

SYNTHESIS OF Cu-CONTAINING LAYERED DOUBLE HYDROXIDES WITH A NARROW CRYSTALLITE-SIZE DISTRIBUTION

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Abstract—Hydrotalcite-like layered double hydroxides (LDHs) containing different ratios of Ni²⁺, Cu²⁺, Mg²⁺ and Al³⁺ in the layers have been prepared by a new method, the key features of which are a very rapid mixing and nucleation process in a colloid mill followed by a separate ageing process. The compositions and structural parameters of the materials synthesized using the two routes are very similar, although the degree of crystallinity is slightly higher for the LDHs produced using the new method. The major advantage of the new method is that it produces smaller crystallites, having a very narrow range of distribution of crystallite size. In the conventional coprecipitation process at constant pH, the mixing process takes a considerable time during which nuclei formed at the beginning of the process have a much longer time to undergo crystal growth than those formed at the end of the process. The consequence is that a wide dispersion of crystallite sizes is obtained. In the colloid mill process, however, the mixing and nucleation is complete in a very short time and is followed by a separate ageing process.

Key Words—Copper; Hydrotalcite; Layered Double Hydroxide; Nickel; Particle-size Distribution.

INTRODUCTION

Layered double hydroxides are a class of synthetic anionic clays the structure of which is based on brucite (Mg(OH)₂)-like sheets in which some of the divalent cations have been replaced by trivalent ions giving positively charged sheets. This charge is balanced by intercalation of anions in the hydrated interlayer regions. The LDHs can be represented by the general formula [M_{1-x}^{II}M_x^{III}(OH)₂]^{x+}(Aⁿ⁻)_{x/n}·yH₂O. The identities of the di- and trivalent cations (M^{II} and M^{III}, respectively) and the interlayer anion (Aⁿ⁻) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. The parent material of this class is the naturally occurring mineral hydrotalcite which has the formula Mg₆Al₂(OH)₁₆CO₃·4H₂O and LDHs are consequently also known as hydrotalcite-like materials. The LDHs have found a wide variety of uses, e.g. as anion exchangers, adsorbents, catalysts and catalyst supports and as additives to plastics (Cavani *et al.*, 1991; Zhang *et al.*, 1999). In addition to the composition and degree of crystallinity, the crystallite size and its distribution are important considerations for many potential applications of LDHs.

The LDH materials are traditionally synthesized by coprecipitation reactions from aqueous solution (Pausch *et al.*, 1986). The method of mixing and the pH during the nucleation and precipitation process can have a significant influence on the particle size and texture of the resulting products. In the so-called variable-pH

precipitation process (Fornasari *et al.*, 1995), hydro-talcite-type LDH carbonates are prepared by adding a solution containing divalent and trivalent cations to solution of Na₂CO₃ until the pH of the reaction mixture reaches a specified value (typically around 10) and a solution of NaOH is then used to maintain the pH value until the precipitation is complete. More commonly used is the constant-pH coprecipitation method at low supersaturation which involves simultaneous drop-wise addition of mixed salt and base solutions to a reaction vessel at such a rate that the pH remains constant (Yun and Pinnavaia, 1995). In either case, once mixing is complete the resulting suspension is subsequently aged at elevated temperatures.

It is difficult to control the particle size and distribution of LDHs using the traditional methods. This is because the addition process takes a considerable time so that nuclei formed at the start of the addition process have a much longer time in which to undergo ageing than those formed at the end of the addition process. We (Zhao *et al.*, 2002) have recently reported a new method for the preparation of LDHs of the type [Mg_{1-x}Al_x(OH)₂](CO₃)_{x/2}·yH₂O with different (Mg²⁺/Al³⁺) ratios which involves a very rapid mixing and nucleation process in a colloid mill (King *et al.*, 1994; Perry and Green, 1997) followed by a separate ageing process. For each Mg²⁺/Al³⁺ ratio, the particle-size distribution for the LDH material produced using the new method was considerably narrower than that for the LDH sample produced by precipitation at constant pH.

