

Control of crystallite and particle size in the synthesis of layered double hydroxides: Macromolecular insights and a complementary modeling tool



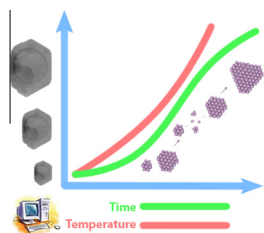
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GRAPHICAL ABSTRACT



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ABSTRACT

Zinc–aluminum layered double hydroxides with nitrate intercalated ($\text{Zn}(n)\text{Al-NO}_3$, $n = \text{Zn}/\text{Al}$) is an intermediate material for the intercalation of different functional molecules used in a wide range of industrial applications. The synthesis of $\text{Zn}(2)\text{Al-NO}_3$ was investigated considering the time and temperature of hydrothermal treatment. By examining the crystallite size in two different directions, hydrodynamic particle size, morphology, crystal structure and chemical species in solution, it was possible to understand the crystallization and dissolution processes involved in the mechanisms of crystallite and particle growth. In addition, hydrogeochemical modeling rendered insights on the speciation of different metal cations in solution. Therefore, this tool can be a promising solution to model and optimize the synthesis of layered double hydroxide-based materials for industrial applications.

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1. Introduction

Layered double hydroxides (LDHs) belong to a class of synthetic nanostructured anionic exchangers, which can be synthesized in a relatively inexpensive and potentially recyclable manner [1]. The

most common compositions of LDHs reported in literature have the general formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n}m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di- and trivalent cations, respectively, A^{n-} is an anion, and x is equal to the molar ratio $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ which is usually between 0.22 and 0.33 [1]. For $x > 0.33$ the formation of a higher number of less stable $\text{M}^{\text{III}}\text{-O-M}^{\text{III}}$ linkages [2] would be necessary [3], but possible to occur under specific conditions of LDH formation [4]. Combining different cations and anions through different

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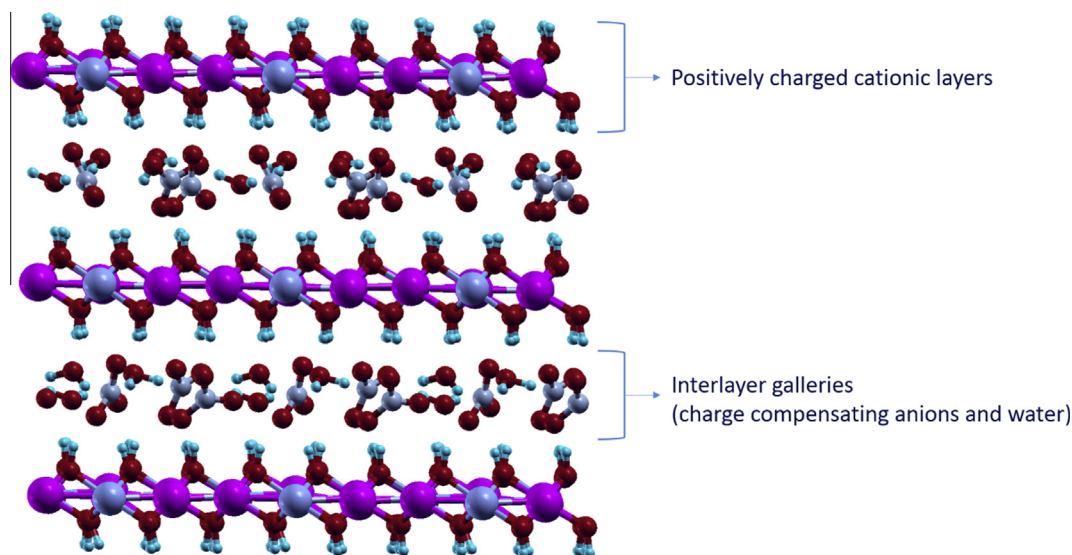


Fig. 1. Schematic representation of the structure of LDH-NO₃.

synthetic routes gives a large number of tailored LDH compositions with desirable physical and chemical properties depending on their application [1].

