Chem. Mater. **1997,** *9,* 417−419

Synthesis of a Low-Carbonate High-Charge Hydrotalcite-like Compound at Ambient Pressure and Atmosphere

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Received October 14, 1996
Revised Manuscript Received December 6, 1996

Hydrotalcite (HT), a clay mineral, is constructed of brucite-like layers $[Mg(OH)_2]$ in which substitution of Al^{3+} for Mg^{2+} at a mole ratio of 1:3 yields a net positive charge. This layer charge is compensated by exchangeable $CO_3{}^{2-}$ anions located (along with adsorbed water molecules) in the interlayer region. Numerous analogues of HT [i.e., "hydrotalcite-like" compounds (HTLCs)] have been synthesized with a variety of M^{2+}/M^{3+} combinations, M^{2+}/M^{3+} ratios, and interlayer anions.[1−10] The compositions of these HTLCs are usually expressed using a generalized form of the formula for a substituted-brucite, i.e., $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}(A^{m-}{}_{x/m})\cdot nH_2O$, where A is the interlayer charge-compensating anion, and x is the $M^{3+}/(M^{2+} + M^{3+})$ mole fraction.

Hydrotalcite and HTLCs have found use as anion exchangers, catalyst precursors, and catalyst supports.[1] For applications involving catalysis or ion exchange it is desirable that the HTLCs be CO_3-free and have high layer charge. The absence of $CO_3{}^{2-}$ is desirable because this anion is retained so strongly that access to the interlayer region by other ions and molecules is restricted and the effective anion-exchange capacity and reactive surface area are low. High layer charge (i.e., $x > 0.33$) is desirable because it increases the maximum possible exchange capacity. In addition to bulk-chemical analyses of phase-pure materials, layer charge can be estimated from the a_0 lattice parameter ($a_0 = 2d_{110}$ for a hexagonal unit cell) provided the ionic radii of the two cations in the hydroxide sheet (e.g., Mg^{2+} and Al^{3+}) are sufficiently different. To our knowledge, only one report of low-CO_3 HTLCs having a layer charge ≥ 0.33 has been published,[3] and these samples had between 15 and 33% of the interlayer sites occupied by $CO_3{}^{2-}$.

In this communication, we report a new synthetic route under *ambient pressure and atmosphere* leading to a high-charge HTLC *nearly free of inorganic C.* This HTLC, which we synthesized with an x value of 0.45, consists of Mg^{2+} and Al^{3+} as the structural cations and the terephthalate dianion $[C_6H_4(COO^-)_2$ or TA] as the compensating anion. Our synthesis procedure was modified from Drezdzon.[11] Briefly, 5.95 g (0.035 mol) of TA free-acid was added to a beaker containing 70 mL of deionized water. While stirring the TA solution, 15−17 mL (0.19−0.21 mol) of 50 wt % NaOH solution (freshly prepared and cooled to room temperature) was added dropwise to the beaker over a period of 30 min. To this, a solution containing 17.94 g (0.07 mol) of $Mg(NO_3)_2\cdot 6H_2O$ and 13.13 g (0.035 mol) of $Al(NO_3)_3\cdot 9H_2O$ in 56 mL of water was added dropwise while stirring the suspension vigorously at ambient temperature and pressure (the relative amounts of Mg and Al added correspond to a mole fraction, x, of 0.33). When the suspension pH decreased to 10, 25 mL of the suspension was removed. Titration with the Mg and Al solution continued. Another 25-mL aliquot was removed when the pH reached 8.5 and a third aliquot was taken at pH 7.5. Finally, addition of 1−2 mL of metal nitrate solution to the remaining suspension (~65 mL) resulted in a pH drop to about 6.5. The four suspensions were then placed in an oven and aged at 74 ± 1 °C overnight. After aging, the suspensions were washed by centrifugation with water until NO_3-free and dried at 100 °C overnight. These oven-dried samples are referred to as samples A (pH 10), B (pH 8.5), C (pH 7.5), and D (pH 6.5). All centrifugates (washings) were saved and analyzed for Mg and Al by inductively coupled plasma atomic-emission spectroscopy (ICP-AES). The oven-dried samples were analyzed for crystalline constituents by powder XRD (smear mounts on zero-background slides, Co Kα X-rays), for total and inorganic C, and for Mg and Al by ICP-AES after digestion in HNO_3.

