CRYSTALLIZATION OF LAYERED DOUBLE HYDROXIDES BY ULTRASOUND AND THE EFFECT OF CRYSTAL QUALITY ON THEIR SURFACE PROPERTIES

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Abstract—The ultrasound technique was applied to the synthesis of layered double hydroxides. The use of ultrasound in the synthesis of these compounds was studied in terms of its effect on their crystal qualities and surface properties. The crystal qualities of the compounds synthesized with ultrasound were compared with those of compounds synthesized without ultrasound to elucidate the effect of the ultrasound on the synthesis. The effect of crystal quality (crystallite size) on the adsorption behavior of humic substances was examined. The compounds synthesized under ultrasonic conditions showed a larger crystallite size and a larger adsorption capacity for humic substances than those synthesized without ultrasonic treatment. The degree of adsorption correlated well with crystal quality.

Key Words—Crystal Quality, Humic Acids, Hydrotalcite, Layered Double Hydroxide, Pyroaurite, Synthesis, Ultrasound, Water Treatment.

INTRODUCTION

Layered double hydroxides (LDHs) such as hydrotalcite and hydrotalcite-like compounds $M_x^{2+}M_y^{3+}(OH)_{2(x+y)}A_{y/n}^{n-} \cdot mH_2O$ (where M^{2+} is a divalent metal ion, M^{3+} is a trivalent metal ion, and A^{n-} is an intercalated anion) are well known as inorganic anion exchangers. Because of their large ion-exchange capacity and structural thermal stability, which are difficult to achieve simultaneously in conventional anion-exchange resins, these compounds are used in many industrial processes, *e.g.* for polymer synthesis, and as coatings that are halogen scavengers and neutralizers (Cavani *et al.*, 1991).

These compounds are commonly synthesized by precipitation from a parent salt solution of divalent and trivalent metal ions, followed by ageing at an elevated temperature (hydrothermal treatment) in the laboratory. The conditions of synthesis, such as solution pH, temperature and metal composition, along with physicochemical structure of the compounds have been studied extensively by many researchers (Allmann *et al.*, 1970; Bellotto *et al.*, 1996; Cavani *et al.*, 1991; Feiknecht, 1942; Kukkadapu *et al.*, 1997; Labajos *et al.*, 1992; Miyata 1980, 1983; Reichle *et al.*, 1986; Taylor, 1969).

Recently, evaluations of the effectiveness of hydrotalcite and the hydrotalcite-like compounds as insoluble adsorbents for the removal of humic substances from water were reported (Amin and Jayson, 1996; Seida and Nakano, 2000). Humic substances are known to constitute a major fraction of organic matter in natural waters and can be difficult to remove with common adsorbents used for drinking water treatment. Hydrotalcite and hydrotalcite-like compounds are believed to remove humic substances by ion exchange in an inner layer and adsorption on their surface (Amin and Jayson, 1996). The effect of metal composition of the hydrotalcite and hydrotalcite-like compounds on adsorption capacities for humic substances was reported by Seida and Nakano (2000). They also found that the crystal quality of hydrotalcite affected its surface properties. The effect of the crystal quality of hydrotalcite on its adsorption capacity for humic substances is not well understood. A simple method for synthesis of a highly crystalline form is also needed.

Ultrasound has attracted much attention in the synthesis of inorganic and organic materials, owing to its specific effects on material processing. It is widely recognized that the effects caused by ultrasound can be mainly attributed to: (1) rapid movement of fluids due to variation of sonic pressure, which accelerates mass transfer; (2) formation and collapse of microbubbles (cavitation), creating localized high-temperature and high-pressure conditions; and (3) micro-streaming, in which a large amount of vibrational energy is applied to small volumes with little heating (Mason, 1990).

Several studies show that sonication enhances and/or alters the dissolution process, chemical reactions, and nucleation and growth of precipitates in some inorganic powder syntheses (Fang *et al.*, 1992; Jiashan *et al.*, 1993; Enomoto *et al.*, 1994). Kooli *et al.* (1997) used ultrasound to promote anion exchange in LDHs. They noted the possibility that ultrasound may improve the crystal quality of the LDH, although they did not study its effects extensively.

In this paper, we describe an ultrasound technique that was applied to improve simply and rapidly the crystal quality of LDHs. A rapid synthesis of highly-

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Table 1. Experimental conditions (HT: without ultrasound, US: with ultrasound).

