Formation of Hydrotalcite-Acrylate Intercalation Compounds and Their Heat-Treated Products

Masahito TANAKA, In Yong PARK, Kazuyuki KURODA, and Chuzo KATO*
Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169

(Received March 29, 1989)

Hydrotalcite-like compounds (HT), layered double hydroxides with a few kinds of interlayer anions ($X=CO_3^{2-}$, Cl^-, and NO_3^-) were allowed to react with acrylate anions in order to prepare a novel inorganic–organic interstratified layered material by anion exchange. When HT-CO_3 was used the anion exchange reaction did not occur. When HT-NO_3 was employed the reaction proceeded to form a HT-acrylate intercalation compound. The formation of the intercalation compound from HT-Cl was observed only under a reaction condition using a concentrated acrylate solution. When the intercalation compound was heated at 80 °C with the addition of an initiator, the interlayer acrylate anions were polymerized to form a HT-polyacrylate intercalation compound.

Hydrotalcite-like compounds (abbreviated HT) are layered double hydroxides, expressed as $[Mg_{1-x}Al_x(OH)_2]^{x+}[A_{x/n}^{n-}\cdot mH_2O]^{x-}$, where A^{n-} is an exchangeable anion, and $0.2\leqq x\leqq 0.33$.[1,2] A part of Mg in the brucite layer $[Mg(OH)_2]$ is replaced with Al, and the positively charged layers are compensated with interlayer anions. The metals in the layers are not limited to Mg and Al, since many divalent and trivalent metals are employed to form different types of layered double hydroxides.[3] Interlayer anions and water occupy the interlayer space. Since these interlayer anions are exchangeable, hydrotalcite-like compounds have been investigated from the viewpoint of an inorganic anion exchanger. Regarding the selectivity of the interlayer inorganic anions, the high selectivity of anions with higher valency and smaller size has been reported.[4]

In general, HT does not exhibit a swelling property. The layer charge density is also relatively higher than those of intercalating layered oxide materials, such as smectite clay. Accordingly, there have been only several reports on exchange with organic anions in HT. Dicarboxylic acids (Zn^{2+}-Al^{3+} hydroxide),[5] D,L-histidines (Mg^{2+}-Al^{3+}),[6] acetic acid (Ni^{2+}-Fe^{3+} (Co^{3+})),[7] and alkyl sulfates (Zn^{2+}-Cr^{3+}),[8] (Mg^{2+}-Al^{3+})[9] have been investigated so far.

In the present study, as a course of our study on the intercalation chemistry of hydrotalcite, the acrylate anion was selected as the guest anion and the possibility of an anion exchange was examined, since the acrylate anion is small in size and polymerizable. Thus, the interlayer polymerization of acrylate anions by thermal treatment was also investigated.

Experimental

Materials. The HT used in this study was a CO_3-exchanged type (Kyowaad 500 manufactured by Kyowa Chemical Industry Co.). The ratio of aluminum in the total metals (x=Al/(Mg+Al)) was 0.25. The XRD, IR, and thermoanalytical data coincided with the previous results.[4]

The Cl- and NO_3-exchanged types were prepared by the following procedure. HT-CO_3 (5 g) and sodium chloride (ca. 20 g) were mixed with decarbonated water to make a suspension (200 ml) by stirring. The suspension was stirred under a nitrogen flow and 2 M hydrochloric acid (1 M= 1 mol dm^{-3}) was added into the reaction mixture and the pH was maintained at 4.2—4.5 for 10 min. The mixture was centrifuged and washed with decarbonated water twice. The end of the washing was checked by ion chromatography. The ion-exchanged product was dried under reduced pressure at room temperature. The XRD, IR, and thermal analyses of the products showed the same results as the previous data of the HT-Cl.[4] HT-NO_3[10] was prepared with sodium nitrate and 2 M nitric acid instead of sodium chloride and hydrochloric acid, respectively. The other procedure was the same as that for the preparation of HT-Cl.

The ion exchange capacities of both HT-Cl and HT-NO_3 were ca. 270 mequiv/100 g HT, which was ca. 90% of the calculated values based on the chemical formulae of the fully exchanged HT-Cl and HT-NO_3. This finding suggested that a part of interlayer carbonate anions was not exchanged with Cl^- or NO_3^-. Commercially available acrylic acid (Tokyo Kasei Co.) was used without further purification.

