Effects of pH and concentration on ability of Cl^- and NO_3^- to intercalate into a hydrotalcite-like compound during its synthesis

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Abstract. In this study, we confirmed that the characteristics of anion intercalation into the interlayer of a hydrotalcite-like compound (HT) during synthesis are similar to those of the anion-exchange reaction of HTs as well as the reconstruction reaction of HTs from Mg–Al oxide. We demonstrated that (i) Cl^-, which has a higher charge density than NO_3^-, more easily reacted with Mg and Al species to form HT structure, resulting in greater intercalation of Cl^- into the HT interlayer; and (ii) for HTs with lower Mg : Al molar ratios, OH^-, which has a higher charge density than Cl^- and NO_3^-, was more likely to interact with Mg and Al species to form HT structure, blocking the intercalation of Cl^- and NO_3^-. Furthermore, we showed that high concentrations of Cl^- and NO_3^- in solution regulated their intercalation into the HT interlayer. The high activity of Cl^- and NO_3^- in solution would facilitate the anions' reactions with Mg and Al species to form HTs, resulting in a high degree of anion intercalation into the interlayer of HTs.

Keywords. Hydrotalcite-like compound; synthesis process; intercalation; anion; concentration; pH.

1. Introduction

Hydrotalcite-like compounds (HTs) are layered, double hydroxides with anion-exchange properties (Miyata 1983). HTs are composed of brucite-like octahedral layers that are positively charged by the partial substitution of Al^{3+} for Mg^{2+}. This charge is neutralized by interlayer anions. Water molecules occupy the remaining spaces in the interlayer. The overall composition can be represented as $[Mg_{1-x}^{2+}Al_x^{3+}(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, where x denotes the Al : (Mg + Al) molar ratio ($0.20 \leqq x \leqq 0.33$) and A^{n-} the concentration of anions such as CO_3^{2-} or Cl^- (Ingram and Taylor 1967; Allmann 1968). HTs are used in wastewater treatment to remove contaminants such as iodate, benzoate, phosphate, and thiocyanate from aqueous solutions (Toraishi *et al* 2002; Cardoso *et al* 2003; Lazaridis 2003). Organically modified HTs can potentially absorb heavy metal ions and aromatic compounds from aqueous solutions (Kameda *et al* 2005a, b, 2006).

The anion-exchange properties of HTs are governed by the charge density of the anions, i.e. anions with higher charge density in solution will replace the anions with lower charge density in the interlayer of HTs (Miyata 1983). HTs are converted to magnesium–aluminum oxide

(Mg–Al oxide) by calcination at 450–800°C. The Mg–Al oxide is able to rehydrate and combine with anions in solution to reconstruct the HT structure. Mg–Al oxide combines more easily with anions that have a high charge density than with anions that have a low charge density (Sato *et al* 1986, 1993; Kameda *et al* 2003). Furthermore, Mg–Al oxide compounds with a low Mg : Al molar ratio combine with anions having high charge densities (Sato *et al* 1992, 1993; Kameda *et al* 2003), because decreasing the Mg : Al molar ratio increases the overall positive charge in the reconstructed HT, thus promoting the intercalation of anions with high charge density to compensate for the increased positive charge (Sato *et al* 1987). It is unclear whether the characteristics of anion intercalation during HT synthesis are similar to those of HT anion-exchange and HT reconstruction. Lukashin *et al* (1999) explored the correlation between the solution pH and the formation of HTs; however, they did not elucidate the effect of preparation conditions on anion intercalation during HT formation. To comprehensively understand anion intercalation into the interlayer of HTs, this effect must be examined.

In the present study, we prepared HTs intercalated with Cl^- and NO_3^- (Cl^-–HT and NO_3^-–HT, respectively). We examined the effects of pH after the reaction, the concentrations of Cl^- and NO_3^- in the solutions, and the Mg : Al molar ratio of the HTs in relation to anion intercalation into the interlayer during synthesis.