Sample no.	M(II)/M(III)$_{ini}$ (mol/mol)	Method	Treatment time (min)	Treatment Temp. (K)	Initial solution pH	Applied power of ultrasound (W)	Additional treatment
1	Mg/Al = 2	HT	10	363	10		Agitation
2	Mg/Al = 2	HT	60	363	10		Agitation
3	Mg/Al = 2	HT	600	363	10		Agitation
4	Mg/Al = 2	US	5		10	190	
5	Mg/Al = 2	US	30		10	210	
6	Mg/Al = 2	US	60		10	225	
7	Mg/Al = 3	HT	10	363	10		
8	Mg/Al = 3	HT	60	363	10		
9	Mg/Al = 3	HT	600	363	10		
10	Mg/Al = 3	HT	10	363	10		Agitation
11	Mg/Al = 3	HT	60	363	10		Agitation
12	Mg/Al = 3	HT	600	363	10		Agitation
13	Mg/Al = 3	US	15		10	67	
14	Mg/Al = 3	US	30		10	71	
15	Mg/Al = 3	US	60		10	76	
16	Mg/Al = 3	US	5		10	190	
17	Mg/Al = 3	US	15		10	198	
18	Mg/Al = 3	US	30		10	210	
19	Mg/Al = 3	US	30		10	213	Cooling
20	Mg/Al = 3	US	45		10	217	
21	Mg/Al = 3	US	60		10	225	
22	Mg/Al = 3	US	10		10	285	
23	Mg/Al = 3	US	30		10	290	
24	Mg/Fe = 3	HT	60	363	10		Agitation
25	Mg/Fe = 3	HT	15	363	10		Agitation
26	Mg/Fe = 3	HT	30	363	10		Agitation
27	Mg/Fe = 3	US	5		10	190	
28	Mg/Fe = 3	US	30		10	210	
29	Mg/Fe = 3	US	60		10	225	

crystallized LDHs was performed under ultrasonic conditions. The effect of ultrasound on the synthesis and/or crystal quality of LDHs was studied as a function of intercalating anions, crystallite size, specific surface area and surface properties of the compounds. The study of the surface properties of the LDHs was based on the adsorption of humic substance onto the compounds with a view to deriving a relationship between crystallite size of the compounds and the efficiency with which they removed humic substances.

EXPERIMENTAL

Preparation of reaction mixtures

The reaction mixtures were prepared based on the procedure reported by Reichle (1986). Magnesium nitrate, $Mg(NO_3)_2.6H_2O$ and aluminum nitrate, $Al(NO_3)_3.6H_2O$ (or magnesium chloride, $MgCl_2.6H_2O$, and ferric chloride, $FeCl_3.6H_2O$) were dissolved in 200 mL of distilled water. The mole ratio of the divalent to trivalent metal ions (*i.e.* Mg(II)/M(III)) in these solutions was set to 2 or 3 and the total concentration of metal ions was set to 0.1 M. Next, an aqueous solution of 10 wt.% NaOH was added dropwise into the solutions with vigorous stirring under N_2 atmosphere until the pH reached 10.0. A 25 wt.% NH_3 solution was added

instead of NaOH in the case of those solutions containing Fe. The reaction mixtures were stirred thoroughly for 4 h at room temperature, without further pH control, under a N_2 atmosphere. Reaction mixtures prepared in this manner were used as the starting slurries for the following syntheses of LDHs.

