

NOTES

SYNTHESIS OF CARBON-HYDROTALCITE COMPLEX AND ITS THERMAL DEGRADATION BEHAVIOR

Key Words—Carbon, Decarbonation, Heat treatment, Hydrotalcite, Intercalation.

Hydrotalcite-like compound (HTlc), an anionic clay, has attracted considerable interest due to its unusual intercalation properties. Various anions have been intercalated into its interlayers, similar to the intercalation of cations into the interlayers of smectite clays. For instance, immobilization of photoactive or electroactive anions in HTlc is an area of interest (Gianellis et al. 1987; Itaya et al. 1987). Also, a molecular

sieve effect is expected by intercalating anions of appropriate size (Miyata and Hirose 1978; Mao et al. 1993).

Although various HTlc intercalation compounds have been synthesized and investigated, all HTlcs reported to date have homogeneous interlayers. HTlcs containing a single anion have been investigated. Co-existence of more than two different anions or clus-

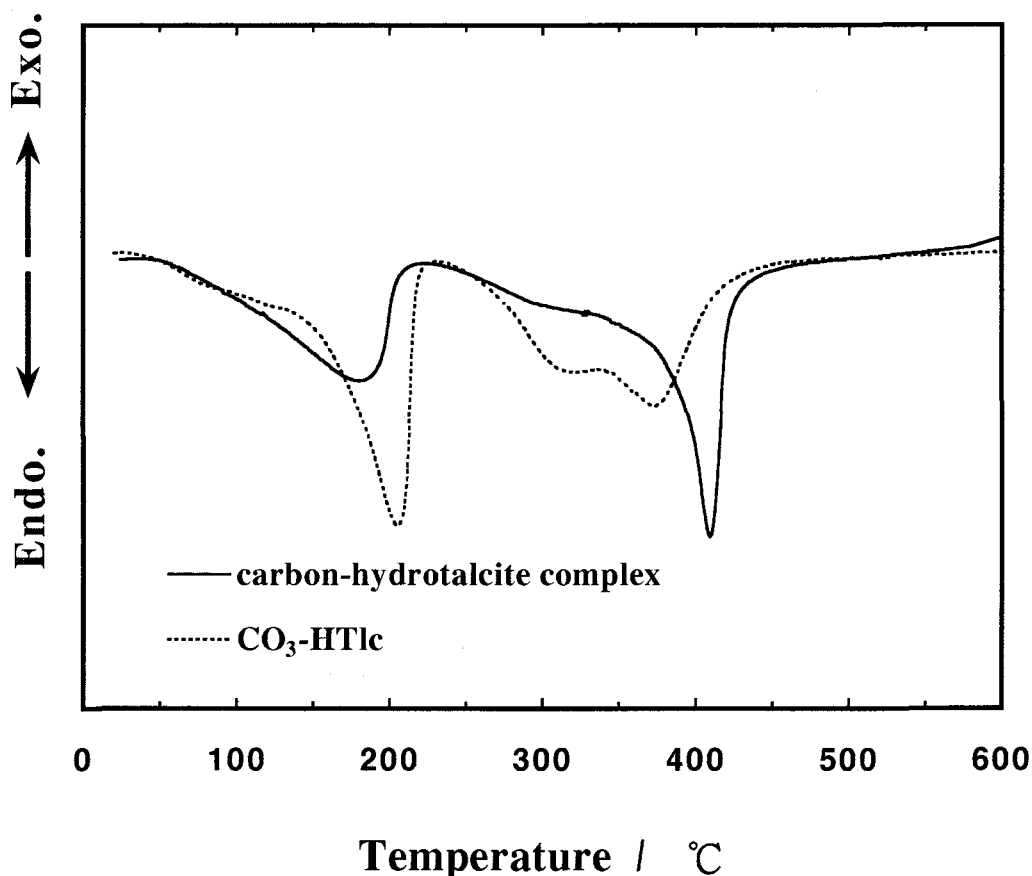


Figure 1. DTA curves (heating rate 3°C/min.) of CO₃-HTlc and carbon-hydrotalcite complex in nitrogen.