The range of metal cations incorporated in the layers of LDHs has been extended in recent years and LDHs containing three and four different metal ions, including

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Table 1. Chemical formulae of Cu-Ni-Al-CO₃ LDHs.

Sample	Formula	c (nm)	a (nm)
1A	[Cu _{0.16} Ni _{0.48} Al _{0.36} (OH) _{2.0}](CO ₃) _{0.18} ·0.73H ₂ O	2.262	0.3032
2A	[Cu _{0.16} Ni _{0.47} Al _{0.36} (OH) _{2.0}](CO ₃) _{0.18} ·0.73H ₂ O	2.265	0.3033
3A	[Cu _{0.23} Ni _{0.43} Al _{0.34} (OH) _{2.0}](CO ₃) _{0.17} ·0.68H ₂ O	2.267	0.3038
4A	[Cu _{0.23} Ni _{0.43} Al _{0.34} (OH) _{2.0}](CO ₃) _{0.17} ·0.68H ₂ O	2.270	0.3038
5A	[Cu _{0.28} Ni _{0.39} Al _{0.33} (OH) _{2.0}](CO ₃) _{0.16} ·0.65H ₂ O	2.260	0.3042
6A	[Cu _{0.28} Ni _{0.38} Al _{0.33} (OH) _{2.0}](CO ₃) _{0.16} ·0.65H ₂ O	2.265	0.3044

a wide variety of transition metal ions, have been reported (Rives, 2001). Transition metal-containing LDH materials are of particular interest as catalysts in their own right and as precursors to other catalysts. Studies of Cu-containing LDHs are less common in the literature, although the synthesis of Cu-Ni-Al-CO₃ LDHs by coprecipitation at constant pH has recently been reported (Rives and Kannan, 2000). The possibility exists of a synergistic effect between Cu²⁺ and Ni²⁺ in catalysts prepared from such materials (Jyothi *et al.*, 2000). Indeed the calcination products of similar materials have been shown to be active in the wet air oxidation of aqueous phenol solutions (Alejandre *et al.*, 2001) as well as phenol hydroxylation (Zhu *et al.*, 1998).

In this paper we extend our work with the colloid mill method to the more complicated case of Cu-Ni-Al-CO₃ LDHs and Cu-Ni-Mg-Al-CO₃ LDHs in order to see whether the same effects are observed as with the simplest Mg-Al-CO₃ system studied previously. If the LDH precursors can be prepared with a narrow range of small particle sizes, it can be expected that it will be possible to prepare more uniform catalysts with a higher surface area on calcination.

EXPERIMENTAL

Chemicals

Reagents were all of AR grade obtained from Beijing Yili Fine Chemical Reagent Co. and used directly without further purification. Water used in the synthesis and washing was deionized with a conductance below 10⁻⁶ S cm⁻¹.

Precursor solutions. Solution A: mixtures of Cu(NO₃)₂·3H₂O, Ni(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with a (Cu²⁺ + Ni²⁺ + Mg²⁺)/Al³⁺ ratio of 2.0 and different ratios of divalent cations were

dissolved in deionized water to give solutions (100 mL) with a {[Cu²⁺] + [Ni²⁺] + [Mg²⁺]} concentration of 0.8 M. Solution B: NaOH and Na₂CO₃ were dissolved in deionized water to form the mixed-base solution (100 mL). The concentrations of the base were related to the concentrations of metal ions in solution A as follows: [NaOH] = 1.6 [Cu²⁺ + Ni²⁺ + Mg²⁺ + Al³⁺] and [CO₃²⁻] = 2.0 [Al³⁺].