Syntheses with ultrasound. Sonic energy was provided by an ultrasonicator (Branson Sonic Power Co., Model 450D) which generates 20 kHz ultrasound waves. A sonic probe made of Ti (10 mm in diameter and 100 mm long) was dipped in 50 mL of reaction mixture. Reaction mixtures were exposed to ultrasound for periods ranging from 5 to 60 min under normal atmospheric conditions without any other experimental controls. The ultrasound was applied to the reaction mixtures at three different output levels (Level 1 (100 W), Level 2 (250 W) and Level 3 (300 W)). Due to the input of sonic energy, the temperature of the reaction mixtures typically increased to ~360 K within 30 min of the onset of ultrasonication. As heating is known to improve LDH crystal quality, a synthesis using ultrasound but also cooling the reaction mixture was also conducted to reduce the reaction temperature effect on crystallization. The reaction mixture was cooled in an ice water bath during ultrasound treatment. The time-averaged ultrasound
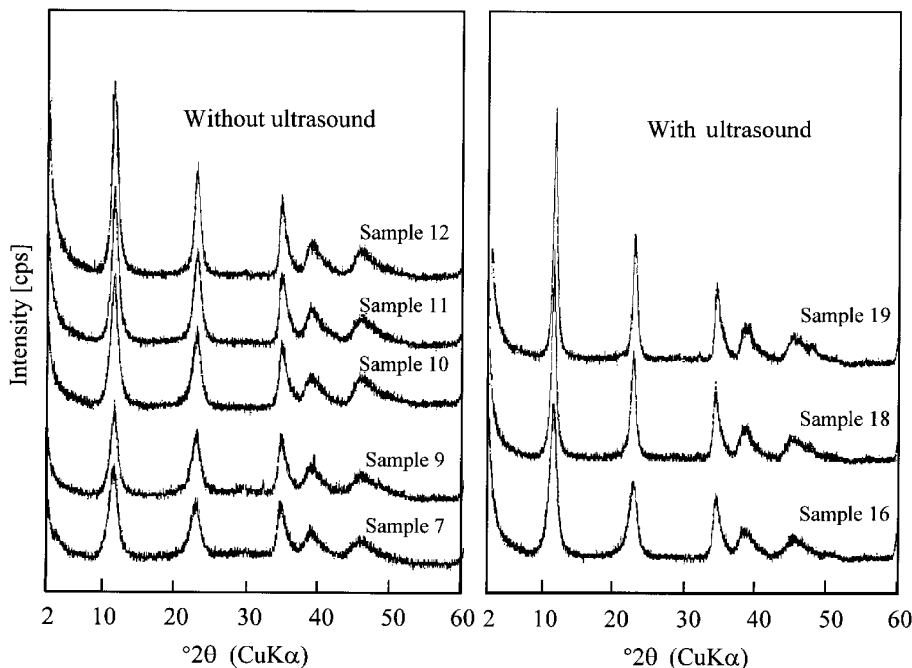
Figure 1. XRD patterns of the compounds synthesized with and without ultrasound.

energy added to the reaction mixtures was calculated from a load-power output chart.

Syntheses without ultrasound (conventional method). Some reaction mixtures were not treated with ultrasound. As ultrasound heats the reaction mixture during the synthesis, other syntheses were conducted without ultrasound. Ultrasound also causes a vigorous mixing of the reaction mixtures. Syntheses with, and without, vigorous stirring of the reaction mixtures were also conducted. In these syntheses, 50 mL of reaction mixtures were heated to 363 K for periods ranging from 10 min to 10 h in a temperature-controlled water bath.

All synthesized compounds were washed with a large amount of distilled water to remove residual chemicals, and then dried at 353 K in an electric oven for 24 h. The dried compounds were crushed with an agate mortar to a particle size of <250 μm. The conditions of synthesis are also listed in Table 1, where the synthesized LDH compounds are abbreviated to $M(II)/M(III)_{ini} = x$, based on their respective constituent metal ions and the molar ratio (x) used in the preparation stage of the starting slurry.

Characterization

Powder X-ray diffraction (XRD) patterns of the synthesized compounds were obtained with an X-ray diffractometer (Rigaku Co. Ltd, RAD-R) using CuKα radiation. The crystallite sizes along the c axis of the compounds were evaluated from the full width at half maximum (FWHM) of the 003 reflection in the XRD pattern. The FWHM of the reflection peaks was calculated using software installed in the instrument. A smaller FWHM means a larger crystallite size. Crystallite sizes were estimated using Scherrer's equation (Cullity, 1956) based on the FWHM of the 003 reflection peak. The intercalating anions of the compounds were elucidated using thermogravimetry (TG) and differential thermal analysis (DTA) with simultaneous mass spectral analysis (MASS), TG/DTA-MASS (Falconer and Schwarz, 1983). The TG analysis was performed under a N_2 atmosphere at a heating rate of 3 K/min. The gases evolved during the heating were monitored by a mass spectrometer (Seiko Instrument Co. Ltd, SSC5200). The anions intercalated in the synthesized compounds were measured in the evolved gases. The specific surface areas of the synthesized compounds were measured by the BET method with nitrogen after drying at 423 K for 5 h.