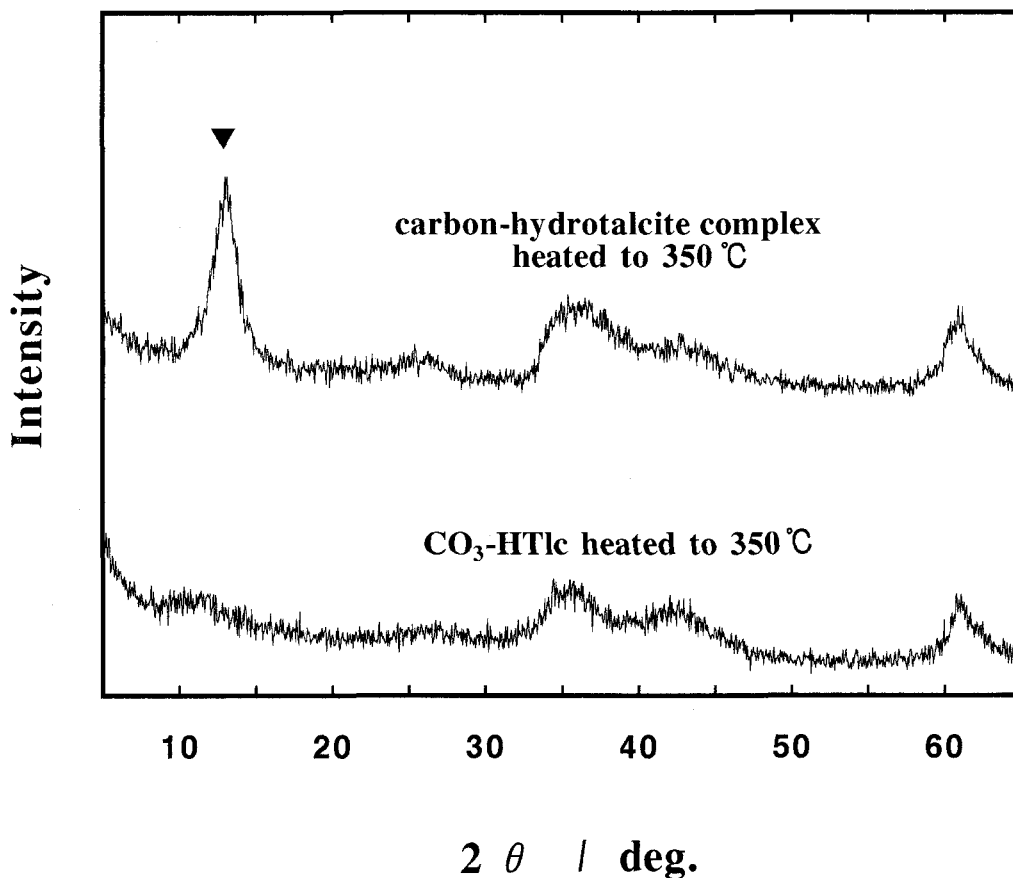


Figure 2. XRD patterns of $\text{CO}_3\text{-HTlc}$ and carbon-hydroxalcalcite complex when they are heated to 350°C . The (001) reflection is marked.

ters in interlayers would appear to be a novel potential of HTlc. The present work was undertaken initially to explore further the potential of HTlcs possessing complex interlayers. Here we report incorporating carbonate and carbon-like clusters into HTlc interlayers and then compare the resulting compounds with HTlc incorporating only carbonate whose thermal behavior has already been thoroughly investigated (Rey et al. 1992; Pesic et al. 1992; MacKenzie et al. 1993; Hudson et al. 1995). This carbon-hydroxalcalcite complex could be expected to have higher thermostability than HTlc without carbon, just as the thermostability of smectite clays increased by the intercalation of carbon into their interlayers (Oya et al. 1985, 1990).

SAMPLE PREPARATION

Organic-anion intercalates of HTlc were prepared by coprecipitation. An aqueous solution of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($\text{Mg}:\text{Al} = 2:1$) was continuously added to an organic anion solution (malonate, glutarate, pimelate and phthalate) at a flow rate of 50 mL/min. The mixture was maintained at $\text{pH} =$

10 by drop-wise addition of a NaOH solution and the mixture was vigorously stirred. The precipitate was washed ultrasonically with distilled water and then centrifuged. This procedure was repeated 10 times. The thoroughly washed precipitate was dried at 80°C . As references, HTlc containing carbonate (abbreviated as $\text{CO}_3\text{-HTlc}$) was prepared by the same method. Also, well-crystallized $\text{CO}_3\text{-HTlc}$ was prepared by a subsequent hydrothermal treatment at 150°C and 500 kPa for 12 h.