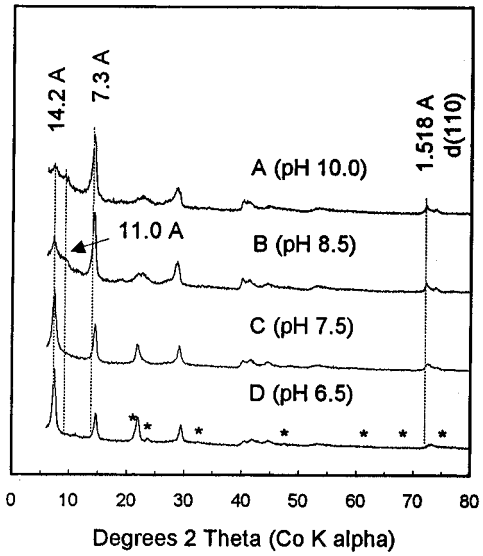

Figure 1. Powder-XRD patterns of the HTLCs obtained at pH 10, 8.5, 7.5, and 6.5. Asterisk denotes major peak positions for bayerite impurity in sample D.

Figure 1 shows powder XRD patterns of the oven-dried materials obtained at different pHs. For sample A (pH 10), the three peaks with d spacings corresponding to 14.2, 11.0, and 7.3 Å reveal information about the interlayer region. The 14.2-Å peak is likely due to interlayer TA anions with the long axis perpendicular to the hydroxide layers.[11] The relatively sharp intense

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S0897-4756(96)00536-4 CCC: $14.00

Table 1. Characteristics of HTLCs Synthesized

sample	d_{003}[a] (Å)	a_0[a] (Å)	x[b]	anion distribution[c] (mol %) TA	CO_3^{2-}	HCO_3^-	charge balance[d]
A (pH 10.0)	14.2, 11.0, 7.3	3.036	0.34	69	13	18	1.00
B (pH 8.5)	14.2, 11.0, 7.3	3.038	0.34	76	0	24	1.02
C (pH 7.5)	14.1	3.024	0.37	95	0	5	0.96
D (pH 6.5)	13.9	3.002	0.45	98	0	2	1.00
			0.47[e]				0.96[e]

[a] Assumes 3-layer polytype; $a_0 = 2d_{110}$. [b] x of starting solution was 0.33. [c] Based on total C and inorganic C analyses; CO_3^{2-} and HCO_3^- fractions assigned to fit x values. [d] Sum of equivalents of TA, CO_3^{2-}, and HCO_3^- divided by charge from Al^{3+} substitution (all calculated on a unit-cell basis). [e] Nominal values assuming no bayerite present.

peak at 7.3 Å is probably a mixture of closely spaced reflections from two or three different sources. It is close to the d_{003} peak observed in CO_3–HTLCs at 7.65 Å[10] and thus could represent reflections from interlayers containing only C_{inorg} anions (i.e., CO_3^{2-} and HCO_3^-). More likely it represents reflections from interlayers containing a mixture of TA anions oriented parallel to the hydroxide layers and C_{inorg} anions. Last, it could contain a small contribution from the second-order reflection of the TA peak at 14.2 Å. The nature of the 11.0 Å peak is less certain. This peak could be due to interlayer TA anions oriented at an oblique angle to the hydroxide sheet, or it could represent random interstratification of 14.2-Å TA layers and 7.6-Å TA/C_{inorg} layers.

