A Simple Environmentally Friendly Method to Prepare Versatile Hydrotalcite-like Compounds

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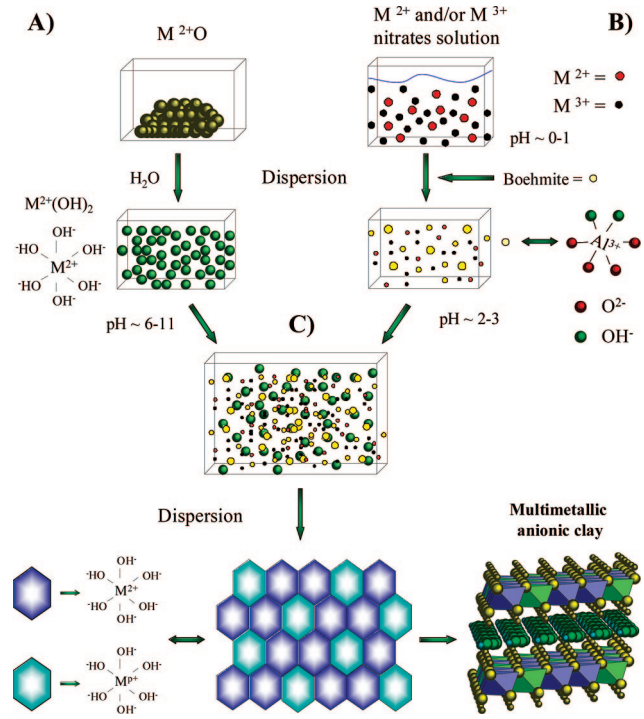
The hydrotalcite-like materials (HT), also called layered double hydroxides, are a class of naturally occurring anionic clays. Their structure resembles that of brucite and is created by replacing some of the M^{2+} in the brucite lattice by M^{3+} cations, turning the layer positively charged. These layers are electrically compensated by anions that are located in the interlayer region. A wide variety of compounds with HT structure can be prepared, represented by the general formula: $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$, where $M^{2+} = Mg^{2+}$, Ni^{2+}, etc.; $M^{3+} = Al^{3+}$, Fe^{3+}, Ga^{3+}, etc.; $A^{n-} = [CO_3]^{2-}$, NO_3^-, Cl^-, etc.[1] Because calcination of HTs yields mixed oxides, which are basic solids, HTs have found important applications in many organic base-catalyzed reactions.[2] HTs could find widescale technological applications as hybrid composites, drug delivery carriers, antiacid agents, flame retardants and PVC additives, catalysts for SO_x and NO_x removal, among others.[3–7] Given the importance of hydrotalcite-like materials, the preparation of multimetallic anionic clays through a simple, environmentally friendly, and economically viable method is of paramount importance. Conventionally, HTs are prepared through the coprecipitation of metallic salts with a concentrated alkaline solution. Nevertheless, this method requires thermal treatments to crystallize HT and intensive washing to eliminate undesirable ions.[8] Although the preparation of anionic clays using metal oxides/hydroxides or an in-line dispersion-precipitation method has been reported,[9–12] long aging times were used (from days to months) and the final product required purifying. In the patent's literature, a method similar to the one here presented has been reported;[13–15] however, it usually required prolonged aging times, and in some cases, relatively pure compounds were obtained only after hydrothermal treatment. Besides, to avoid the presence of unreacted precursors and secondary crystalline phases, the researchers necessarily adjusted the pH with an acid (such as formic and nitric acid) or with a base (such as NaOH or ammonium hydroxide). Moreover, all those patents are focused mainly on bimetallic anionic clays. Hence, this work reports an easy, environmentally friendly, and economical way for the preparation of multimetallic anionic clays.

Scheme 1. Proposed Hydrotalcite-like Structure Formation Pathway



The general reaction pathway is illustrated in Scheme 1. Before and during the HT formation, several reactions take place, such as the dissociation, hydrolysis, and peptization of the insoluble oxides. In Scheme 1, part A, the insoluble bimetallic oxide is dispersed and hydrolyzed in order to obtain small and reactive hydroxide particles. Depending on the nature of the pristine oxide, the fresh hydroxide can provide a pH medium from 6 to 11.[16,17]

In parallel, nitrate salts are dissolved in water, engendering a pH of 0 to 1, depending on their nature and concentration.