Surface property of the compounds

A humic acid sodium salt purchased from Aldrich was used as an adsorbate for the evaluation of surface properties of the synthesized compounds. The humic acid was used as supplied. Each of a set of the compounds (weighing 0.05 g), synthesized with and without ultrasound, was placed into 20 mL of a 100 mg L^{-1} solution of the humic acid. The mixture was kept at room temperature with shaking for 7 days in order to attain adsorptive equilibrium. The residual concentration of humic substances in the solution after 1 and 7 days was measured by ultraviolet spectrophotometer (Hitachi Co. Ltd, UV-2000, wavelength 280 nm)
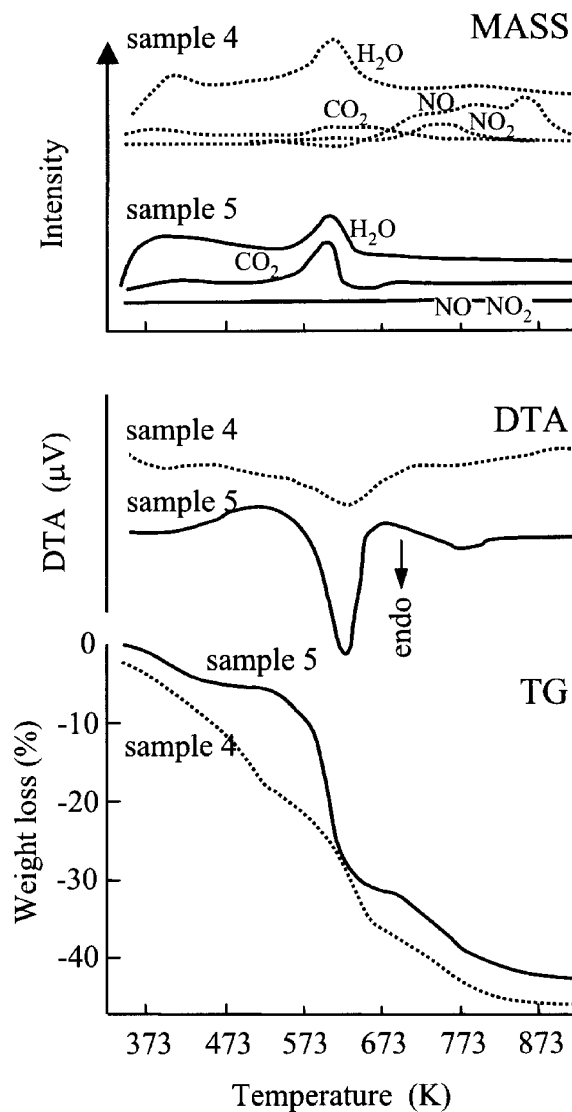
Figure 2. Thermal behavior (TG/DTA charts) of the ultrasonically synthesized compounds with Mg/Al = 2 and gases that are released during the thermal decomposition of the compounds (MASS chart).

after filtering the insoluble LDH compound from solution using a microporous membrane (pore diameter 0.45 μm). The fraction of the total added humic acid adsorbed from solution by the LDH was calculated by mass balance.

RESULTS

Intercalates during the synthesis

All the synthesized compounds showed the typical diffraction pattern of a hydrotalcite, e.g. in Figure 1 where compounds were synthesized with and without ultrasound. Table 2 shows the d_{003} value of the compounds (Mg/Al = 2) synthesized with (US), and

without (HT), ultrasound (Samples 1−6). The d_{003} value of the compounds decreased from 0.88 nm to 0.77 nm with synthesis time, and this occurred faster in the ultrasonically synthesized compound. The changes in d_{003} value should be induced by an exchange of the intercalated anion between NO_3^- and CO_3^{2-} ions. It is noted that the reported d_{003} values are 0.879 nm for NO_3^- and 0.765 nm for CO_3^{2-}, respectively (Cavani *et al.*, 1991). Figure 2 shows the TG/DTA-MASS diagrams of the compounds synthesized with ultrasound (Mg/Al = 2, Samples 4 and 5). The dominant gases released during the decomposition of the layered structure of the compound which occurs along with both maximum weight loss (TG) and maximum endothermic peak (DTA) at ~723 K, were NO_x and water vapor, H_2O, in the compound treated ultrasonically for 5 min (sample 4). The dominant gases were CO_2 and H_2O in the compound treated for 30 min (sample 5). These results, along with the results shown in Table 2 prove that the intercalating NO_3^- ions were exchanged rapidly for CO_3^{2-} ions during the ultrasonic treatment.