Bulk analysis for total C and C_{inorg} was used to estimate the anionic composition of the interlayer region (Table 1). These results show that sample A contained both TA and C_{inorg} at a ratio of about 2:1. Analyses by Fourier transform infrared spectroscopy and ^{13}C cross-polarization magic-angle-spinning nuclear magnetic resonance spectrometry (data not shown) confirmed these results. Thus, even though no C_{inorg} was intentionally added to the system and excess TA was present during the precipitation process, substantial amounts of presumably atmospheric-derived C_{inorg} were found in the HTLC we synthesized at pH 10.

Bulk analysis of sample A for Mg and Al yielded a value for x nearly identical with that of the starting solution (Table 1). The sum of the charges associated with the exchangeable divalent anions (i.e., assuming only CO_3^{2-} and TA) was about 10% greater than the layer charge derived from the Al^{3+} content. With the assumption that HCO_3^- is also present in the interlayer, a more realistic charge balance of 1.00 was obtained (Table 1). Last, the a_0 value obtained from the d_{110} peak located at about 72° 2θ, which is sensitive to x values, is comparable to the values reported for CO_3-HTLCs with similar degrees of Al substitution.[12] These results suggest that Al and Mg coprecipitated to yield a single phase as would be expected from the comparable solubilities of $Mg(OH)_2$ and $Al(OH)_3$ at pH 10.[13]

Sample B (pH 8.5) was similar to sample A, except for an increase in the intensity of the 14.2-Å TA peak, a corresponding decrease in the amount of C_{inorg} in the interlayer, and a higher anion-charge excess (Figure 1 and Table 1). The decrease in C_{inorg} and the size of the anion-charge excess suggest that all the C_{inorg} is HCO_3^-, which is held much less strongly than the divalent CO_3^{2-} or TA anions. Such a shift to HCO_3^- would be driven by the decrease in solution-phase CO_3^{2-} (i.e., the conversion of CO_3^{2-} to HCO_3^-) as the pH decreases.[14]

Sample C (pH 7.5), on the other hand, was substantially different from samples A and B. The XRD pattern (Figure 1) shows a strong TA peak at 14.1 Å with three higher-order reflections. The peak at 11.0 Å in patterns for samples A and B is absent, and that at 7.3 Å has "shifted" to 7.1 Å, indicating that it is primarily a second-order reflection of the 14.1-Å TA peak. These results suggest that TA oriented perpendicularly to the hydroxide sheet is the dominant interlayer anion. Further evidence for this is given by the bulk carbon data (Table 1), which show that 95% of the interlayer C is in the form of TA and only 5% is present as C_{inorg} (presumably all HCO_3^-). The bulk-chemical data show an increase in the x value to 0.37 and a corresponding decrease is seen in the a_0 value obtained from the d_{110} peak (Table 1). Charge-balance data (i.e., TA and HCO_3^- relative to x) show a slight anion "deficit", which could be due to a separate Al phase or a small quantity of NO_3^- (not determined) present in the sample (Table 1). The XRD pattern, however, suggests that the sample is phase-pure (Figure 1). The slight decrease in the d spacing of the TA XRD peak (i.e., from 14.2 to 14.1 Å) may be a result of the higher layer charge exhibited by this sample.

Sample D (pH 6.5) continues the trends set by samples B and C. It is essentially free of C_{inorg}, has a nominal x value of 0.47 and an a_0 value of 3.002 Å (Table 1). This a_0 value is lower than the 3.016-Å value reported[3] for the Mg–Al–$Fe(CN)_6$/CO_3 HTLC with similar x and suggests that the nature of the interlayer anions also contributes to the extent of lattice compression. As with sample C, the amounts of TA and HCO_3^- present correspond to 96% of the nominal layer charge, x, calculated from bulk-chemical analyses (Table 1). A small XRD peak at 4.36 Å and the additional intensity of the peak at 4.71 Å (relative to sample C), however, suggests the presence of a small amount of Al in a separate bayerite phase (Figure 1). Assuming that the true value is given by the anion charge, a value of 0.45 for x is obtained (Table 1). Finally, the first-order TA peak has a d spacing of 13.9 Å, thus continuing the trend for compression along the c axis with higher layer charge. To our knowledge, sample D represents the first example of an essentially C_{inorg}-free, high-charge HTLC.