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2. Experimental

All reagents were purchased from Kanto Chemical (Tokyo, Japan). The two Mg–Al solutions ($[Mg^{2+} + Al^{3+}]$ = 0·04–2·5 M; Mg : Al = 2–4), i.e. Mg–Al chloride solution and Mg–Al nitrate solution, were prepared by dissolving $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$, as well as $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, in deionized water. The Mg–Al solution (100 mL), followed by deionized water (100 mL), was added at a rate of 5 mL/min to 200 mL of deionized water at 25°C with vigorous agitation. Simultaneously, 0·5 M NaOH was added to the solution to achieve the experimental pH, which ranged from 8 to 13. Deionized water was also added to give a total volume of 500 mL. The mixture was stirred continuously for 1 h at 60°C and then incubated at room temperature for 12 h. Nitrogen gas was bubbled into the solution throughout the coprecipitation to minimize the dissolved CO_2. After incubation, the resulting suspension was repeatedly washed with deionized water and collected by centrifugation. The precipitate was dried at 105°C for 24 h.

The Cl^-–HT and NO_3^-–HT were identified through X-ray diffraction (XRD) using Ni-filtered Cu-Kα radiation (40 kV, 20 mA). The Cl^-–HT and NO_3^-–HT were dissolved in 1 M HNO_3 and HCl, respectively and analysed for Mg^{2+} and Al^{3+} concentrations using inductively coupled plasma–atomic emission spectrometry (ICP–AES) and for Cl^- and NO_3^- concentrations using a Dionex QIC ion chromatograph and Dionex model AS4A column (eluent: 1·8 mM Na_2CO_3 and 1·7 mM $NaHCO_3$; flow rate: 1·5 mL min^{-1}; Dionex Corp., Sunnyvale, CA).

3. Results and discussion

The very important points for examining the results obtained in this study will be described as follows. In this case, the intercalation of anion into the interlayer of HT is not caused by the insertion of species as guest into the host compound. HTs are formed through the reactions of Mg^{2+}, $Al(OH)_4^-$, and anions, as expressed by (1), resulting in the intercalation of anion into the interlayer of HT.

$$(1 - x)Mg^{2+} + xAl(OH)_4^- + (2 - 4x)OH^- + xA^{n-} \rightarrow$$

$$[Mg_{1-x}Al_x(OH)_2](A^{n-})_{x/n}. \tag{1}$$
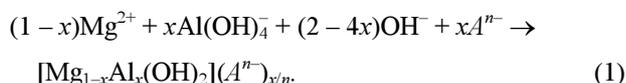
In this study, Mg–Al solution, together with NaOH (pH control), were added dropwise to deionized water. In the local environment where the droplets of NaOH were added, the pH was very high. This high pH resulted from the formation of $Al(OH)_4^-$ from $Al(OH)_3$, which formed in solution with the addition of Mg–Al. The $Al(OH)_4^-$ quickly reacted with Mg^{2+} and anions, leading to the formation of HTs.

Figure 1 shows the effect of 'pH after the reaction', which refers to the final pH of the mixture after 12 h at room temperature, on the molar ratio of Cl : Al and NO_3 : Al in