Crystal quality of the compounds

Figure 3 shows the FWHM of the 003 reflection as the function of treatment time for the series of compounds with a mole ratio of Mg/Al = 3 (Samples 7−23). All these compounds had d_{003} values of 0.77 nm, which indicates the formation of compounds with CO_3^{2-} ions as the intercalated anion. In the compounds synthesized without ultrasound, the crystallite size increased in those compounds when treated over a long period (600 min). The crystallite size of the compounds treated without stirring showed little increase, even for longer treatment times (600 min). The compounds synthesized in the presence of ultrasound showed a faster decrease in the width of the 003 reflections regardless of the treatment, in comparison with those synthesized without ultrasound. The crystallite size of the compound increased more rapidly in the presence of ultrasound. A larger ultrasound application power and longer treatment time resulted in an increase in crystallite size. The crystallite size of the compound synthesized in the presence of ultrasound, but with slurry cooling as well, was also much larger than those synthesized without ultrasound (sample 19). However, the crystallite size of the cooled compound was some-

Table 2. d_{003} value of the compounds with Mg/Al = 2.

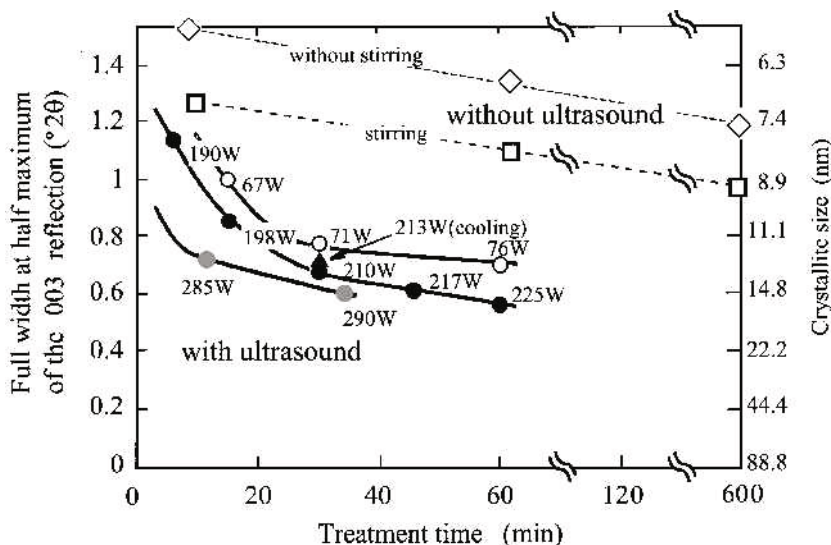| Sample no.	Synthetic method	Treatment time (min)	d_{003} (nm)
1	HT	10	0.84
2	HT	60	0.79
3	HT	600	0.77
4	US	5	0.82
5	US	30	0.78
6	US	60	0.77

Figure 3. Relationship between the treatment time and the full width at half maximum of the 003 reflection and crystallite size. The numerical values in the Figure show the application power of the ultrasound. (Without ultrasound: ◇; without stirring: □; with stirring, with ultrasound: ○; level 1: ●; level 2: ▲; level 2 with cooling: ⬤).

what less than that synthesized in the absence of slurry cooling but with ultrasound (sample 18).

The effect of ultrasound on the synthesis of LDHs was confirmed in a synthesis of pyroaurite-type compounds $(Mg_6^{2+}Fe_2^{3+}(OH)_{16}(CO_3^{2-})_2 \cdot mH_2O)$. Figure 4 shows the FWHM of the 003 reflection of the synthesized compounds as a function of treatment time (samples 24−29). The crystallite size increased more rapidly with the use of ultrasound than without, as shown by the FWHM of the 003 reflection in Figure 4. Together, these data illustrate the effectiveness of ultrasound in bringing about a simple and rapid synthesis of LDHs under ambient conditions.

Specific surface area

The specific surface area for the series of compounds with a mole ratio of Mg/Al = 3 and common treatment times are shown in Table 3 (samples 10−12, 16, 18, 21). The specific surface area of the compounds increased with increased treatment time in compounds synthesized, both with and without ultrasound. A faster increase in the surface area was observed in those compounds synthesized in the presence of ultrasound.

Figure 5 shows the relationship between the specific surface areas and the FWHM of the 003 reflections for the series of the compounds. The specific surface areas of the compounds increased with an increase of the crystallite size (with a decrease in the FWHM of the 003 reflections).

