



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 Castellón 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 $[\text{NH}_4(\text{NH}_3)_n]^+$ 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 an unusual *sensu stricto* intercalation process into a LDH without exchanging nitrate ions.

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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 ($\text{Mg}(\text{OH})_2$) structure. The isomorphous substitution of divalent cations by trivalent cations leaves a residual positive charge that is stabilized by interlayer anions. The formula can be generalized to $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, 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 oxalates 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. $180 \text{ cm}^3 \text{ min}^{-1}$ 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:



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 isomorphous 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

* Corresponding author. Fax: +52 646 174 46 03.

E-mail address: gregoriocarbjal@yahoo.com.mx (G.G. Carbajal Arizaga).

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 $180\text{ cm}^3\text{ min}^{-1}$, 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 $3.36 \times 10^{-2}\text{ mol}$ of $\text{Zn}(\text{NO}_3)_2$ and $1.12 \times 10^{-2}\text{ mol}$ of $\text{Al}(\text{NO}_3)_3$, representing a molar ratio of $\text{Zn}:\text{Al}=3$. Since the CVD reactions were conducted at different times, precipitation control depended on pH. The bubbling was stopped when $\text{pH}=10$ 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 $\text{Cu K}\alpha$ ray ($\lambda=0.15418\text{ nm}$) 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 $\text{C}1\text{s}$ 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 $10^\circ\text{C min}^{-1}$. 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 \AA 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 \AA basal spacing. The second, shifted to lower 2θ angles, belonged to a layered phase with basal distance of 13.9 \AA (identified with asterisks in Fig. 2b).

The interlayer LDH distances were determined by subtracting the layer thickness (4.8 \AA) [17] from the basal space; thus, being of 9.1 \AA 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 \AA 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 \AA large and it is enough to allocate nitrate ions, whose ionic radii is around 2.19 \AA [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

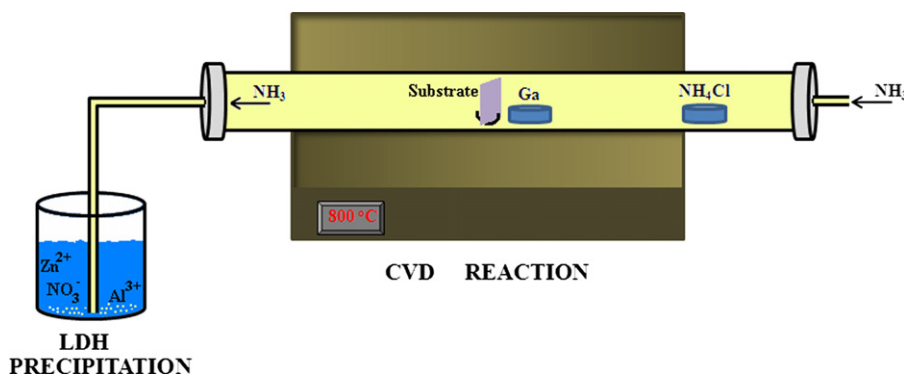


Fig. 1. Scheme of the tubular reactor to synthesize GaN by CVD and the precipitation of LDH structures with residual ammonia.

occupy the interlayer space. EDS only showed the presence of Zn and Al. EDS analysis was also done on the calcined sample at 500 °C. If gallium were present, the concentration of gallium in the calcined sample should increase and appear in the spectra, but no signal of gallium or even of chlorine was detected.

The LDH-CVD XPS spectrum was also obtained (Fig. 3). The atoms detected in the spectrum corresponded to zinc, aluminum and oxygen. High-resolution analysis conducted in the region where the gallium $2p_{1/2}$ and $2p_{3/2}$ bands were expected to appear (inset in Fig. 3) did not reveal the presence of this metal.

3.3. Thermal analysis

Fig. 4 shows the decomposition profile of LDH-CVD formed by four mass loss events, whose values and temperature intervals are listed in Table 1. Event I (25–158 °C) in LDH structures is commonly associated to release of physisorbed water molecules [11], although some authors report that this event ends at 220 °C [10].