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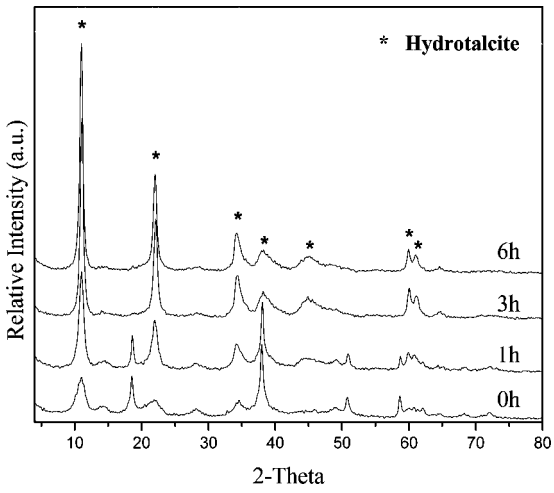

Figure 1. X-ray powder diffraction of the MgAl hydrotalcite evolution at increasing aging times.

Here, an insoluble metallic oxide source (boehmite for instance) is added and dispersed into the reaction medium, which facilitates the dissociation and homogenization of particles. This causes a slight pH increase. The metallic nitrates have a double function: (1) provide cations to reach an intended M^{2+}/M^{3+} molar ratio and (2) adjust the pH, and thus produce an adequate environment for the incorporation of the insoluble divalent and/or trivalent metal precursors (part B). Finally, the suspension A and the gel B are mixed and dispersed, step C.

In the case of the MgAl sample, the pH attained after dispersion was ~9. The reaction's evolution was monitored by the precursor's disappearance from the final dispersed slurry (Figure 1). A sample was taken immediately after dispersion, labeled as 0 h. The XRD analysis demonstrated that this sample consisted of a mixture of brucite, boehmite, and hydrotalcite phases. The slurry was poured into a glass reactor and heated to 80 °C; samples were taken at 1, 3, and 6 h. After 1 h, boehmite and brucite reflections diminished substantially, and at 3 h, they almost disappeared. Only a negligible amount of boehmite remained after 6 h. It is worth noting that the solids were not washed in any of the synthesis steps.

The following reaction mechanism is proposed for the MgAl formation

$$MgO(s) + H_2O \rightarrow Mg(OH)_2(s) \quad (1)$$

$$Mg(OH)_2(s) \leftrightarrow Mg^{2+} + 2OH^- \quad (2)$$

$$2AlOOH(s) + 2H^+ \leftrightarrow 2Al^{3+} + 2H_2O + O_2 \quad (3)$$

$$2Al^{3+} + 6OH^- \leftrightarrow 2Al(OH)^{2+} + 4OH^- \quad (4)$$

$$2Al(OH)^{2+} + 4OH^- \leftrightarrow 2Al(OH)_2^+ + 2OH^- \quad (5)$$

$$2Al(OH)_2^+ + 2OH^- \leftrightarrow 2Al(OH)_3(s) \quad (6)$$

$$Al(OH)_3(s) + OH^- \leftrightarrow Al(OH)_4^- \quad (7)$$

Equations 1 and 2 belong to the steps shown in Scheme 1A, where $M^{2+}O$ and $M^{2+}(OH)_2$ are assigned to magnesium oxide and magnesium hydroxide, respectively. $Mg(OH)_2$ formation (eq 1) begins at pH ~9.5, whereas $Mg(OH)_2$ dissociation (eq 2) is obtained at pH well below 9. By means of XRD, we corroborated the complete transformation of MgO to $Mg(OH)_2$.

Boehmite peptization/dissociation/precipitation reactions are given in eqs 3−7. Depending on the pH value, several aluminum species are obtained. The reaction shown in eq 3 occurs at pH below 3, whereas reactions illustrated by eqs 5−7 are achieved in basic environments.[16–18] When both boehmite and magnesium hydroxide's dispersions are completed, the suspension A and the gel obtained in B are mixed and dispersed again. Here, reactions 2 and 4−7 take place simultaneously, giving rise to the hydrotalcite formation.

A general mechanism is proposed for the formation of multimetallic anionic clays, illustrated by eqs 8−11.

$$(1 - x)M^{2+}(OH)_2(s) + x[M^{p+}(OH)_p(s)] + (x/n)A^{n-} + 2OH^- + mH_2O \leftrightarrow [M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O \quad (8)$$

$$(1 - x)M^{2+}(OH)_2(s) + x[M^{p+}(OH)_4^{y-}] + (x/n)A^{n-} + 2OH^- + mH_2O \leftrightarrow [M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O \quad (9)$$

$$(1 - x)M^{2+} + x[M^{p+}(OH)_p(s)] + (x/n)A^{n-} + 2OH^- + mH_2O \leftrightarrow [M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O \quad (10)$$

$$(1 - x)M^{2+} + x[M^{p+}(OH)_4^{y-}] + (x/n)A^{n-} + 2OH^- + mH_2O \leftrightarrow [M^{2+}_{(1-x)}M^{3+}_x(OH)_2]A^{n-}_{x/n}\cdot mH_2O \quad (11)$$

When the metal nitrates are dissolved in water, the cationic M^{p+} species exists, whereas at basic conditions the $M^{p+}(OH)_4^{y-}$ species are found, for instance, when $p = 2$, $y = 2m$ and when $p = 3$, $y = 1$, respectively.[13] We consider that reaction 8 takes place immediately after mixing (step C). Depending on the nature of M^{p+}, the corresponding hydroxide $M^{p+}(OH)_p(s)$ will form in acidic medium, as in the cases of the iron and aluminum hydroxides or in neutral-basic medium for the magnesium, copper, nickel, and zinc hydroxides. As the reaction proceeds and the medium becomes alkaline, the $M^{p+}(OH)_4^{y-}$ species will appear. It is important to control the final pH to facilitate the dissociation of the insoluble bimetallic hydroxide $M^{2+}(OH)_2(s)$.

