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 Ni^{2+}, Cu^{2+}, Mg^{2+} and Al^{3+} 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clays the structure of which is based on brucite (Mg(OH)_{2})-like sheets in which some of the divalent cations have been replaced by trivalent ions giving positively charged sheets.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_{II}^{x-}M_{III}^{x}(OH)_{2}]^{x+}(A_{n}^{m-})_{y}H_{2}O. The identities of the di- and trivalent cations (M_{II}^{x-} and M_{III}^{x}) and the interlayer anion (A_{n}^{m-}) 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 Mg_{6}Al_{2}(OH)_{16}CO_{3}.4H_{2}O 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), hydrotalcite-type LDH carbonates are prepared by adding a solution containing divalent and trivalent cations to solution of Na_{2}CO_{3} 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}]_{0.5}(CO_{3})_{x/2}.yH_{2}O with different (Mg^{2+}/Al^{3+}) 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 Mg^{2+}/Al^{3+} 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