Ion Exchange with Acrylate Anions. The amount of acrylate anions used in the anion exchange was calculated on the basis of the anion exchange capacity of hydrotalcite. The amounts were 3, 5, 7, 10, 20, and 50 times the anion exchange capacity when HT-NO_3 was used. The amounts of 5, 10, and 50 times the capacity were selected for experiments with HT-CO_3 and HT-Cl. A given amount of acrylic acid was dissolved in water and the pH of the solution was adjusted to be 7 with a NaOH aq. solution to form acrylate anions; the total volume of the final solution was 400 ml. Thus, the concentrations of acrylate anions were varied from 0.10 to 1.69 mol dm^{-3} for HT-NO_3, and from 0.17 to 1.69 mol dm^{-3} for HT-CO_3 and HT-Cl. When HT-Cl was employed, an exchange reaction using a highly concentrated acrylate solution (6.75 mol dm^{-3}, the total volume was 100 ml, the amount of acrylate anions was 50-times the ion exchange capacity of HT, pH 7) was also performed.

HT (5 g each) was added into these solutions and the reaction mixtures were stirred for 1 week at room temperature. When a shorter reaction time, e.g. 5 days, was attempted, the unreacted HT partly remained. After centrifugation, the products were washed with decarbonated water. The completion of the washing was checked by CHN analyses of the products. After a few repetitions of washing, the carbon contents reached a constant value. After washing, the products were dried under reduced pressure at room temperature and analyzed. All of the anion-exchange experiments were performed under a nitrogen atmosphere.

Polymerization. The HT-acrylate intercalation compounds were heat-treated at 80 °C for 1 day after the addition of potassium peroxodisulfate (an initiator for polymerization) into the undried products followed by homogeneous mixing.

Analyses. X-Ray powder diffraction patterns were obtained with a Rigaku Rad-IB diffractometer using Ni-filtered Cu $K\alpha$ radiation. IR analyses were performed with a Perkin-Elmer FT-IR 1640 using a KBr disk technique. DTA curves were recorded on a Shimadzu DT-20 thermal analyzer at a heating rate of 10 °C min^{-1} under an air atmosphere. TG curves were recorded on a Shimadzu DT-40 apparatus.

Results and Discussion

Hydrotalcite-Acrylate Intercalation Compound.
The formation of intercalation compounds was primarily judged by the variation in the X-ray diffraction patterns. The ratio of the intercalation compound to unreacted HT was roughly estimated by the peak intensities of their (003) diffraction lines. When HT–NO$_3$ was used as the starting material, the reaction with acrylate solutions of lower concentrations yielded the intercalation compound at a very low ratio with a large amount of unreacted HT. With the increase in the concentration, the formation of the intercalation compound became pronounced. The intercalation compound obtained from the highest concentration formed a single phase and the reproducibility was highest. Therefore, the compound obtained from the acrylate solution (1.69 M) was employed for the following analyses.

Figure 1 shows the X-ray powder diffraction patterns of the reaction products obtained from HT–NO$_3$. In the profile of the HT–acrylate reaction product (Fig. 1(b)), the diffraction peak due to (003), which corresponded to the basal spacing, shifted to a lower 2θ angle at 6.4° (d=13.8 Å). Correspondingly, the peaks due to (006) and (009) shifted to lower angles in a similar manner.

The IR spectra of HT–NO$_3$, sodium acrylate, and the reaction product are shown in Fig. 2. In the spectrum of the HT–acrylate reaction product (Fig. 2(c)), the absorption peak due to nitrate anions at 1380 cm^{-1} (ν_3) almost disappeared, whereas peaks due to acrylate anions at 1640 cm^{-1} ($\nu_{C=C}$), 1560 cm^{-1} (ν_{asCOO^-}), and 1450 cm^{-1} (ν_{sCOO^-})[11,12] appeared. A slight deformation in the peak profile at 1360 cm^{-1} (δ_{C-H}) can be explained by considering that the small peak due to carbonate anions ($\nu_{CO_3^{2-}}$) overlapped. As described in Experimental, carbonate anions partly remained in the original HT–NO$_3$. However,

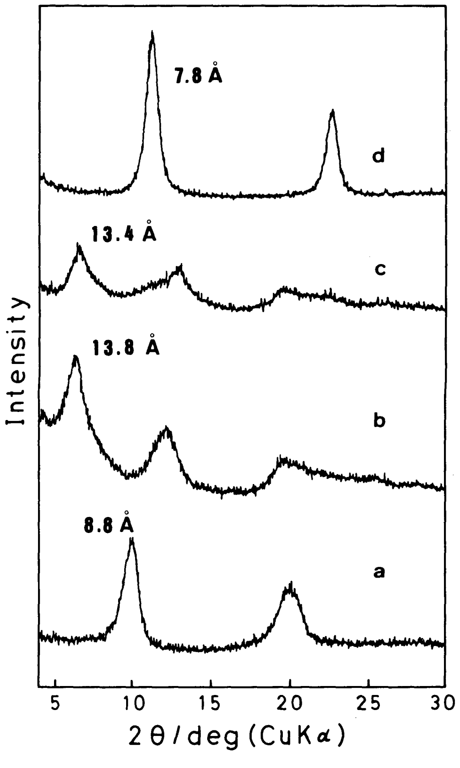

Fig. 1. X-Ray powder diffraction patterns of a) HT–NO$_3$, b) HT–acrylate intercalation compound, c) HT–polyacrylate intercalation compound, and d) CO$_3$ re-exchanged HT.

