

## 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 (Giannelis 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-

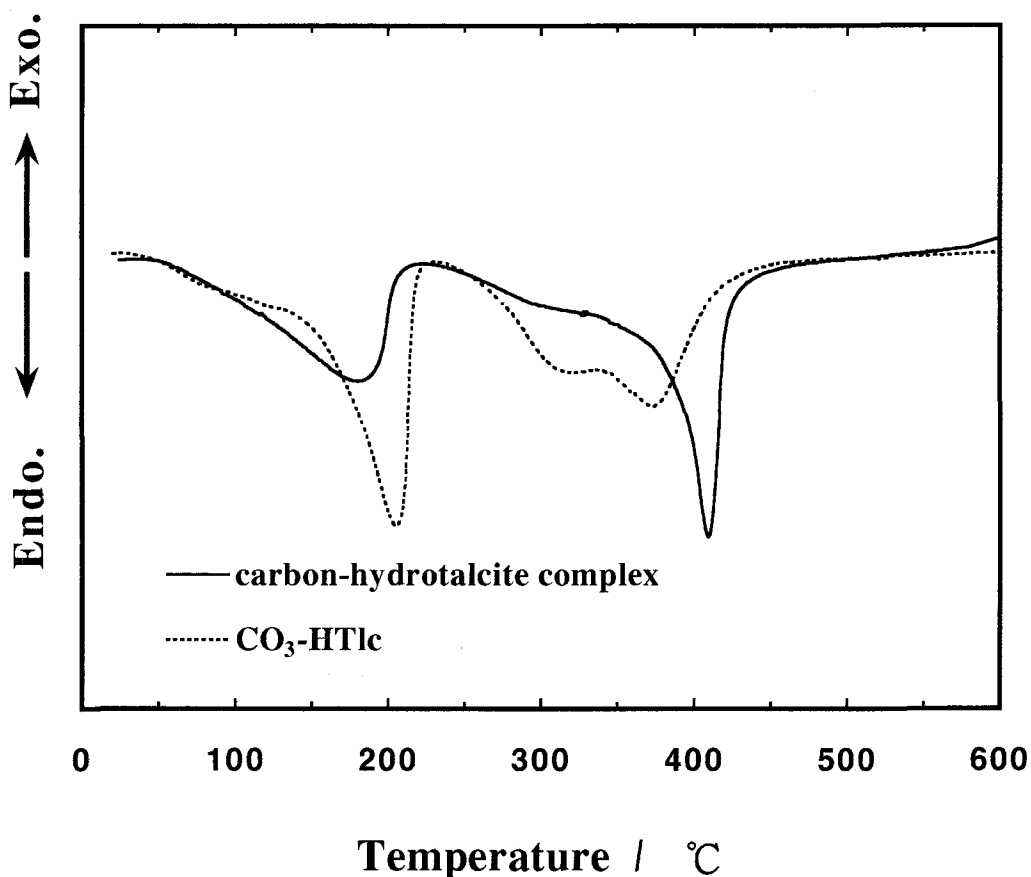


Figure 1. DTA curves (heating rate 3°C/min.) of CO<sub>3</sub>-HTlc and carbon-hydrotalcite complex in nitrogen.