the precipitates. The terms $[Cl^-]_T$ and $[NO_3^-]_T$ (figure 1) are the theoretical concentrations of Cl^- or NO_3^-, respectively, in 500 mL of the prepared solution. The precipitates for all plots in figure 1 were confirmed to be Cl^-–HT or NO_3^-–HT by XRD. The molar ratio of Cl : Al or NO_3 : Al in the precipitates relates to the degree of intercalation of the anions into the interlayer of the HTs. At the $[Cl^-]_T$ of 0·11 M, the Cl : Al molar ratio in the Cl^-–HT remained at around 0·9, even when the pH after the reaction was increased. The diameter of Cl^- (3·62 Å) is larger than that of OH^- (2·80 Å) (Kapustinskii 1956; Sato *et al* 1986) and therefore, Cl^- has a lower charge density than OH^-. Thus we expected a preferential intercalation of OH^- into the HT interlayer. However, the prepared Cl^-–HT often contained Cl^- as the intercalated anion. This suggests Cl^-, rather than OH^-, reacted preferentially as the A^{n-} with Mg and Al species in the synthesis process of Cl^-–HT, according to (1). During Cl^-–HT preparation, a high Cl^- concentration was shown to prevent the reaction of OH^- with Mg and Al species, preventing the intercalation of OH^- into the HT interlayer. At the $[Cl^-]_T$ of 0·02 M, the Cl : Al molar ratio in the Cl^-–HT was around 0·9 until pH 11·5. For pH values higher than 11·5, the Cl : Al molar ratio decreased with increasing pH. With increasing OH^- concentration, OH^-, rather than Cl^-, preferentially reacted as the A^{n-} with Mg and Al species according to (1), intercalating into the HT interlayer. At the $[NO_3^-]_T$ of 0·11 M, the NO_3 : Al molar ratio in the NO_3^-–HT decreased with increasing pH after the reaction, in contrast to the behaviour of the $[Cl^-]_T$ of 0·11 M. Given that NO_3^- has a larger diameter than Cl^- (3·78 vs 3·62 Å,
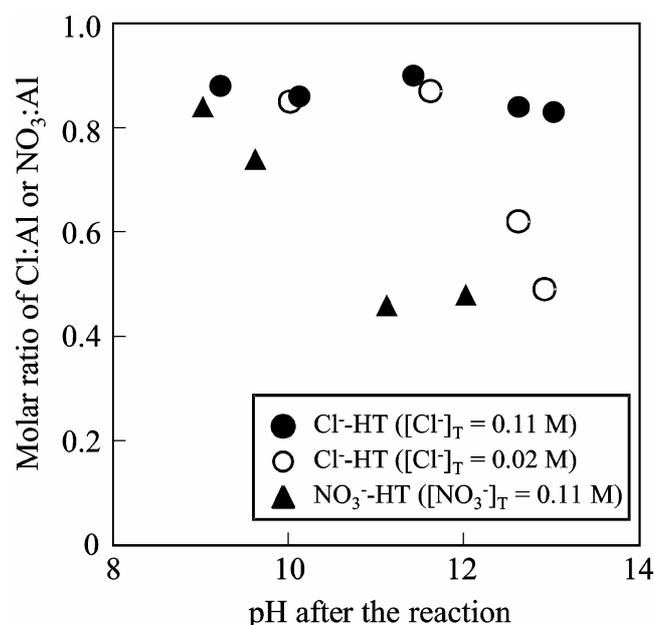

Figure 1. Effect of pH after the reaction on the molar ratio of Cl : Al or NO_3 : Al in the precipitates. (Initial Mg : Al molar ratio in solution: 4).

respectively (Kapustinskii 1956)), NO_3^- may be hard to be interposed between the brucite-like layers during HT formation. Accordingly OH^-, which has a smaller diameter, reacts more readily with Mg and Al species, preventing NO_3^- intercalation.