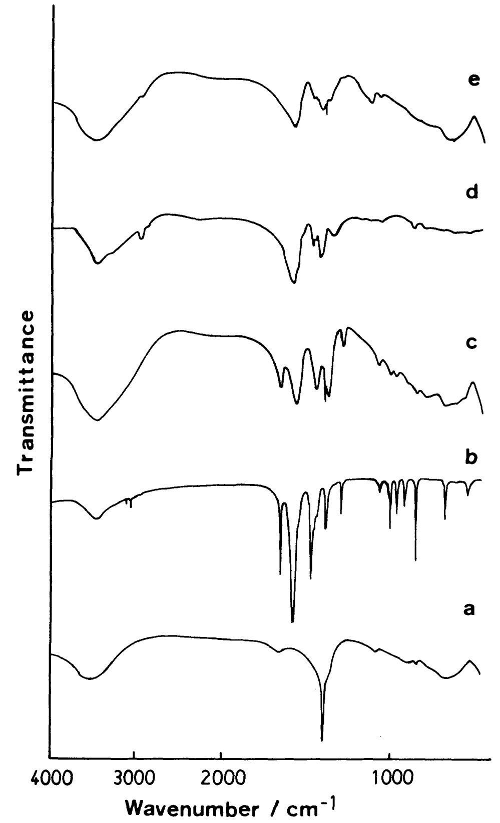

Fig. 2. Infrared spectra of a) HT–NO$_3$, b) sodium acrylate, c) HT–acrylate intercalation compound, d) sodium polyacrylate, and e) HT–polyacrylate intercalation compound.

carbonate anions must have been partly intercalated during the procedure of ion exchange or washing, since these anions have the highest selectivity in HT.[4)]

Part of the product was re-exchanged with carbonate anions by being immersed in a sodium carbonate aqueous solution (2 M) for one day. The XRD result of the re-exchanged product is shown in Fig. 1(d). The peaks shifted to higher angles and showed the characteristic pattern of HT–CO_3. The IR spectrum of the product also showed the presence of carbonate anions along with a disappearance of acrylate anions. From these results, it can be concluded that the reaction can be treated as an interlayer anion exchange and that the double hydroxide layer was retained.

The Mg and Al contents (Mg/Al=0.74/0.26) analyzed by ICP, carbon contents (8.8%) determined by CHN analysis, and the amount of the interlayer water ($0.33H_2O$) calculated from the thermogravimetric curve led to the following chemical formula of the HT-acrylate intercalation compound: $[Mg_{0.74}Al_{0.26}(OH)_2](Ac)_{0.18}(CO_3)_{0.04}\cdot 0.33H_2O$, where Ac represents the acrylate anion. The amounts of acrylate anions and CO_3^{2-} could not be determined separately by TG curves because their weight losses overlapped each other. Therefore, the amounts was deduced from the relationship among the anion exchange capacity, total carbon contents, and the charges of acrylates and carbonates.

When HT–CO_3 was employed as the starting material, the XRD results did not show any variation in their profiles, indicating no reactions. Since the basal spacing of HT is dependent on the size of unhydrated interlayer anions,[4)] the increase in the basal spacing should have been detected if acrylate anions were intercalated. The IR results also showed no absorption peaks due to acrylate anions. From these findings, an anion exchange did not take place in a system using HT–CO_3.

When HT–Cl was used, the HT-acrylate intercalation compound was partly obtained only in the case when a highly concentrated acrylate solution was used. The basal spacing of the intercalation compound showed the same value of 13.8 Å. Based on the intensities of (003) diffraction lines of HT-acrylate and HT–Cl, the ratio of the HT-acrylate to the unreacted HT–Cl was roughly estimated to be 3 : 1. In all other cases, however, the intercalation compounds could not be prepared. Therefore, the reactivity of HT–Cl was much lower than that of HT–NO_3.