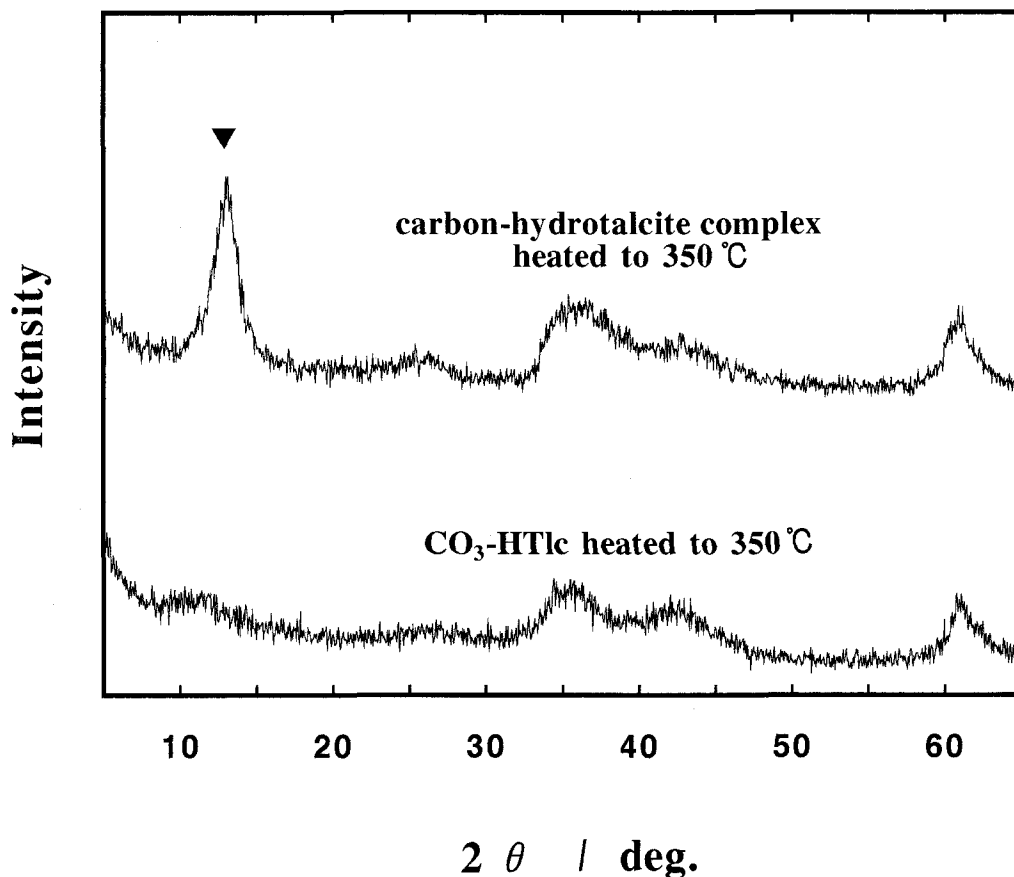


Figure 2. XRD patterns of CO<sub>3</sub>-HTlc and carbon-hydrotalcite complex when they are heated to 350°C. The (001) reflection is marked.

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-hydrotalcite 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 Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Mg: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 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 CO<sub>3</sub>-HTlc) was prepared by the same method. Also, well-crystallized CO<sub>3</sub>-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 hydrotalcite-carbon complex, in a Na<sub>2</sub>CO<sub>3</sub> aqueous solution.