Effect of crystallite size on the surface property of the compounds

Figure 6 shows the relationship between the FWHM of the 003 reflections and the fractions of humic acid removed from the solution by the compounds (Mg/Al=3, samples 10−12, 16−18, 20, 21). The degree of removed humic acid correlated well with the width of the 003 reflection for both compounds. These results suggest that the adsorption capacity of these compounds increased with increasing crystallite size. This is also consistent with the increase in specific surface area with increasing crystallite size, as shown in Figure 5. A greater degree of removal of humic acid after 1 day was achieved with those compounds synthesized in the absence of ultrasound, than by those synthesized in the presence of ultrasound for an equivalent common width at half

Table 3. The Mg/Al ratio, specific surface area and crystallite size of the synthesized compounds as a function of synthesis conditions.

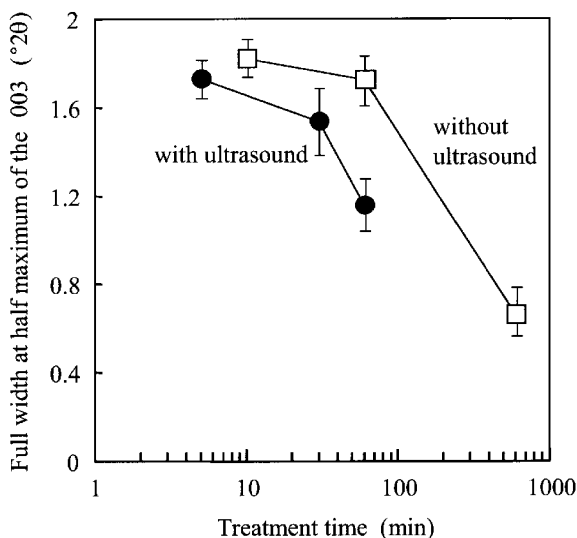| Sample No.	Synthetic method	Treatment time (min)	Specific surface area (m²/g)	Crystallite size (nm)
10	HT	10	2.2	7.2
11	HT	60	8.0	7.9
12	HT	600	65.5	9.6
16	US	5	48.4	7.8
18	US	30	69.9	10.3
21	US	60	71.7	15.5

Figure 4. Relationship between the treatment time and the full width at half maximum of the 003 reflection for pyroaurite-like compounds.

maximum of the 003 reflection. A slight increase in pH of the solutions was observed as shown by the pH values given beside each symbol (initial pH of the solution was 6.8). The pH increased depending on the decrease in the crystallite size of the compounds used. The effect of the crystallite size of the LDH compounds on the solution pH was also confirmed in the previous study (Seida and Nakano, 2001). A larger change of the pH was observed for the solutions with compounds synthesized in the absence of ultrasound than for those with the compounds synthesized in the presence of ultrasound. Adsorption capacity for humic acid of all compounds correlated well with their crystallite size after 7 days.

DISCUSSION

It was observed that the application of ultrasound caused vigorous mixing of the bulk of the reaction mixture at the beginning of its application. This disappeared after ~10 min of ultrasound due to gelation of the reaction mixture. Regardless, the compounds synthesized over a longer period of ultrasonic treatment showed further improvement in the crystallite size as shown in Figures 3 and 4. Ultrasonic energy must have still propagated into the reaction mixture after the disappearance of bulk mixing, as also confirmed by the averaged applied ultrasound power shown in Table 1. Vigorous mixing of the reaction mixture during gelation would have significantly affected the further crystallization of the LDH compounds after gelation. The vigorous mixing induced by ultrasound probably produces an homogeneous dispersion of the reaction mixture that results in rapid crystallization. The effects on crystallite size in those compounds synthesized with, and without, vigorous stirring, but without the applica-
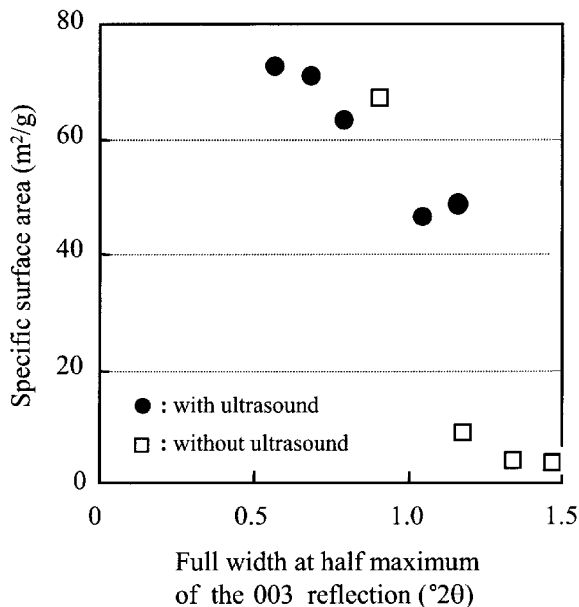