As shown in figure 1, the Cl : Al molar ratio in the Cl^-–HT decreased with increasing pH at low $[Cl^-]_T$, suggesting that the anion concentration has a significant effect on its intercalation into the HT interlayer. The relationships between the Cl^- and NO_3^- concentrations and the molar ratios of Cl : Al and NO_3 : Al in the precipitates are shown in figure 2. For the Cl^-–HT, the Cl : Al molar ratio was around 0·5 at the lowest $[Cl^-]_T$. With slight increase in the $[Cl^-]_T$, Cl : Al increased to greater than 0·8. Despite further increases in the $[Cl^-]_T$, the Cl : Al molar ratio remained between 0·7 and 0·9. For the NO_3^-–HT, the NO_3 : Al molar ratio was around 0·5 at the lowest $[NO_3^-]_T$, similar to the Cl^-–HT. With slight increase in the $[NO_3^-]_T$, NO_3 : Al increased to around 0·7. Further increases in the $[NO_3^-]_T$ did not change the NO_3 : Al molar ratio. For molar ratios of around 0·5 at the lowest $[Cl^-]_T$ or $[NO_3^-]_T$, OH^- accounted for the remaining intercalated anions. In addition to the hydroxyl groups contained in the HT host layers, OH^- is found to intercalate to a high degree during the formation of HTs. Although Cl^- and NO_3^- appeared to easily react with Mg and Al species and intercalated to high degrees into the HT interlayer with increasing $[Cl^-]_T$ and $[NO_3^-]_T$, the molar ratio of neither Cl : Al nor NO_3 : Al ever increased to 1, even at high $[Cl^-]_T$ or $[NO_3^-]_T$. Thus, OH^- could not be completely excluded. During the formation of HT host layer, some OH^- certainly exists in the

vicinity of the layer in solution. This proximity of the formed host layer to OH^- in solution dictates that OH^- will also function as an intercalation anion in all solution conditions.

The results shown in figures 1 and 2 illustrate that, when the solution concentrations of Cl^- and NO_3^- were similar, the Cl : Al molar ratio was greater than the NO_3 : Al molar ratio in the precipitate. This indicates that Cl^-, which has a higher charge density than NO_3^-, preferentially reacted with Mg and Al species to form a HT structure and that intercalation was governed by the charge density of the anion. This conclusion is in good agreement with the anion-exchange property of HTs and the reconstruction of HTs from Mg–Al oxide (Miyata 1983; Sato *et al* 1986, 1993; Kameda *et al* 2003). The solution concentration of Cl^- or NO_3^- controlled the degree of intercalation. Although Cl^- and NO_3^- have lower charge densities than OH^-, they more readily reacted with Mg and Al species because of their high activity in solution, resulting in the high degree of intercalation demonstrated in this study.

The relationship between the Mg : Al molar ratio and that of Cl : Al or NO_3 : Al in the precipitates is shown in figure 3, where the Mg : Al value reflects that of the precipitate. The molar ratios of both Cl : Al and NO_3 : Al were decreased at a lower Mg : Al molar ratio owing to the intercalation of OH^-. These results are in agreement with the properties for the reconstruction reaction of HTs from Mg–Al oxide (Sato *et al* 1992, 1993; Kameda *et al* 2003). For HT synthesis, larger amounts of negative charge, i.e. anions with a high charge density, are required to com-
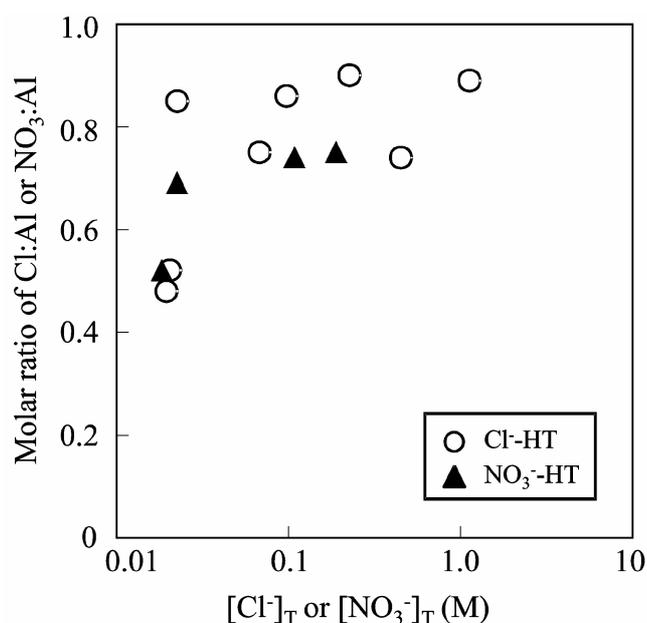

