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Reversible intercalation of ammonia molecules into a layered double hydroxide structure without exchanging nitrate counter-ions

Gregorio Guadalupe Carbajal Arizaga [a],*, Fernando Wypych [b],
Felipe Castillón Barraza [a], Oscar Edel Contreras Lopez [a]

[a] *Universidad Nacional Autónoma de México, Centro de Nanociencias y Nanotecnología, Km. 107 Carretera Tijuana-Ensenada, Apdo. Postal 14, C.P. 22800. Ensenada, Baja California, México*
[b] *CEPESQ—Research Centre of Applied Chemistry, Department of Chemistry, Federal University of Paraná, P.O. Box 19081, 81531-980 Curitiba, PR, Brazil*

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ABSTRACT

A zinc/aluminum LDH was precipitated with recycled ammonia from a chemical vapor deposition reaction. The LDH presented a crystalline phase with basal distance of 8.9 Å, typical for nitrate-containing LDHs, and another phase with a basal distance of 13.9 Å. Thermal treatment at 150 °C eliminated the phase with the bigger basal distance leaving only the anhydrous nitrate-intercalated LDH structure with 8.9 Å. Intense N–H stretching modes in the FTIR spectra suggested that the expansion was due to intercalation of ammonia in the form of $[NH_4(NH_3)_n]^+$ species. When additional samples were precipitated with pure ammonia, the conventional LDH nitrate structure was obtained (8.9 Å basal distance) at pH = 7, as well as a pure crystalline phase with 13.9 Å basal distance at pH = 10 due to ammonia intercalation that can be removed by heating at 150 °C or by stirring in acetone, confirming a unusual *sensu stricto* intercalation process into a LDH without exchanging nitrate ions.

1. Introduction

Layered double hydroxides (LDH), also known as hydrotalcite-like compounds, are formed by layered units in which metal cations are octahedrally coordinated with hydroxyl groups, as in the brucite ($Mg(OH)_2$) structure. The isomorphic substitution of divalent cations by trivalent cations leaves a residual positive charge that is stabilized by interlayer anions. The formula can be generalized to $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{3+} and M^{2+} are the metal cations and A^{n-} is a counter-ion [1–7].

The well-known anion exchange property of LDHs [1,2] has been used to exchange counter-ions for inorganic or organic ions that modify the properties of the layered structures [1,2] and allow to produce new materials with pharmacological applications [1], UV-absorbers that can be added to polymers [3,4], enzyme supports [5,6], organic molecule separators [7] and water pollutant retainers [2], for instance.

LDHs are synthesized by soft methods and alkaline precipitation is the most common procedure. This particular method involves a salt solution with M^{3+} and M^{2+} cations. Direct alkaline precipitants are NaOH, KOH and NH_4OH, but urea or ammonium carbonate hydrolysis reactions are also used to generate hydroxyls *in situ* [8–10]. Other less used methods are the milling of metal hydroxides and metal salts to form LDH structures [11] or urea and oxisalts melting (fusion) reactions [9].

Considering the relevance of an alkaline medium to obtain LDHs, our group decided to reuse the ammonia stream discharged from a chemical vapor deposition (CVD) reactor in which GaN rods were prepared with gallium metal, ammonium chloride and ammonia [12]. Such CVD reaction is conducted at constant ammonia flow of ca. 180 cm^3 min^{-1} and this stream is normally dissolved in water and then neutralized, because in solution, ammonia induces formation of hydroxyl groups according to the following equation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \tag{1}$$

Thus it seemed a good opportunity to synthesize LDH structures by reusing the ammonia. However, during the characterization of these compounds, unexpected results suggested an intercalation phenomenon in the structures. We stress here that in an exchange reaction the pristine counter-ions are displaced by new ones [1–8]. On the other hand, an intercalation reaction is defined as an isomorphic insertion (sometimes reversible) of mobile species (molecular or ionic) into the interstices of a host, i.e. the host does not change its structure but its interlayer distance [13]. Under this concept, an intercalation process in a LDH containing nitrate as counter-ions, for example, would involve the insertion of new chemical species in the interlayer space (interstice) without displacing nitrate ions and to the best of our knowledge, there are no reports regarding

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* Corresponding author. Fax: +52 646 174 46 03.
E-mail address: gregoriocarbajal@yahoo.com.mx (G.G. Carbajal Arizaga).

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to *strictu sensu* intercalation reactions in LDH. We report here the synthesis of a LDH with recycled ammonia as well as the intercalation compounds obtained.

2. Experimental

2.1. Synthesis

The system from which ammonia (NH_3) was obtained is described as follows: gallium nitride (GaN) was synthesized in a tubular reactor with one heating zone with two precursors at atmospheric pressure. One was NH_3 gas introduced at the entrance of the tube and the second precursor was formed in the heat zone with metallic gallium and NH_4Cl as shown in Fig. 1. Above 300 °C, NH_4Cl dissociates and forms a gaseous unstable gallium monochloride intermediate, which reacts with NH_3 [12].