Figure 5. Relationship between the full width at half maximum of the 003 reflection and the specific surface area.

tion of ultrasound, support this assumption. Temperature and pressure are the key factors in the use of hydrothermal treatments to enhance both dissolution of hydroxide precipitates, and their subsequent crystal growth (Tomonaga, 1987). The dissolution-recrystallization process of hydroxide precipitates that constitute the LDH would also be enhanced under the higher temperature and pressure conditions used in conventional hydrothermal syntheses of LDHs. The compound synthesized with ultrasound showed a higher crystal quality even with synthesis performed under cooled conditions. From the effects that the ultrasound potentially produces along with the results shown in the previous sections, it is considered that: (1) vigorous
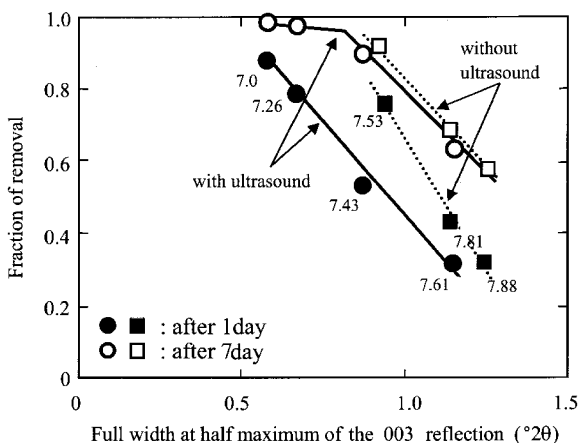

Figure 6. Relationship between the full width at half maximum of the 003 reflection and the fraction of humic substance removal. The numerical values beside each symbol show final solution pH.

mixing of the reaction mixture by ultrasound during its gelation causes homogeneous dispersion of metal ions; (2) acceleration of ion exchange processes induced by the ultrasound enhances production of the carbonate-type LDH phase which crystallizes more readily than the nitrate-type LDH because the LDH preferentially adsorbs carbonate ions (Miyata, 1983); and (3) cavitation caused by ultrasound accelerates the dissolution-crystallization processes. These effects would all result in a larger crystallite size of the compound.

The humic acids would be difficult to adsorb in the inner layer gallery of the compound due to its larger molecular size (MW = 2000–50000 Dalton). From the results shown in Figure 6 and Table 3, the removal of humic acid by these compounds was inferred to occur through adsorption to the surfaces of the compounds. The compounds synthesized without ultrasound, however, showed faster removal of humic acid than the compounds synthesized with ultrasound, in spite of their small surface area, for a common width at half maximum of their 003 reflections at 1 day in Figure 6.

A slight increase of solution pH may be induced by a slight dissolution of the compound due to a buffering pH effect of the compound. Hydrotalcite is known to buffer solution pH to a weak basic region through its slight dissolution (Seida and Nakano, 2002). The dissolution depends on the crystal quality and metal composition of the compound (Seida and Nakano, 2001). Both Mg and Al were detected in the solutions by the ICP analysis of the solutions, the amount being almost stoichiometrically equivalent to the increase in solution pH on the basis of the hydroxides that are produced by Mg and Al dissolution (Seida and Nakano, 2000). The release of metal cations and/or their hydroxides may be enhanced in those compounds with a low Mg/Al ratio. The removal of humic acid in the LDH compound with the smaller Mg/Al ratio, smaller crystallite size and specific surface area, may be enhanced through coagulation and/or precipitation by the cations and hydroxides produced from the dissolution of the LDH compound. Further study is required to clarify the exact mechanism of the humic acid removal.

The crystallite size of these LDH compounds can be used to estimate their surface properties.

CONCLUSIONS

Ultrasound was found to be an effective tool in the synthesis of LDHs, even with only a few minutes application. It enables a simple and rapid synthesis of these compounds under ambient conditions.

The crystallite size of these compounds is increased by a greater duration and power of ultrasound application.

The adsorption capacity of these compounds for humic acids depends on the crystal quality of the compound and can be estimated by the crystallite size of the compound.

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