Plots of x vs a_0 and c_0 (i.e., $3d_{003}$) for the four HTLCs we synthesized (Figure 2) show that both cell dimensions decrease linearly with increasing x and that Vegard's law is valid for these samples. The slope of

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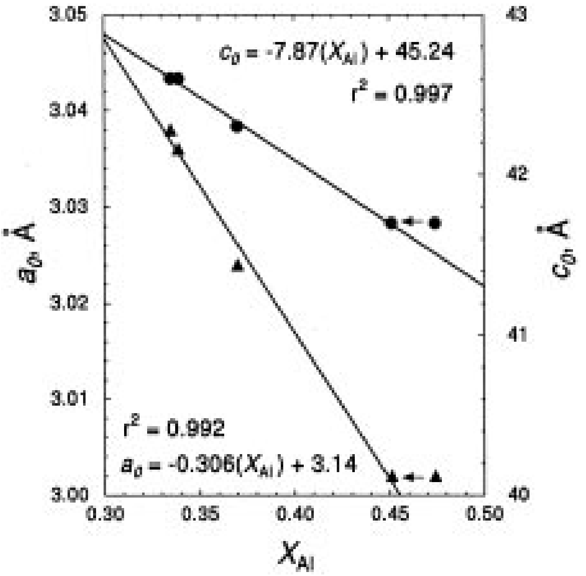

Figure 2. Relationship between a_0, c_0, and x for the HTLCs synthesized. Values for c_0 calculated using TA peaks only and assuming a three-layer polytype, i.e., $c_0 = 3d_{003}$. Arrows denote correction of nominal x values for bayerite impurity in sample D.

the a_0 plot is about 20% steeper than that reported by Miyata,[12] but the y intercept (3.14 Å) is closer to the theoretical value for brucite (3.147 Å).[15] By fixing a_0 for brucite at 3.147 and incorporating the results for samples A, B, and C, Vegard's law can be used to estimate a value of x for sample D. A value of 0.444 is obtained, which is very close to the value estimated earlier on the basis of charge balance.

Elemental analysis of the washings (data not shown) shows a net increase in Mg^{2+} concentration and a net decrease in Al^{3+} concentration in the washings from sample D (pH 6.5) relative to those for sample C (pH 7.5). These results are consonant with changes in the relative solubilities of the end-member hydroxides as pH decreases. As they are coupled with changes in the a_0 parameter, it seems likely that they correspond primarily to homogeneous changes in the structure of the HTLC rather than to simple dissolution of the HTLC and precipitation of an end-member $Al(OH)_3$ phase. Further support for this hypothesis comes from preliminary elemental analysis data (not shown) collected by transmission electron microscopy showing that sample D is compositionally homogeneous on at least a 20-Å scale. Similar losses of Mg^{2+} from CO_3−HTLCs treated by acidic solutions have been noted by Kooli et al.[16] and, together with our data, suggest that the composition of the hydroxide sheet is labile to some extent. The labile nature of the hydroxide sheet, however, depends on the interlayer anion. With CO_3^{2-}, it seems that the maximum x attainable is 0.33 (data not shown), whereas, with TA, values approaching 0.5 are possible. This result adds new flexibility to our ability to synthesize HTLCs and has important implications for synthesis of other layered compounds with oxide or hydroxide structures.

Acknowledgment. Work funded by the Laboratory-Directed Research and Development program of the Pacific Northwest National Laboratory (PNNL) as part of the support for the Environmental Molecular Sciences Laboratory project. Funding for R.K.K. was facilitated by Associated Western Universities, Northwest Division. PNNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

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