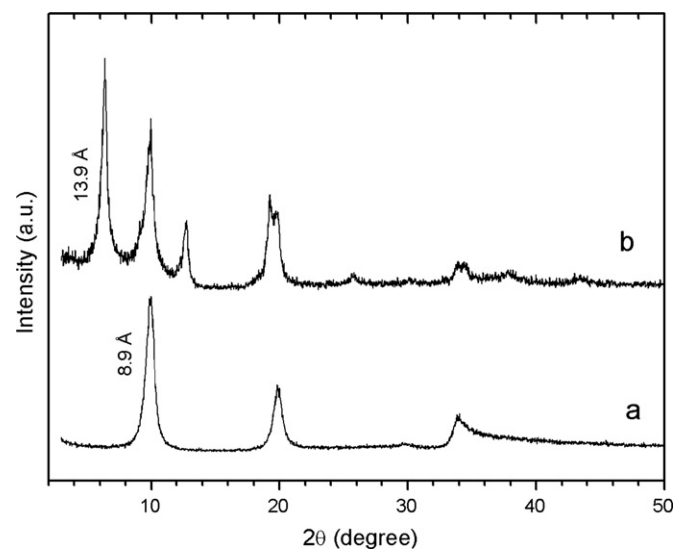


Fig. 2. X-ray diffraction patterns of the LDH precipitated with (a) 14% NH_4OH solution and (b) with ammonia discharged from the CVD reactor.

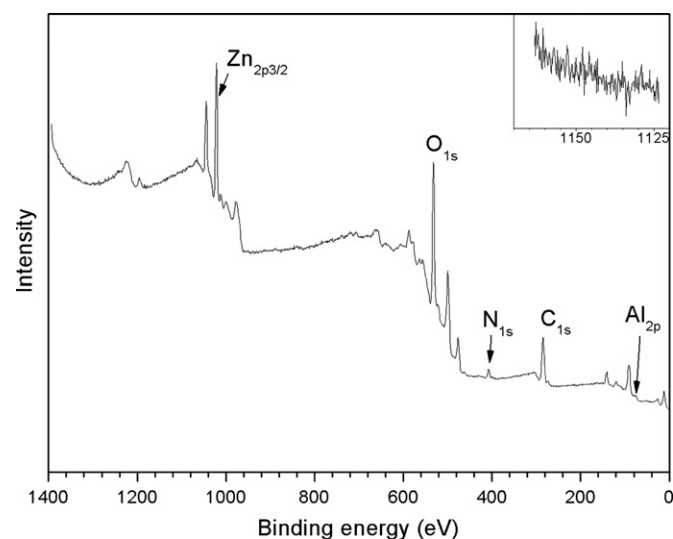


Fig. 3. Low resolution LDH-CVD XPS spectrum. Inset: high-resolution spectrum where gallium $2p_{1/2}$ and $2p_{3/2}$ bands were expected to appear.

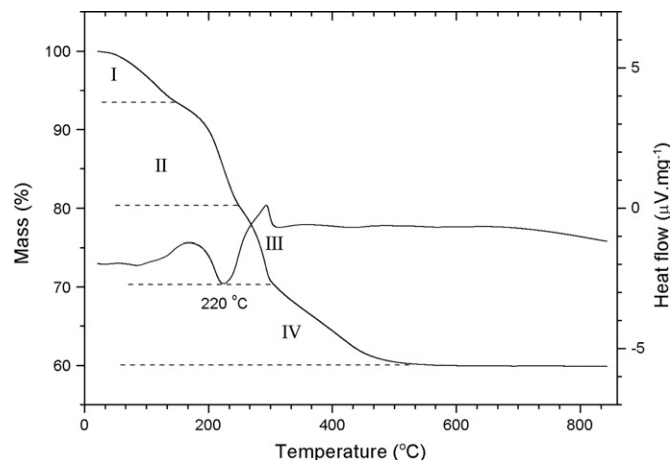


Fig. 4. Thermogravimetric profile of LDH precipitated with ammonia discharged from the CVD reactor.