The layers of LDHs consist of approximately octahedral units of cations surrounded by edge-sharing hydroxide ions, forming brucite-like layers, (Mg(OH)₂), where some divalent cations are replaced by trivalent cations, which result in positively charged layers. These layers are relatively weakly bound to charge-balancing anions in the interlayer region through hydrogen bonds, electrostatic effects and dispersive forces involving layer hydroxyl groups and interlayer anions and water molecules, resulting in a three-dimensional structure such as that represented in Fig. 1. The weak interlayer bonding allows LDHs to expand and intercalate, for example, different functional organic molecules, which makes them ideal host-guest structures with applications in catalysis [5,6], adsorption [7,8], pharmaceuticals [9,10], photochemistry [7,11], electrochemistry [12,13], purification [14] and functional polymers [12].

One particular application of LDHs explored in our research group is in active corrosion protection of metallic surfaces [15–19]. In this case LDHs are loaded with corrosion inhibitors and used as coating additives. This approach takes full use of LDHs anionic exchange capability by locally releasing the inhibitors, while trapping aggressive species, such as chlorides. The intercalation of functional molecules into LDHs also contributes to the stabilization of the latter against possible undesirable effects caused by light, temperature or the presence of oxygen.

The route used in this work for the preparation of LDH materials involves the intercalation of nitrate by co-precipitation, followed by hydrothermal treatment. The Zn:Al ratio was 2:1, since it has been demonstrated to produce well defined layered materials [16], while the nitrate anion was chosen as the intercalated species because it can be easily replaced by functional molecules [15–19] through an anion exchange reaction, which make Zn(2)Al-NO₃ ideal precursors for many applications, including corrosion protection. Nevertheless, Zn(2)Al-NO₃ is already a anticorrosion material on its own, acting as a chloride nanotrap by anion exchange in functional coatings, thereby reducing their permeability to aggressive species [20].

Due to the wide range of applications of LDHs and, particularly, in active corrosion protection, there is a general interest to establish the industrial production of these materials.

Due to the wide range of applications of LDHs and, particularly, in active corrosion protection, there is a general interest to establish the industrial production of these materials [21,22], which also make the LDHs formation mechanism still a matter of great interest [23,24]. For this reason, the relation between the physicochemical properties capable of influencing the synthesis (pH, time and temperature), and the characteristics of the produced materials was investigated, not only considering the more usual hydrodynamic particle size, but also the crystallite size in two different directions (parallel and perpendicular to the cationic layers). Moreover, analytical evidence of the dissolution of LDHs was gathered. This study allowed elucidating the mechanisms behind the synthesis of these materials (crystallite and particle growth, material dissolution, Ostwald ripening phenomenon and main reactive species in solution). Furthermore, one approach based on hydrogeochemical modeling software was proposed, allowing to model the synthesis of LDH-based materials.

The crystal structure of LDHs is often difficult to determine by X-ray diffraction (XRD) due to poor crystallinity of these materials [25]. The particular case of LDH-NO₃ is still a matter of discussion regarding the parallel [26,27] or non-parallel [28,29] orientation of nitrate anions in the interlayer toward the cationic layer. Thus, the molecular crystal structure of this material was investigated employing density functional theory (DFT) calculations together with the periodic slab approach, which allowed to gain insights into the structure of the synthesized material and the conformation adopted by the nitrate anions in the interlayer.

2. Experimental section

2.1. Materials

Zn(NO₃)₂·6H₂O (99%), Al(NO₃)₃·9H₂O (98.5%), NaNO₃ (99.5%) and NaOH (98%) were obtained from Sigma-Aldrich and used without any further purification.

2.2. Synthesis of layered double hydroxides

The synthetic pathway of Zn(2)Al-NO₃ investigated in this work involved a two-step methodology, starting by a nucleation process based on low supersaturation co-precipitation at constant pH

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