LDH synthesis with separate nucleation and ageing steps. Solution A (100 mL) and solution B (100 mL) were added simultaneously to a colloid mill rotating at 5000 rpm and mixed for 2 min. The resulting slurry was transferred from the colloid mill to a flask (500 mL) and aged at 100°C for 6 h. The precipitate was filtered and washed thoroughly with deionized water until the pH of the washings was <8. The resulting solids (samples 1A, 3A and 5A in Table 1 when [Mg²⁺] = 0 and samples 1B, 3B and 5B in Table 2) were dried at 100°C for 24 h.

LDH synthesis by the constant-pH method. Solution A (100 mL) and solution B (100 mL) were added simultaneously drop-wise to a flask (1000 mL) containing stirred deionized water (300 mL) at such a rate that the pH of the reaction mixture was maintained at 10±0.5. The mixing process was carried out at room temperature. The resulting slurry was aged at 100°C for 6 h. The precipitate was then filtered and washed well with deionized water until the pH of the washings was <8. The resulting solid (samples 2A, 4A and 6A in Table 1 when [Mg²⁺] = 0 and samples 2B, 4B and 6B in Table 2) was dried at 100°C for 24 h.

Characterization. Powder X-ray diffraction (XRD) patterns of the samples were recorded using a Shimadzu XRD-6000 diffractometer under the following conditions: 40 kV, 30 mA, CuKα (λ = 0.15406 nm) radiation.

Table 2. Chemical formulae of Cu-Ni-Mg-Al-CO₃ LDHs.

Sample	Formula	c (nm)	a (nm)
1B	[Cu _{0.18} Ni _{0.32} Mg _{0.18} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.64H ₂ O	2.257	0.3038
2B	[Cu _{0.18} Ni _{0.32} Mg _{0.18} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.68H ₂ O	2.253	0.3031
3B	[Cu _{0.09} Ni _{0.24} Mg _{0.35} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.65H ₂ O	2.259	0.3036
4B	[Cu _{0.09} Ni _{0.25} Mg _{0.35} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.61H ₂ O	2.265	0.3037
5B	[Cu _{0.14} Ni _{0.36} Mg _{0.18} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.69H ₂ O	2.254	0.3031
6B	[Cu _{0.14} Ni _{0.37} Mg _{0.18} Al _{0.32} (OH) _{2.0}](CO ₃) _{0.16} ·0.63H ₂ O	2.257	0.3032

The samples, as unoriented powders, were step-scanned in steps of $0.02^\circ 2\theta$ in the range from 3 to 70° using a count time of 4 s per step.

Elemental analyses were performed by ICP emission spectroscopy using an Ultima instrument on solutions prepared by dissolving the samples in dilute HNO_3 .

The particle-size distribution was determined using a Malvern Mastersizer 2000 laser particle-size analyzer, which gives accurate results for particle diameters in the range 0.020 – 2000 μm .

RESULTS AND DISCUSSION

Elemental analysis of LDHs

The powder XRD patterns (not shown) for all the products show the characteristic reflections of LDH materials (Cavani *et al.*, 1991). The intensities of the peaks of LDHs prepared using the colloid mill method are greater than those of the materials prepared using the traditional method, suggesting that the former have greater crystallinity. In each case, no other crystalline phases have been formed. The calculated values of the structural parameters are shown in Tables 1 and 2 and are consistent with previous reports in the literature (Rives and Kannan, 2000). Tables 1 and 2 also list the calculated formulae for the Cu-Ni-Al-CO_3 LDHs and Cu-Ni-Mg-Al-CO_3 LDHs respectively, prepared using the colloid mill method (samples 1, 3, 5) and the conventional method of coprecipitation at constant pH (samples 2, 4, 6). The carbonate content was calculated on the assumption that it is the only interlayer anion since LDHs are known to have a strong affinity for carbonate ions and the FTIR spectra (not shown) show no evidence of nitrate ions.