Figure 2. Effect of the concentration of Cl^- or NO_3^- on the molar ratio of Cl : Al or NO_3 : Al in the precipitates. (Initial pH: 10; Initial Mg : Al molar ratio in solution: 4).
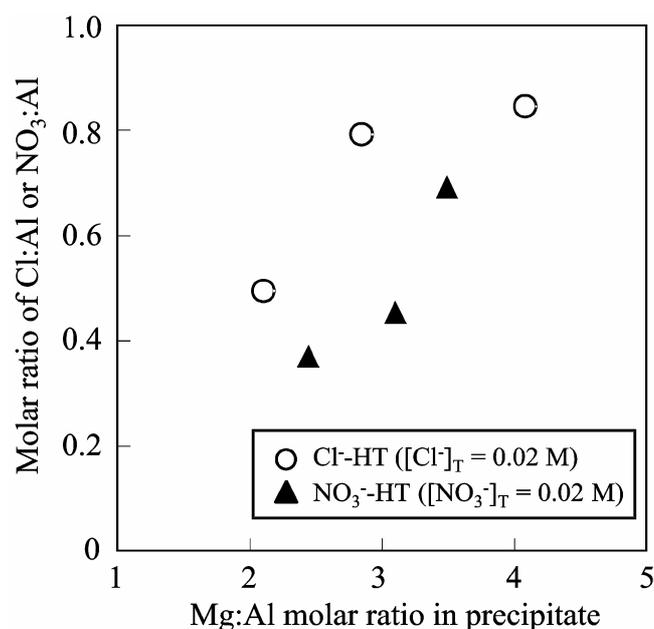

Figure 3. Effect of Mg : Al molar ratio on the molar ratio of Cl : Al or NO_3 : Al in the precipitates. (Initial pH: 10).

pensate for an increased percentage of Al^{3+} in a HT with a lower Mg : Al molar ratio, i.e. with a high value of x in (1).

Figure 4 shows the XRD patterns of precipitates prepared from a mixed solution of $MgCl_2$ and $AlCl_3$ at the initial Mg : Al molar ratios of (a) 2, (b) 3 and (c) 4. In this case, the initial Mg : Al molar ratios of 2, 3 and 4 correspond to the ratios of 2·1, 2·8 and 4·1 in precipitates, as shown in figure 3. It was confirmed that the XRD peaks of all precipitates were ascribed to hydrotalcite (JCPDS card
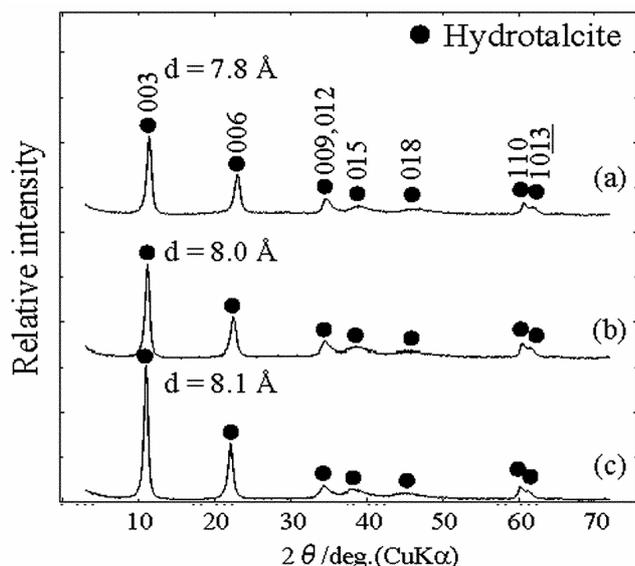