#### RESULTS

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

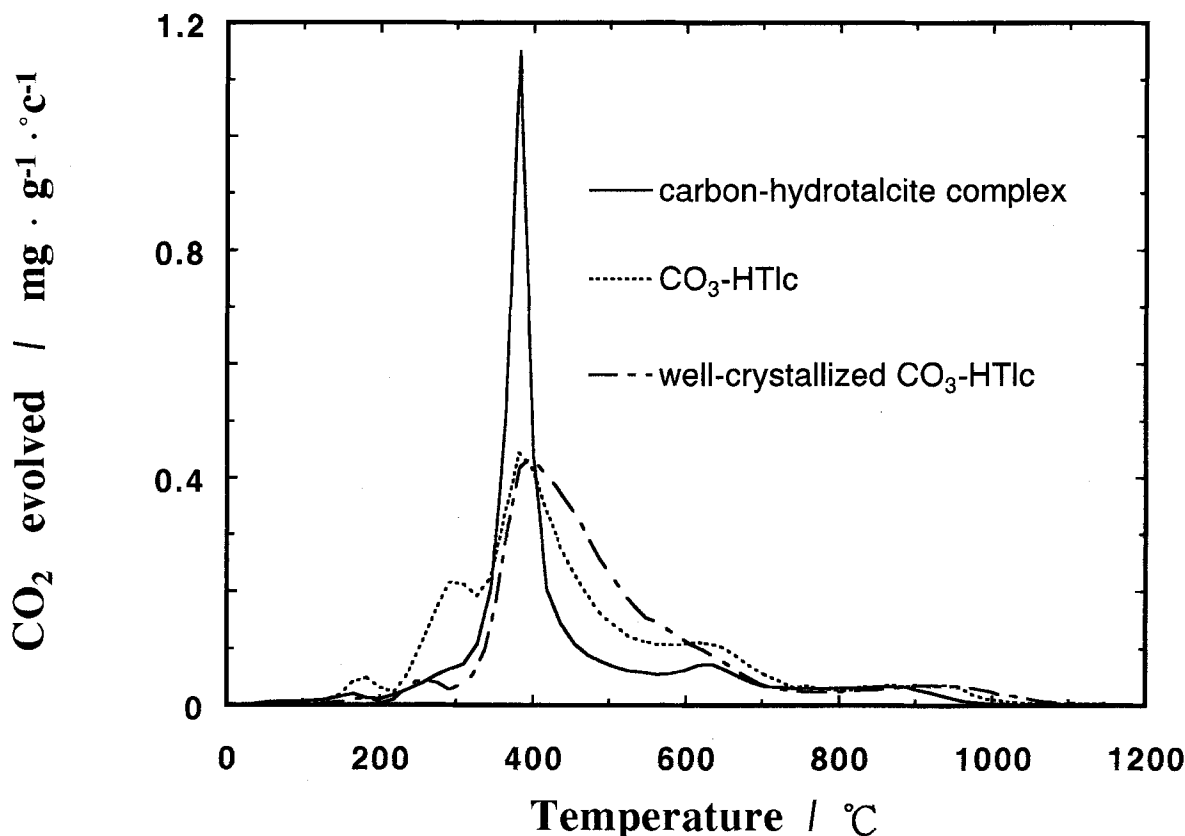


Figure 3. Amounts of  $\text{CO}_2$  evolved from  $\text{CO}_3\text{-HTlc}$ , well-crystallized  $\text{CO}_3\text{-HTlc}$  and carbon-hydroxalcite complex at various temperatures.  $\text{CO}_2$  evolution from the TG experiment (heating rate  $3^\circ\text{C}/\text{min.}$ ) was measured by gas chromatography (GC) with nitrogen carrier gas.

hydroxalcite complexes prepared with all organic-anion intercalates examined have shown the same thermal behavior. Here we describe the thermal behavior of the carbon-hydroxalcite 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-hydroxalcite complex as shown by X-ray microanalysis with an energy dispersive spectrometer (EDS). The carbon content of the carbon-hydroxalcite 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-hydroxalcite complex. Differential thermal analysis (DTA) curves show endothermic peaks at 210, 305 and  $410^\circ\text{C}$  for  $\text{CO}_3\text{-HTlc}$ , and peaks at 180 and  $410^\circ\text{C}$  and a shoulder at around  $300^\circ\text{C}$  for the carbon-hydroxalcite complex (Figure 1). The layer structure collapsed at the second DTA peak temperature for both the carbon-hydroxalcite complex and the  $\text{CO}_3\text{-HTlc}$ . However the second DTA peak temperature of the carbon-hydroxalcite complex ( $410^\circ\text{C}$ ) is  $100^\circ\text{C}$  higher than that of the  $\text{CO}_3\text{-HTlc}$  ( $305^\circ\text{C}$ ). This was confirmed by the XRD patterns of samples calcined at  $350^\circ\text{C}$ , a temperature between the second DTA peak temperatures of the  $\text{CO}_3\text{-HTlc}$  and the carbon-hydroxalcite complex (Figure 2). The (001) reflection was observed for the carbon-hydroxalcite complex but not for the  $\text{CO}_3\text{-HTlc}$ .

The carbon-hydroxalcite complex evolved  $\text{CO}_2$  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-hydroxalcite complex.

Calcination atmosphere <sup>a</sup>	Carbon content <sup>b</sup> wt %
Air	0.36
Nitrogen	2.0

<sup>a</sup> 'Calcination atmosphere' refers to the atmosphere when the calcination of pimelate intercalate was carried out.