Organic-anion intercalates were calcined in air or in an inert gas at the temperature at which weight loss was completed (600°C for phthalate intercalate and 500°C for other intercalates), and then interlayer organic anions were carbonized. Well-ground calcined material was regenerated to HTlc, which was a hydroxalcalcite-carbon complex, in a Na_2CO_3 aqueous solution.

RESULTS

After calcination, organic-anion intercalates of HTlc, which form a white powder became brown in air or black in nitrogen. Carbon-hydroxalcalcite complex was the same color as its calcined material. Carbon-

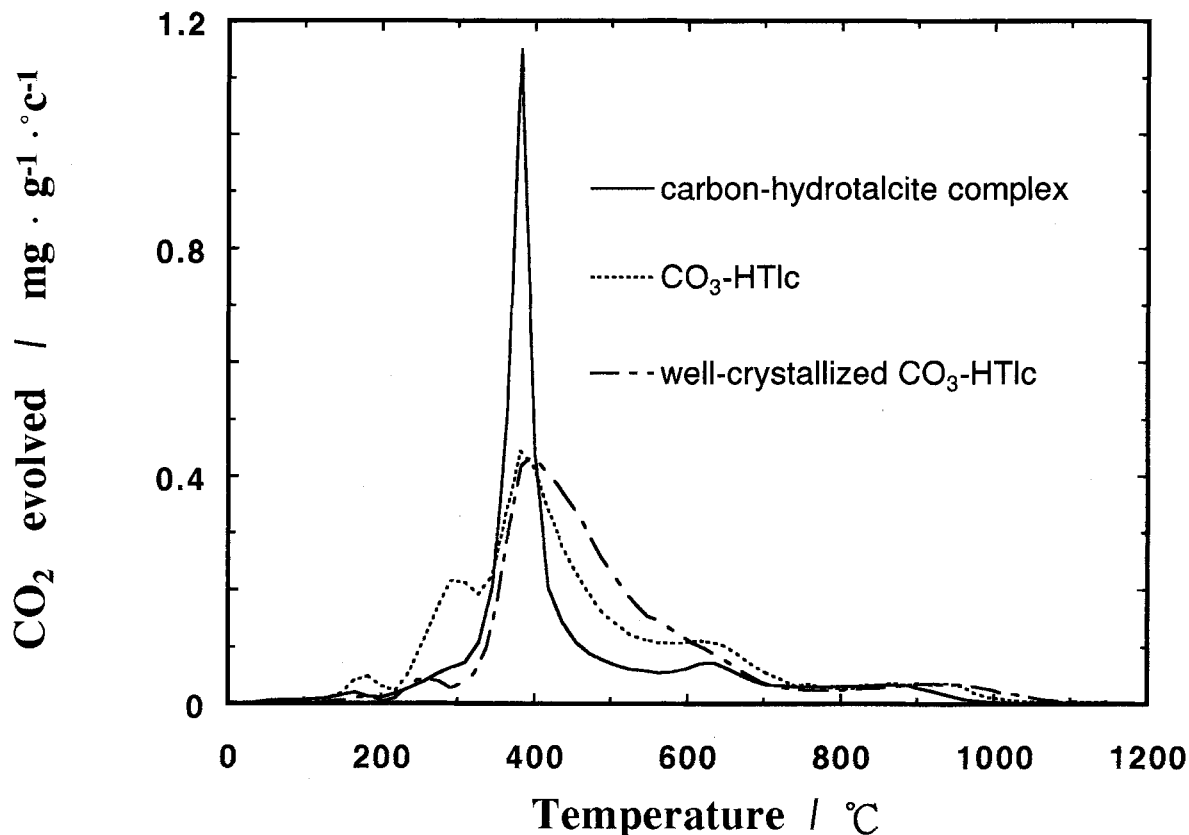


Figure 3. Amounts of CO_2 evolved from $\text{CO}_3\text{-HTlc}$, well-crystallized $\text{CO}_3\text{-HTlc}$ and carbon-hydroxalcalite complex at various temperatures. CO_2 evolution from the TG experiment (heating rate $3^\circ\text{C}/\text{min.}$) was measured by gas chromatography (GC) with nitrogen carrier gas.

hydroxalcalite complexes prepared with all organic-anion intercalates examined have shown the same thermal behavior. Here we describe the thermal behavior of the carbon-hydroxalcalite complex with pimelate intercalate as a typical example.