Figure 4. XRD patterns of precipitates prepared from a mixed solution of $MgCl_2$ and $AlCl_3$ at the initial Mg : Al molar ratios of (a) 2, (b) 3, and (c) 4. (Initial pH: 10; $[Cl^-]_T = 0.02$ M).
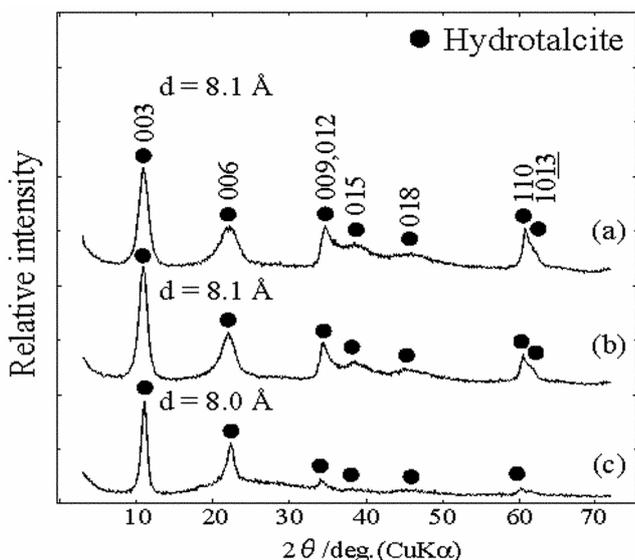

Figure 5. XRD patterns of precipitates prepared from a mixed solution of $Mg(NO_3)_2$ and $Al(NO_3)_3$ at the initial Mg : Al molar ratios of (a) 2, (b) 3, and (c) 4. (Initial pH: 10; $[NO_3^-]_T = 0.02$ M).

22-700), a hydroxycarbonate of magnesium and aluminum formulated as $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ that occurs in nature. The basal spacing, $d(003)$, of HT is composed of the brucite-like layer thickness (4·8 Å) and interlayer spacing. The basal spacing, shown in figure 4, is larger than the brucite-like layer thickness, indicating the presence of interlayer spacing, i.e. the intercalation of Cl^- and OH^- in the interlayer of HT. The basal spacing, $d(003)$, value of the precipitate increased with increasing initial Mg : Al molar ratio, i.e. the ratio in the precipitate. As shown in figure 3, the increase of Mg : Al molar ratio in precipitate results in the increase of Cl : Al molar ratio. Therefore, increase of the basal spacing is attributed to the high degree of intercalation of Cl^- in the interlayer of HT. In contrast, for the XRD patterns of NO_3^-–HTs (figure 5), the change of the initial Mg : Al molar ratio hardly led to the change of the basal spacing of precipitate. It was found that some degree of intercalation of NO_3^- in the interlayer of HT had less effect on the basal spacing.

4. Conclusions

This study examined the characteristics of anion intercalation into the interlayer of HTs during their synthesis. Our results agree with those for HT anion-exchange and HT reconstruction from Mg–Al oxide. Furthermore, we show that the concentrations of Cl^- and NO_3^- in solution regulate their intercalations into the interlayer of HTs.

(I) When the solution concentration of Cl^- is higher than that of OH^-, Cl^- preferentially reacts with Mg and Al species to form a HT structure, leading to the intercalation of Cl^- into the interlayer of the HT. Increasing the OH^- concentration in solution blocks the reaction of Cl^- with Mg and Al species. At similar concentrations of NO_3^- and Cl^-, the larger anionic diameter of NO_3^- leads to preferential Cl^- intercalation.

(II) At pH 10, Cl^- or NO_3^- at high concentrations reacts readily with Mg and Al, resulting in a high degree of intercalation of Cl^- or NO_3^- into the HT interlayer. The co-intercalation of OH^- cannot be excluded, because OH^- is required for the formation of the HT host layer.

(III) The preparation of HTs with lower Mg : Al molar ratios prevents the intercalation of Cl^- and NO_3^-, each of which has a lower charge density than OH^-.

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