From these results, the kind of interlayer anions in the starting materials greatly affected the formation of HT-acrylate intercalation compounds. The reason why only HT–NO_3 has a high intercalating ability may be explained by the following two points: the difference in selectivity (or stability) of the interlayer anions and the difference in the interlayer spacings. Regarding the former factor, it has been known[4)] that the selectivity decreases in the order

$$CO_3^{2-} \gg Cl^- > NO_3^-.$$

With regard to the latter point, the interlayer distances of both HT–Cl and HT–CO_3 are ca. 3 Å, while that of HT–NO_3 is ca. 4 Å. On the other hand, the thickness of the acrylate anion, which takes a planar geometry, is 2.8 Å. If acrylate anions are intercalated in a flat arrangement during the initial stage of intercalation, it is preferable to use HT–NO_3 due to its larger interlayer thickness. Consequently, it is supposed that acrylate anions can be intercalated more easily. For both of these reasons, HT–NO_3 was most successful for the inclusion of acrylate anions.

Hydrotalcite-Polyacrylate Intercalation Compound. Figure 1(c) shows the XRD data of the polymerized product. The IR spectrum of the product is shown in Fig. 2(e). In the XRD data, the d_{003} value became slightly smaller (d=13.4 Å) than that for a monomer-intercalated substance. Although the peak intensities were weakened, the layer structure was retained. The IR spectrum showed the main characteristic bands due to polyacrylate anions.[13,14)] In particular, the absorption peak arising from $\nu_{C=C}$ at 1640 cm^{-1} disappeared and the total profile was similar to that of sodium

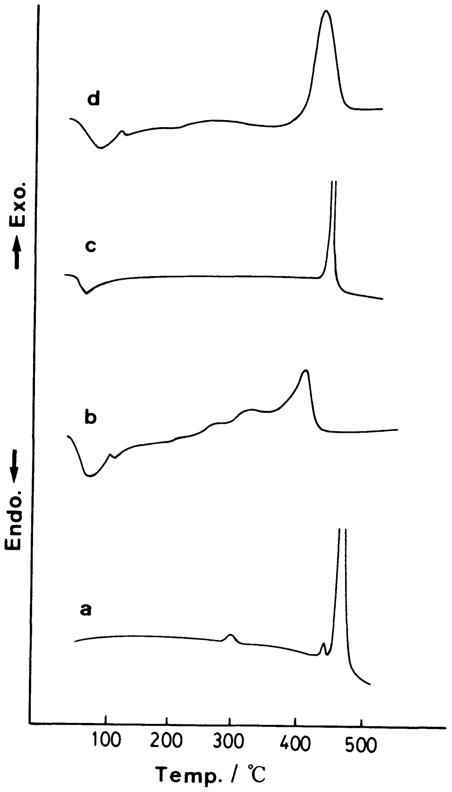

Fig. 3. DTA curves of a) sodium acrylate, b) HT-acrylate intercalation compound, c) sodium polyacrylate, and d) HT-polyacrylate intercalation compound.

polyacrylate, indicating a polymerization of acrylate anions in the interlayer space.

The DTA curves of the intercalation compounds before and after polymerization, sodium acrylate, and sodium polyacrylate are shown in Fig. 3. The DTA curve of sodium acrylate showed exothermic peaks due to polymerization at 280—290 °C and oxidative decomposition starting at 430—440 °C.[15] The reason why decomposition occurred at a comparatively higher temperature may be attributed to the formation of a thermally stable polymer with three-dimensionality which was prepared by bulk polymerization. The DTA curve of sodium polyacrylate did not show an exothermic peak due to polymerization but, rather, exhibited a similar sharp exothermic peak due to its oxidative decomposition.

The complex DTA curve was observed in the HT–acrylate intercalation compound. The several exothermic peaks overlapped and the first started at 250 °C. The XRD data of the heat-treated product at 250 °C for 1 h showed a decrease in the basal spacing to ca. 9 Å. The IR spectrum of the heat-treated product also showed a drastic decrease in the absorption peaks due to acrylate anions. Therefore, the oxidative decomposition of the HT–acrylate intercalation compound proceeded at much lower temperatures than that of the polymerized intercalation compound.

The DTA curve of the HT–polyacrylate intercalation compound was similar to that of sodium polyacrylate. The XRD result of the heat-treated product of the intercalation compound at 250 °C showed the retention of the same basal spacing as the HT–polyacrylate intercalation compound. The IR spectrum of the heat-treated product also showed absorption peaks due to polyacrylate anions. Thus, the difference in the thermal behavior of the intercalation compounds before and after polymerization was confirmed.

From these results we can conclude that acrylate anions were polymerized in the interlayer region of hydrotalcite. The difference in the thermal behavior between HT–acrylate and HT–polyacrylate intercalation compounds was observed, which was attributed to the formation of interlayer polymers.

One of the authors (K. K.) thanks the Yazaki Memorial Foundation for financial support. Waseda University also supported us as a Project Study in Science and Engineering Research Laboratory.

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