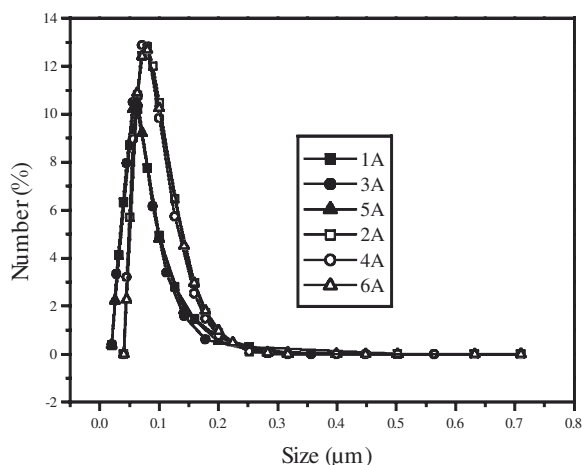


Figure 1. Particle-size distribution of Cu-Ni-Al-CO_3 LDHs. The particle-size distribution of the samples prepared with the colloid mill method (1A, 3A and 5A) is narrower than that of the samples prepared with the conventional method of precipitation at constant pH (2A, 4A and 6A).

Particle-size distribution of LDHs

The results for the particle-size distribution, by number, are shown in Figures 1 and 2. For any given particle, the diameter obtained using this method is that of a sphere of equivalent volume. For all samples, the particle-size distribution of the Cu-Ni-Al-CO_3 LDH and Cu-Ni-Mg-CO_3 LDH obtained by our new method is considerably narrower than that of those prepared at constant pH. In addition, the particle size is smaller. The new synthesis method is apparently responsible for the narrow particle-size distribution, just as is observed in the case of Mg-Al-CO_3 LDHs (Zhao *et al.*, 2002). In the method of precipitation at constant pH, nucleation and crystal growth occur simultaneously during the addition process, and thus it is inevitable that after ageing, a wide range of crystallite sizes is obtained. In the colloid mill method, the nucleation step carried out in the colloid mill is complete in a very short time (~ 1 – 2 min), and in the subsequent separate ageing step, all the nuclei formed grow for the same length of time. The particle-size distribution can thus be controlled using the new method.

We have studied the effect of varying the synthesis parameters such as stator-rotor gap size, rotational speed of the colloid mill and the concentration of reactant solutions on the particle-size distribution. Although reproducible changes in the particle-size distribution are obtained, no clear relationship between the variables is apparent.

CONCLUSIONS

In the present study, we have successfully prepared Cu-Ni-Al-CO_3 LDHs and Cu-Ni-Mg-Al-CO_3 LDHs by a new method involving separate nucleation and ageing steps. Compared with the conventional method of

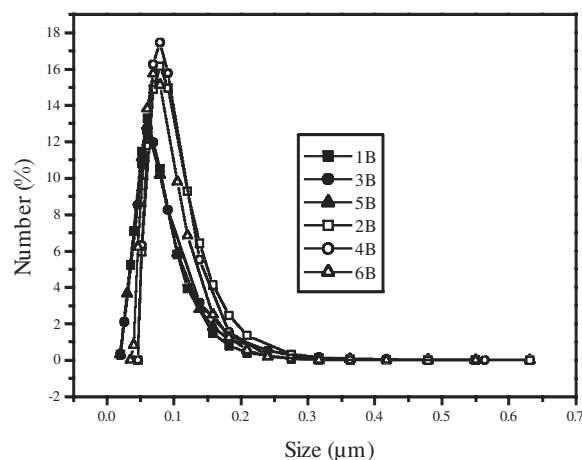


Figure 2. Particle-size distribution of Cu-Ni-Mg-Al-CO_3 LDHs. The particle-size distribution of the samples prepared with the colloid mill method (1B, 3B and 5B) is narrower than that of the samples prepared with the conventional method of precipitation at constant pH (2B, 4B and 6B).

coprecipitation at constant pH, the materials obtained by the new method are of smaller particle size and have a narrow range of particle-size distribution.

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