Table 1

Thermal events and temperature intervals in the decomposition profile of LDH precipitated by bubbling ammonia from the CVD reactor.

| Event | Temperature (°C) | Mass loss (%) |
|-------|------------------|---------------|
| I | 25–158 | 6.8 |
| II | 158–253 | 13.9 |
| III | 253–313 | 8.5 |
| IV | 313–497 | 10.9 |

The 59.9% residue at the end of the TGA analysis is formed by a zinc/aluminum mixed oxide at a molar ratio of $\text{Zn}:\text{Al}=3$ according to the synthesis. Considering the general formula for LHD described in the introduction, the theoretical mass of OH and NO_3^- ions required to form a LDH structure is 34.3%, which is near to the sum of mass lost in events II, III and IV (33.3%). The intensity of the endothermic peak at 200 °C supports the release of anions from the layers. If this amount of mass justifies the amount of hydroxyl groups needed to maintain the layered structure and the nitrate to stabilize the layers' charge, then the 6.6% of mass in event I could include the extra species responsible for the expansion of the interlayer space.

If this is true, thermal event I should contain neutral species instead of counter-ions. Water is discarded since we have observed that LHDs dry well even at room temperature. Water is physisorbed on the outer surfaces of each crystallite or takes part in the hydration shell of intercalated nitrate anions. It is valid to suppose that a species is lost in the first thermal event, which is able to expand the interlayer space and is stable at the drying temperature (100 °C).

In principle, an anion different to nitrate was expected to be intercalated since different types of anions are retained between LDH layers during a co-precipitation [17].

The possibility of finding intercalated ammonium ions seemed not to be valid owing to their positive electric charge, which is the same charge in the LDH layers. On the contrary, if ammonia molecules were considered as ligands in a complex, these molecules would be lost within the temperature range of 80 and 130 °C [19] and this falls in the interval of event I.

3.4. Thermally treated samples

3.4.1. Infrared spectroscopy and X-ray diffraction

FTIR spectroscopy was used to explore the molecular composition of LDH-CVD and the derivative of a thermal treatment based on the first mass loss in the TG profile.

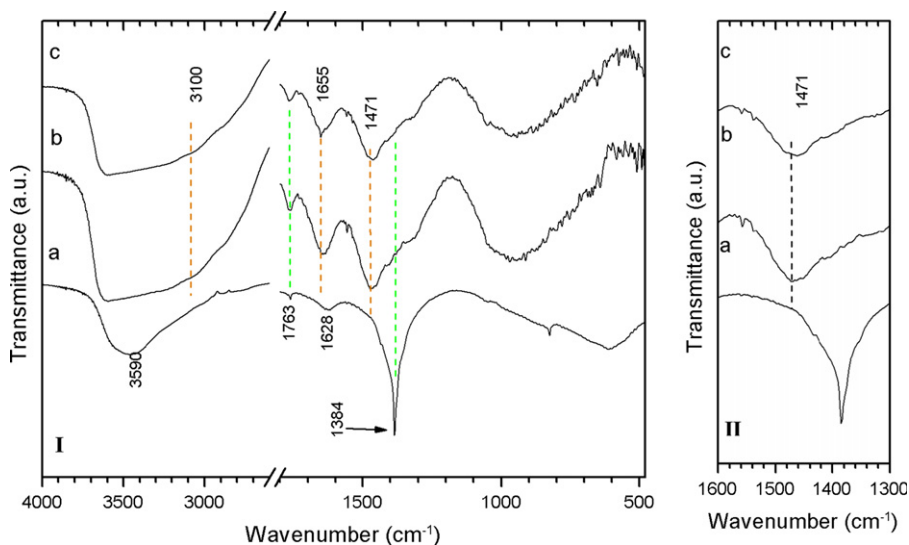


Fig. 5. (I) FTIR spectra of (a) the LDH precipitated with NH_4OH solution, (b) with discharged ammonia from the CVD reactor and (c) the product after heating to 150°C . (II) Zoom of the ammonia band at 1471 cm^{-1} .

First, the spectrum of the LDH prepared as reference with NH_4OH solution presented characteristic bands involving vibration of hydroxyls centered at 3400 cm^{-1} and one sharp intense band of nitrate at 1384 cm^{-1} which has been described elsewhere (Fig. 5-I-a) [20]. In addition, a peculiar band of very low intensity arises at 1763 cm^{-1} and belongs to a nitrate stretching [21]. This band can be seen in published spectra of layered materials containing nitrate [11], even though it has rarely been specifically described by the authors. This band supports the presence of nitrate ions in the next compounds, especially because it does not overlap with vibrational modes involving N–H bonds. The water bending mode is also seen at 1628 cm^{-1} with weak intensity.