<sup>b</sup> 'Carbon content' refers to the carbon content not including carbon of interlayer carbonate.

to that of the virgin CO<sub>3</sub>-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-hydroxalcalite complex. The spacings of (003) and (110) for carbon-hydroxalcalite complex, which are proportional to the Mg/(Mg + Al) ratio, were the same as those for CO<sub>3</sub>-HTlc. These results revealed that the calcined material was regenerated completely to the hydroxalcalite-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-hydroxalcalite 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-hydroxalcalite complex. For example, the layer structure of the carbon-hydroxalcalite complex could be supported by the carbonaceous residues. This improvement in thermal stability promotes CO<sub>2</sub> evolution. The layer structure of the carbon-hydroxalcalite complex is maintained up to the temperature of main decarbonation (380°C) but that of the CO<sub>3</sub>-HTlc collapses before the decarbonation. Perhaps the oxygen atoms, which come closer to the interlayer carbonate anions of CO<sub>3</sub>-HTlc and well-crystallized CO<sub>3</sub>-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-hydroxalcalite complex, carbonate anions might be released more readily because the layer structure is maintained. Consequently, the carbon-hydroxalcalite complex evolved CO<sub>2</sub> more sharply than even well-crystallized CO<sub>3</sub>-HTlc. In addition, small peaks of decarbonation were observed at 600 and 900°C for car-

bon-hydroxalcalite complex as well as CO<sub>3</sub>-HTlcs. Al ions enter MgO in the temperature range of 500–800°C, and MgAl<sub>2</sub>O<sub>4</sub> forms at 900°C. The remaining carbonates are released as the Al ions migrate, as we reported previously (Hibino et al. 1995).

*Materials Processing Department* TOSHIYUKI HIBINO  
*National Institute for Resources* KATSUNORI KOSUGE  
*and Environment*

16-3 Onogawa, Tsukuba, ATSUMU TSUNASHIMA  
305 Japan

#### REFERENCES

- Giannelis EP, Nocera DG, Pinnavaia TJ. 1987. Anionic photocatalysts supported in layered double hydroxides: Intercalation and photophysical properties of a ruthenium complex anion in synthetic hydroxalcalite. *Inorg Chem* 26:203–205.
- Hibino T, Yamashita Y, Kosuge K, Tsunashima A. 1995. Decarbonation behavior of Mg-Al-CO<sub>3</sub> hydroxalcalite-like compounds during heat treatment. *Clays & Clay Miner* 43:427–432.
- Hudson MJ, Carlino S, Apperley DC. 1995. Thermal conversion of layered (Mg/Al) double hydroxide to the oxide. *J Mater Chem* 5:323–329.
- Itaya K, Chang HC, Uchida I. 1987. Anion-exchanged hydroxalcalite-like-clay-modified electrodes. *Inorg Chem* 26:624–626.
- MacKenzie KJD, Meinhold RH, Sherriff BL, Xu Z. 1993. <sup>27</sup>Al and <sup>25</sup>Mg solid-state magic-angle spinning nuclear magnetic resonance study of hydroxalcalite and its thermal decomposition sequence. *J Mater Chem* 3:1263–1269.
- Mao G, Tsuji M, Tamaura Y. 1993. Synthesis and CO<sub>2</sub> adsorption features of a hydroxalcalite-like compound of the Mg<sup>2+</sup>-Al<sup>3+</sup>-Fe(CN)<sub>6</sub><sup>4-</sup> system with high layer-charge density. *Clays & Clay Miner* 41:731–737.
- Miyata S, Hirose T. 1978. Adsorption of N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub> on hydroxalcalite-like system: Mg<sup>2+</sup>-Al<sup>3+</sup>-(Fe(CN)<sub>6</sub>)<sup>4-</sup>. *Clays & Clay Miner* 26:441–447.
- Oya A, Mita H, Tosaka Y, Otani S. 1990. Thermal degradation behavior of hydroxalcalite/flavianic acid complex in nitrogen. *Appl Clay Sci* 5:13–22.
- Oya A, Omata Y, Otani S. 1985. Thermal degradation behavior of montmorillonite- $\alpha$ -naphthylamine complex under nitrogen. *J Mater Sci* 20:255–260.
- Pesic L, Salipurovic S, Markovic V, Vucelic D, Kagunya W, Jones W. 1992. Thermal characteristics of a synthetic hydroxalcalite-like material. *J Mater Chem* 2:1069–1073.
- Rey F, Fornés V, Rojo JM. 1992. Thermal decomposition of hydroxalcalites: An infrared and nuclear magnetic resonance spectroscopic study. *J Chem Soc Faraday* 88:2233–2238.
- (Received 17 January 1995; accepted 6 July 1995; Ms. 2607)