioxide analysis

Fig. 6 shows the CO_2 evolution rate curves for TBZ, the silver-TBZ chelate and TAM. Analogous behaviour was observed among the three samples, i.e. the gas started to evolve around 400 °C and reached a maximum evolution rate at 450 °C.

The CO_2 evolution rate curves for Dode and DoM are shown in Fig. 7. The CO_2 gas began to evolve from Dode at 100 °C, and reached maximum rates around 250 and 450 °C. DoM, on the other hand, showed CO_2 evolution from 200 °C with a maximum at 275 °C.

Fig. 8 shows the CO_2 evolution curves for Hexa and HeM. CO_2 evolution occurred at 200 °C in both samples, but the maximum rates were observed at 250 °C for Hexa and 300 °C for HeM.

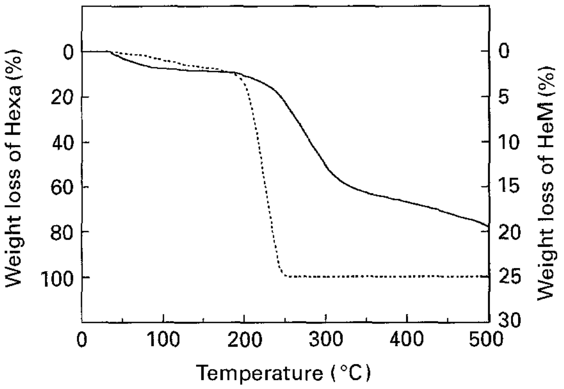

Figure 5 TG curves for (– – –) Hexa and (——) HeM.

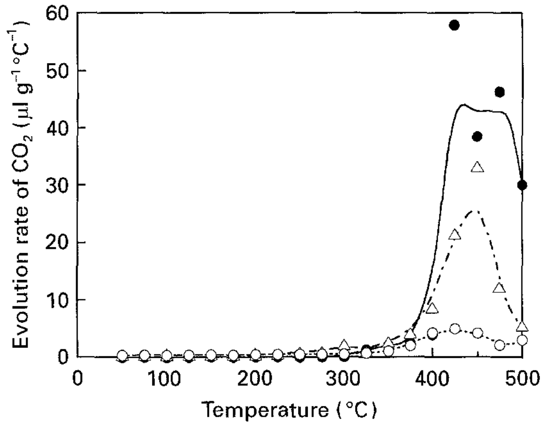

Figure 6 Evolution rate of CO_2 for (—○—) TBZ, (——△——) $Ag(TBZ)_2$ and (—●—) TAM.

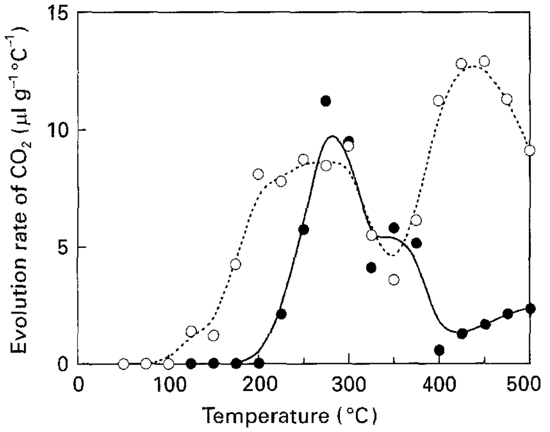

Figure 7 Evolution rate of CO_2 for (○) Dode and (●) DoM.

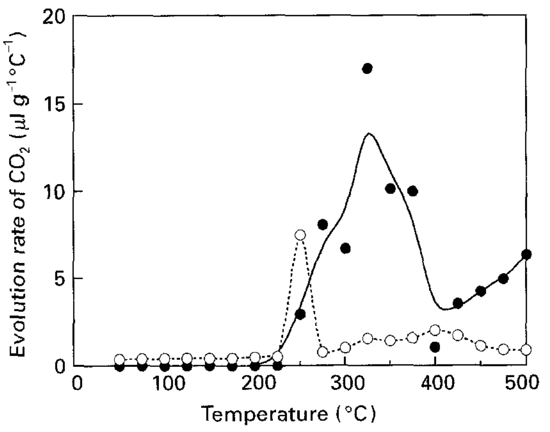

Figure 8 Evolution rate of CO_2 for (○) Hexa and (●) HeM.