The ratio of $\text{Mg}/(\text{Mg} + \text{Al})$ was unchanged by calcination and reconstitution to carbon-hydroxalcalite complex as shown by X-ray microanalysis with an energy dispersive spectrometer (EDS). The carbon content of the carbon-hydroxalcalite complex, although not including carbon of interlayer carbonate, was measured by combustion method (Table 1). When the calcination of organic-anion intercalate was carried out in nitrogen, the carbon content of carbonaceous residue was com-

parable with the carbon content of interlayer carbonate (2.5 wt%).

There was no difference between the X-ray diffraction (XRD) patterns of $\text{CO}_3\text{-HTlc}$ and the carbon-hydroxalcalite complex. Differential thermal analysis (DTA) curves show endothermic peaks at 210, 305 and 410°C for $\text{CO}_3\text{-HTlc}$, and peaks at 180 and 410°C and a shoulder at around 300°C for the carbon-hydroxalcalite complex (Figure 1). The layer structure collapsed at the second DTA peak temperature for both the carbon-hydroxalcalite complex and the $\text{CO}_3\text{-HTlc}$. However the second DTA peak temperature of the carbon-hydroxalcalite complex (410°C) is 100°C higher than that of the $\text{CO}_3\text{-HTlc}$ (305°C). This was confirmed by the XRD patterns of samples calcined at 350°C , a temperature between the second DTA peak temperatures of the $\text{CO}_3\text{-HTlc}$ and the carbon-hydroxalcalite complex (Figure 2). The (001) reflection was observed for the carbon-hydroxalcalite complex but not for the $\text{CO}_3\text{-HTlc}$.

The carbon-hydroxalcalite complex evolved CO_2 more sharply than did the $\text{CO}_3\text{-HTlc}$ and the well-crystallized $\text{CO}_3\text{-HTlc}$ (Figure 3). The decarbonation behavior of regenerated $\text{CO}_3\text{-HTlc}$ was found to be identical

Table 1. Carbon content of carbon-hydroxalcalite complex.

Calcination atmosphere ^a	Carbon content ^b wt %
Air	0.36
Nitrogen	2.0

^a 'Calcination atmosphere' refers to the atmosphere when the calcination of pimelate intercalate was carried out.

^b 'Carbon content' refers to the carbon content not including carbon of interlayer carbonate.

to that of the virgin CO₃-HTlc. Thus, the regeneration procedure does not affect decarbonation behavior.

DISCUSSION

The Mg/(Mg + Al) ratio of organic-anion intercalate of 0.33 was unchanged by regeneration to carbon-hydroxalcalcite complex. The spacings of (003) and (110) for carbon-hydroxalcalcite complex, which are proportional to the Mg/(Mg + Al) ratio, were the same as those for CO₃-HTlc. These results revealed that the calcined material was regenerated completely to the hydroxalcalcite-like structure and that there is no amorphous phase.

There is no XRD and transmission electron microscopic (TEM) information on the site where carbonaceous residues from the organic anions reside. However, judging from the 100°C improvement in thermal stability, we believe that the carbonaceous residues could be located in the interlayers of the carbon-hydroxalcalcite complex. In the case of carbon-smectite clay complexes converted from organic-smectite clay complexes, their layer structures are maintained at temperatures about 200°C higher than those of the corresponding raw clay minerals, because the resulting intercalated carbon hampers sintering of the clay minerals (Oya et al. 1985). A similar effect may occur for the carbon-hydroxalcalcite complex. For example, the layer structure of the carbon-hydroxalcalcite complex could be supported by the carbonaceous residues. This improvement in thermal stability promotes CO₂ evolution. The layer structure of the carbon-hydroxalcalcite complex is maintained up to the temperature of main decarbonation (380°C) but that of the CO₃-HTlc collapses before the decarbonation. Perhaps the oxygen atoms, which come closer to the interlayer carbonate anions of CO₃-HTlc and well-crystallized CO₃-HTlc during collapse of the layer structure, hamper the departure of the carbonate anions during decarbonation. On the other hand, during the decarbonation of the carbon-hydroxalcalcite complex, carbonate anions might be released more readily because the layer structure is maintained. Consequently, the carbon-hydroxalcalcite complex evolved CO₂ more sharply than even well-crystallized CO₃-HTlc. In addition, small peaks of decarbonation were observed at 600 and 900°C for car-

bon-hydroxalcalcite complex as well as CO₃-HTlcs. Al ions enter MgO in the temperature range of 500–800°C, and MgAl₂O₄ forms at 900°C. The remaining carbonates are released as the Al ions migrate, as we reported previously (Hibino et al. 1995).

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