The spectrum taken from the LDH sample precipitated with discharged ammonia (Fig. 5-I-b) also contains the bands assigned to OH and nitrate vibrations. Besides, intense broad bands arose at 3100 , 3000 , 1655 , 1471 and 1344 cm^{-1} , which can be directly assigned to N–H vibrations [22,23], so that the source can be either the ammonium ion (NH_4^+) or ammonia molecules (NH_3). Our previous hypothesis discarded the presence of ammonium owing to the positive charge, which is the same in the layers; nonetheless, if ammonia molecules react with acidic hydroxyls like Si–OH–Al in zeolites, a proton can be transferred to ammonia to form NH_4^+ , which is capable of reacting further with additional ammonia molecules to form a $[\text{NH}_4\cdot\text{NH}_3]^+$ dimer or $[\text{NH}_4(\text{NH}_3)_n]^+$ complex [23]. Although LDHs do not have acidic hydroxyls, water molecules present in the interlayer space that form a salvation shell for nitrate ions could be the proton donor to form NH_4^+ and then $[\text{NH}_4(\text{NH}_3)_n]^+$ species [22].

Among the N–H vibration bands, the one at 1463 cm^{-1} differentiates NH_4^+ from NH_3 molecules. Evidence for this statement was found by Micek-Ilnicka et al. [22] in experiments where an excess of ammonia molecules in a $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ lattice increases the intensity of this band due to the formation of a $[\text{NH}_4(\text{NH}_3)]^+$ dimer. Similarly, Datka and Góra-Marek [23] observed that a low excess of ammonia retained in a zeolite lattice presents a band at 1450 cm^{-1} and when the excess is higher, the intensity of the band increases and shifts to 1465 cm^{-1} .

The LDH precipitated with discharged ammonia presented an intense band at 1471 cm^{-1} (Fig. 5-II-b), which is near to that observed by the authors above, suggesting that a dimer or trimer $[\text{NH}_4(\text{NH}_3)_n]^+$ was allocated between the LDH layers. LDH-CVD was heated in a furnace at $10^\circ\text{C min}^{-1}$ up to 150°C and

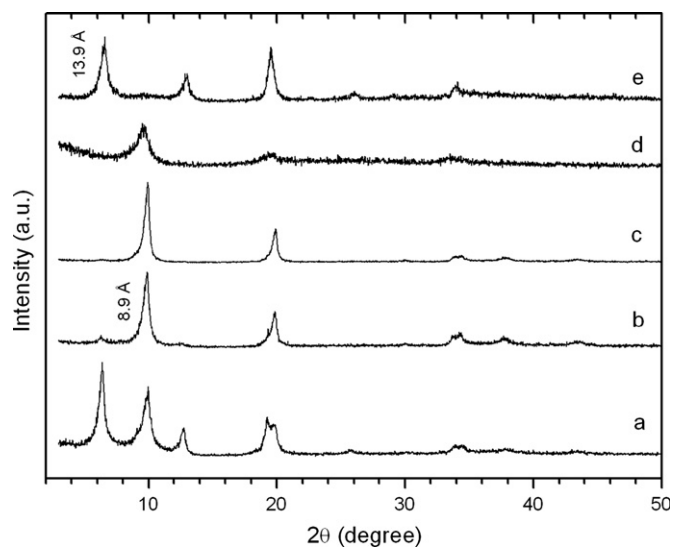


Fig. 6. X-ray diffraction patterns (a) of LDH-CVD, (b) of the reconstituted products after heating to 150°C , (c) or after stirring in acetone and (d) of samples precipitated with pure ammonia at pH 7 and (e) pH 10.

then analyzed by FTIR and X-ray diffraction. This temperature and rate correspond to event I in the TG profile. The X-ray diffraction pattern showed that the predominant 13.9 Å phase (Fig. 6a) was drastically reduced, leaving an almost pure compound with 8.9 Å basal distance (Fig. 6b), which is the common dimension for nitrate-containing LDH as described earlier. The reconstitution was also achieved by stirring the sample 24 h in acetone (Fig. 6c). This experiment evidenced that the chemical species responsible for the interlayer space expansion was lost in event I with the subsequent recovery of the nitrate-containing LDH structure. Therefore, since nitrate ions were not exchanged, the expansion of the interlayer space corresponds to an intercalation process of any ammonia molecular species.