The production of multimetallic HTs ($MgM^{p+}Al$) was performed as follows: MgO was dispersed in water at 5000 rpm/30 min (A). In parallel, M^{2+} or M^{3+} nitrates were dissolved. Afterward, enough boehmite was added to achieve the desired molar ratio (M^{2+}/M^{3+}) and the mixture was dispersed at 5000 rpm/30 min (B). The H_2O/solid ratio was 10. Thereafter, the product resulting from the addition of (A) to (B) was dispersed for 1 h at 8000 rpm (C). The slurry was aged at 80 °C for 6 h with a stirring speed of 400 rpm. Finally, the solid was filtered and dried at 100 °C for 12 h. The results from XRD analysis are shown in Figure 2. In the case of the MgFeAl hydrotalcites, both magnesium oxide (MgFeAl) and magnesium hydroxide (MOHFA) were used as magnesium sources. The production of HTs with Mg^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Al^{3+}, and Fe^{3+} was easily accomplished.

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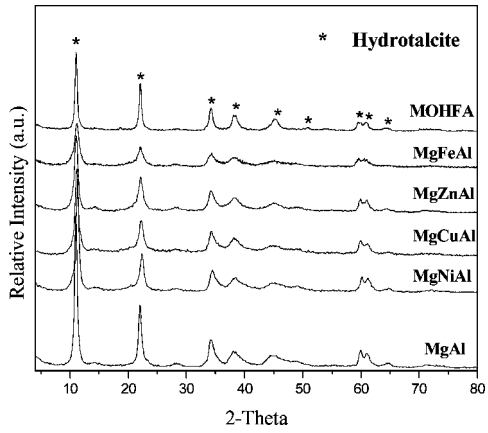

Figure 2. X-ray powder diffraction of several hydrotalcite-like compounds.

To prepare 1 kg of sample MgFeAl, for instance, the following amounts of reagents were employed, 377 g of MgO as dispersed in 2.909 L of water (A). Separately, 364 g of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 2.800 L of water, and then 155 g of boehmite was added and dispersed (B).

The multimetallic anionic clays showed only a small amount of brucite as a secondary phase that disappeared by increasing the aging time and/or adjusting the pH by varying the initial quantity of metal sources.

The chemical composition and the specific surface areas are summarized in Table 1. The M^{2+}/M^{3+} molar ratios were very similar to the nominal one. The BET values ranged from 140 to 256 m^2/g, which indicates that the calcined samples had surface areas similar to those found for coprecipitated samples with similar compositions. From SEM analysis, the solids show a lamellar structure with platelets of about 50 nm of thickness and 0.5 μm of size.

Table 1. Chemical Composition and Surface Areas of the HTs

sample[a]	chemical formulas	BET (m^2/g)
MgAl	$[Mg_{0.754}\ Al_{0.246}\ (OH)_2](NO_3)_{0.246}\ 0.64H_2O$	227
MgNiAl	$[Mg_{0.662}Ni_{0.074}Al_{0.264}(OH)_2](NO_3)_{0.264}\ 0.60H_2O$	230
MgCuAl	$[Mg_{0.708}Cu_{0.051}Al_{0.241}(OH)_2](NO_3)_{0.241}0.50H_2O$	223
MgZnAl	$[Mg_{0.676}Zn_{0.068}Al_{0.256}\ (OH)_2](NO_3)_{0.256}0.54H_2O$	140
MgFeAl	$[Mg_{0.756}Fe_{0.064}Al_{0.180}\ (OH)_2](NO_3)_{0.244}0.59H_2O$	145
MOHFA	$[Mg_{0.812}Fe_{0.058}Al_{0.130}(OH)_2](NO_3)_{0.188}0.48H_2O$	256

[a] Calcined at 500 °C/4 h.

This work shows an easy and economical way for multimetallic anionic clay production. To the best of our knowledge, this is the first time that these materials are produced in such a way. The HT production method does not require washing or purification of the final product, as occurs with the anionic clays prepared by any other method. This allows compliance with the growing environmental regulations imposed upon industrial production processes. This method allows the HT production in high quantities, thus providing a viable alternative for those processes limited by the unavailability of large amounts of these compounds.

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