Ammonia was streamed through the reactor at a rate of 180 $cm^3\,min^{-1}$, and the unreacted NH_{3-x} returned to form ammonia. The temperature at the outlet of the reactor decreased to less than 200 °C, so that gallium and NH_4Cl solidified and ammonia was the main compound released; however, a small content of metal gallium or ammonium chloride were not discarded to be in the stream. The gas at the outlet of the reactor was bubbled with a rubber into 150 mL of a solution containing 3.36×10^{-2} mol of $Zn(NO_3)_2$ and 1.12×10^{-2} mol of $Al(NO_3)_3$, representing a molar ratio of Zn:Al = 3. Since the CVD reactions were conducted at different times, precipitation control depended on pH. The bubbling was stopped when pH = 10 was reached.

Reference samples were precipitated with a 14% NH_4OH solution (Sigma-Aldrich) and with pure NH_3 (99.999%).

The white solids were filtered and rinsed with 500 mL of water. Importantly, samples prepared with residual ammonia were dried at 100 °C for 36 h, because the compounds are stable under these conditions. Finally, samples were ground with a mortar to facilitate their handling during analysis.

The solid precipitated with the ammonia discharged from the CVD reactor was labeled LDH-CVD to differentiate it from the reference compounds prepared with 14% ammonia solution and pure ammonia.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Phillips X'pert diffractometer using a Cu target $K\alpha$ ray ($\lambda = 0.15418$ nm) as X-ray source with 0.02 step scans. Energy dispersive spectra (EDS) were collected with a Jeol JSM-5300 scanning electron microscope. X-ray photoelectron spectra (XPS) were collected with an AES-XPS PHI 548 system with Al anode. An energy step of 100 eV was used for the generation of survey spectra, which was scanned from 0 to 1200 eV. For high-resolution spectra, an energy step of 50 eV was used with 0.8 eV resolution. The C1s binding energy was used to compensate surface charge effects.

Thermogravimetry and differential thermal analysis (TGA/DTA) measurements were obtained with a TA SDT Q600 V20.9 equipment using an alumina crucible. Analyses were carried out under a flow of air at a heating rate of 10 °C min^{-1}. Fourier transform infrared (FTIR) spectra were collected with a NICOLET 6700 spectrometer, using a resolution of 2 cm^{-1} and accumulation of 32 scans.

3. Results

3.1. Powder X-ray diffraction

The X-ray diffraction patterns of the LDH reference precipitated with ammonium hydroxide solution presented a reflection corresponding to 8.9 Å basal distance (Fig. 2a), which is a typical LDH structure with a nitrate ion intercalated between the layers [14–16].

In the LDH-CVD X-ray diffraction pattern, two crystalline phases were detected (Fig. 2b). The first corresponded to the same phase as that for the reference precipitated with NH_4OH with 8.9 Å basal spacing. The second, shifted to lower 2θ angles, belonged to a layered phase with basal distance of 13.9 Å (identified with asterisks in Fig. 2b).

The interlayer LDH distances were determined by subtracting the layer thickness (4.8 Å) [17] from the basal space; thus, being of 9.1 Å in the expanded phase. Additionally, considering similarities in the width and shape of basal reflections, integration of the peak areas added up to 51% of the crystalline phase with 13.9 Å basal space. The interlayer dimension, the content and the stability under the drying conditions of this second phase raised the question of which chemical species ejected from the CVD reactor had been retained between the LDH layers. Ammonia, gallium and ammonium chloride were the reagents used in the CVD reactor; thus, any compound derived from them could have been retained in the LDH structure. The interlayer distance in the reference LDH is only 4.1 Å large and it is enough to allocate nitrate ions, whose ionic radii is around 2.19 Å [18].

3.2. EDS and XPS spectroscopies

EDS spectroscopy was used for qualitative analysis of LDH-CVD to detect if, in addition to the Zn^{2+} and Al^{3+} cations used to precipitate the layered materials, gallium was also present, considering that the interlayer space was much larger than the nitrate ion radii and a possible gallium complex could

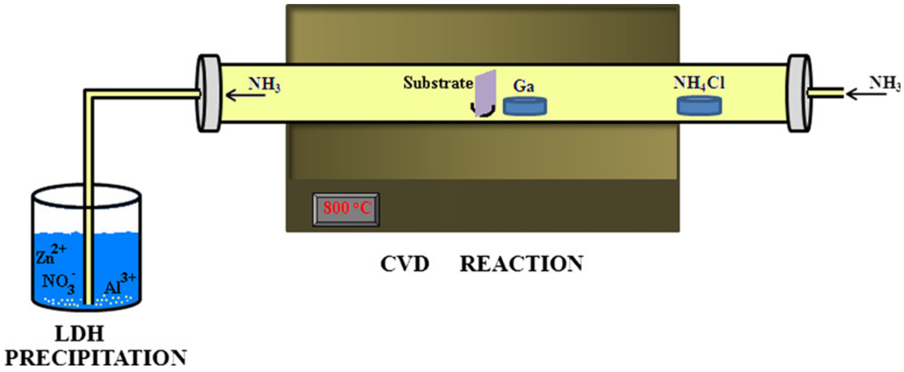

Fig. 1. Scheme of the tubular reactor to synthesize GaN by CVD and the precipitation of LDH structures with residual ammonia.