4. Discussion

4.1. Structure of agents

It is certain from the following phenomena (i–iv) that silver-TBZ chelate, Dode and Hexa were intercalated between the Mont layers; i.e. (i) all samples became more hydrophobic than raw Mont; (ii) the carbon content suggested that more than 90% of the CEC of the Mont was exchanged by the silver-TBZ chelate, Dode and Hexa, respectively; (iii) the interlayer distances of TAM, DoM and HeM were larger than the 0.96 nm of the dried Mont by approximately 0.68–1.08 nm; (iv) some characteristic absorptions from TBZ, Dode and Hexa were observed in the infrared spectra. The broad (0 0 1) X-ray diffraction peak of TAM may also support the intercalation, because TAM is such a bulky chelate, its orientation between the Mont layers may be disturbed, leading to a broad X-ray diffraction profile.

The interlayer distance of the Mont is increased by intercalation of the quaternary alkyl ammonium cation with a longer alkyl chain (the length of the alkyl chain is shown by the number *n*, of carbon atoms in the chain). When a molecule with *n* more than 12 is intercalated, a double or triplelayer of molecules is formed between the Mont layers [7]. Because the diameter of an alkyl chain is 0.4 nm, this means that the alkyl ammonium cations are situated parallel to the Mont layer to form the monolayer stacking [8]. Then *n* for Dode and Hexa is 13 and 16. These must show an equal interlayer distance corresponding to a doublelayer, but the distances of DoM and HeM are 1.64 and 1.92 nm, respectively. This difference is thought to be caused by the lack of the hydrogen bonds between the positive end group of the alkylpyridinium cations and the negative silicate layers [9]. The pyridinium groups in HeM must slightly lift off from the Mont layers [8].

4.2. Thermostability of agents

The TG analysis showed clearly some significant differences among the thermostabilities of the unchelated organic ligand, its chelate with silver cation and the chelate intercalated between the Mont layers. Both quaternary ammonium cations between the Mont layers were released at almost the same temperature, which is higher than the evaporation temperatures of the quaternary ammonium cations themselves. A similar trend was also observed in the TAM series; i.e. TBZ showed a weight loss at 265 °C compared with 353 °C for TAM. These phenomena are thought to be dependent on the bonding strength between the Mont layer and the intercalated organic cation in addition to the intrinsic thermostability of the organic cation.

The thermal decomposition mechanism of the clay/organic complex is not clearly understood, but two quite distinct mechanisms have been proposed. Allaway [10] and Bradley and Grim [11] assumed that the organic intercalant between the Mont layers oxidizes in step-wise oxidation, resulting in a distinct weight loss after each step. According to the second theory, proposed by Ramachadran *et al.* [12], and

Aleshin and Shaimukhametov [13, 14], two weight losses are observed at the heating stage. One, at lower temperature, is the oxidation of the organic molecule attached on the external Mont surface and another, at higher temperature, is due to oxidation of the intercalated organic molecule. As can be seen in Fig. 6, TAM showed a maximum carbon dioxide evolution rate around 400 °C which does not coincide with the weight loss temperatures stated above. The Mont intercalated by the quaternary ammonium cation exhibited a similar phenomenon as observed in the case of TAM. In the present work, however, only carbon dioxide evolution was examined. It is not unreasonable to assume that weight loss was caused by evolution of other kinds of gases.

It is apparent that the thermostability of an organic compound is improved by intercalating between the Mont layers. In turn, the thermostability of the Mont layers is also improved by the carbon derived from the organic material after decomposition.

5. Conclusion

Mont intercalated by silver-TBZ chelate and quaternary ammonium cation (*n*-dodecyltrimethylammonium and hexadecylpyridinium), respectively, have been prepared, and their thermostabilities were examined by using thermogravimetry and carbon dioxide evolution analysis. The degradation temperatures of the ammonium cations were increased by intercalating between Mont layers. Both Dode and Hexa between the Mont layers were released at a nearly equal temperature which was higher than those for the quaternary ammonium cations without intercalation. The TAM-series also showed a similar trend. TAM gave a maximum carbon dioxide evolution rate at around 400 °C which did not coincide with the weight-loss temperature. A similar relation was also observed in the Mont intercalated by quaternary ammonium cations. However, carbon dioxide began to evolve from the quaternary ammonium cation at a lower temperature than that of Mont intercalated by quaternary ammonium cations.

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