The FTIR spectrum of the heated sample (Fig. 5-I-c) was similar to the fresh sample, but it should be considered that ammonia bands are intense even if residual ammonia is still present in the structure. The N–H vibrations are intense to a degree that hides nitrate bands, as seen earlier [24]. The presence of nitrate ions is confirmed with the band at 1763 cm^{-1} .

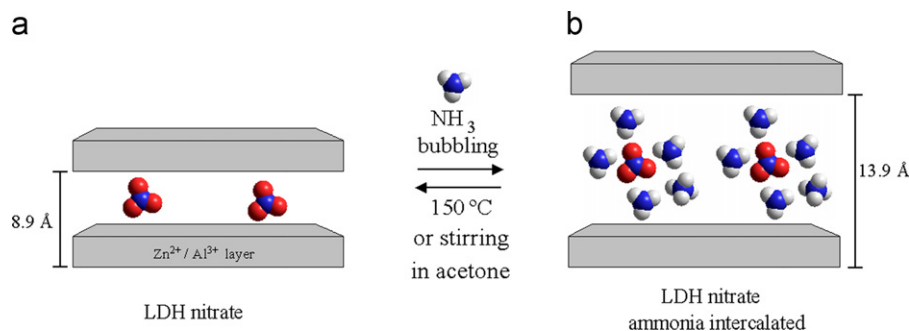


Fig. 7. (a) LDH structure with 8.9 Å basal space obtained at pH 7 with pure or residual ammonia from the CVD reactor, (b) If ammonia is bubbled until pH 10 is reached, the basal space increases to 13.9 Å.

Additional LDH samples were precipitated with pure ammonia in order to compare with LDH precipitated with residual ammonia from the CVD reactor. While the ammonia was bubbled into the solution, a sample of the precipitate formed at pH=7 was removed and the bubbling was stopped when pH=10 was reached. These two samples were dried at 100 °C for 20 h. The XRD pattern of the sample precipitated at pH=7 corresponds to the same LDH structure obtained by precipitation with ammonium hydroxide solution (Fig. 6d), which showed a basal spacing of 8.9 Å. The further bubbling of ammonia into the solution promoted formation of $[\text{NH}_4(\text{NH}_3)_n]^+$ species that expanded the interlayer distance, forming a phase with the basal distance of 13.9 Å (Fig. 6e).

Finally, the insertion of ammonia molecules in the interlayer space of the LDH without exchanging nitrate ions, and the release of this ammonia when the LDH is heated or stirred in acetone, lead to conclude that this reversible process is classified as an intercalation reaction *sensu stricto* according to the definition made by Bruce and O'Hare [13] as depicted in Fig. 7.

4. Conclusions

The ammonia discharged from the GaN synthesis by CVD, where metal gallium and NH₄Cl are also employed, is useful to precipitate LDH structures. The presence of gallium was not detected since the amount of this metal is small compared with the constant flux of ammonia and the reaction is designed to convert all the metal to GaN. The LDH structures precipitated at pH=7 had a conventional basal spacing of 8.9 Å. When ammonia was bubbled until pH=10 was reached, the LDH underwent intercalation of $[\text{NH}_4(\text{NH}_3)_n]^+$ species at the same time as nitrate ions were retained in the interlayer space of LDH giving a basal spacing of 13.9 Å. Ammonia was released from this expanded LDH by heating to 150 °C or by stirring in acetone, thus recovering the LDH structure that contains only nitrate ions (8.9 Å). This reaction can be classified as an intercalation reaction *sensu stricto*, since nitrate counter-ions are not being exchanged and this fact offers the possibility to consider LDHs as gas retainers.

On the other hand, GaN is synthesized nowadays by different CVD procedures, being the type of gallium reagents the main modification but the use of ammonia as source of nitrogen is

common; here we have shown that the precipitation of LDHs is an easy way to use this residue with the advantage that LDH can be further used in other applications or studies.

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