Intercalation studies of zinc hydroxide chloride: Ammonia and amino acids

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ABSTRACT

Zinc hydroxide chloride (ZHC) is a layered hydroxide salt with formula $Zn_5(OH)_8Cl_2 \cdot 2H_2O$. It was tested as intercalation matrix for the first time and results were compared with intercalation products of the well-known zinc hydroxide nitrate and a Zn/Al layered double hydroxide. Ammonia was intercalated into ZHC, while no significant intercalation occurred in ZHN. Aspartic acid intercalation was only achieved by co-precipitation at pH=10 with ZHC and pH=8 with zinc hydroxide nitrate. Higher pH resistance in ZHC favored total deprotonation of both carboxylic groups of the Asp molecule. ZHC conferred more thermal protection against Asp combustion presenting exothermic peaks even at 452 °C while the exothermic event in ZHN was 366 °C and in the LDH at 276 °C.

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1. Introduction

Layered hydroxide salts (LHS) also named layered basic salts or metal hydroxide salts are compounds with a structure comprised of layers where the center is occupied by divalent metal cations and the surfaces are composed of hydroxyl groups. In some cases, the OH sites are partially substituted by small anions like Cl^-, NO_3^- or CH_3COO^-. Another possibility is the substitution by water molecules, which leaves a charge residue in the layers that needs stabilization by anions located near to water molecules [1,2]. In this second category falls the structure of zinc hydroxide chloride and zinc hydroxide nitrate. Although each of these layered salts have different polytype structures, the easier phase to obtain at room temperature and atmospheric pressure is $Zn_5(OH)_8A_2 \cdot 2H_2O$, where $A=Cl^-$ or NO_3^-.

The anion exchange capacity of these two LHSs has been known for years [1,3], but the interest in using the hydroxide salts as intercalation matrices increased in the last 5 years, specifically regarding the intercalation of dicarboxylic acids [4,5], drugs [6], and dyes [7] to prepare drug delivery systems or polymer charges.

Among the LHSs, zinc hydroxide nitrate (ZHN) with formula $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ has been the most studied as intercalation matrix. Other LHS have been seldom intercalated like $Cu_2(OH)_3$ $CH_3COO \cdot H_2O$ [4].

On the other hand, zinc hydroxide chloride (ZHC) with formula $Zn_5(OH)_8Cl_2 \cdot 2H_2O$ was first synthesized by exchanging nitrate anions from the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ structure [1]. Both ZHN and ZHC belong to the IIb group according to the Louer

classification [2]; thus, the anion-exchange properties of ZHC are expected to be similar to those of ZHN. Despite this, there were no reports of intercalation into ZHC, only structural or thermal properties had been published [1,8,9].

The syntheses of LHS follows the procedures described for layered double hydroxides (LDH) like the typical precipitation of metal salts with alkaline solutions such as sodium hydroxide [4,7,10]. An indirect form of precipitation is the thermal decomposition of urea, which generates hydroxyl ions, thus increasing the pH of the reaction medium. The decomposition rate of urea is controlled by means of the temperature, and the crystals obtained by this method acquire normally large size and good crystal quality. Other recent method involves the precipitation with gaseous ammonia. This procedure allows the intercalation of ammonia molecules in addition to the presence of nitrate counter-ions [11].

Properties of LDHs are well-known, specially the anion-exchange capability has been widely explored and used to prepare new materials combining the features of the inorganic LDH matrices with those of the anions exchanged including metal complexes, dyes, pesticides, viruses, DNA and amino acids, among others. The interest to study LDH intercalated with biomolecules lies on the potentiality to act as reservoirs or delivery systems and molecules with carboxylic groups are easy to intercalate [12].

Despite the similarity between LDH and LHS structures, different behaviors towards intercalation or anion-exchange reactions could be found in structures with isomorphic substitution of some crystal sites. For instance, the compositional difference between ZHN and a Zn/Al LDH is the Al(III) ion and the former is more prone to undergo functionalization with carboxylic acids [13]. Similarly, LHSs could have different behaviors between

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isoestructural compounds with the same metal cation but different counter-ion. The aim of this work is to study ZHC as intercalation matrix with amino acids and ammonia molecules due to the lack of information about this salt as a host and compare the behavior with the parent ZHN structure (differing only in the counter-ion) and with a LDH containing Zn/Al layers.

2. Experimental

Two zinc hydroxide salts were synthesized for this study, namely zinc hydroxide chloride (ZHC) and zinc hydroxide nitrate (ZHN). In addition, a Zn/Al layered double hydroxide (LDH) was synthesized to be used as reference in the assessment of the intercalation products of the hydroxide salts.

2.1. Layered compounds precipitation

ZHC and ZHN were precipitated at room temperature from a solution containing 2.5 g of anhydrous $ZnCl_2$ or 5.0 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 100 mL of water. Then, 0.1 mol L^{-1} NaOH solution was added dropwise with stirring until pH$=$7 was reached. The suspensions formed were stirred for 2 h. Before washing of both hydroxide salts, 15 mL of each suspension were separated for the ammonia intercalation experiments.

The solution to precipitate LDH was prepared with 5.85 g $Zn(NO_3)_2 \cdot 6H_2O$ and 2.46 g $Al(NO_3)_3 \cdot 9H_2O$ in 200 mL of water. The Zn:Al molar ratio was equal to 3 and this was maintained for the co-precipitation experiments. The compound was precipitated with NaOH solution at pH$=$8 and stirred for 2 h.

The ZHC, ZHN and LDH solids were recovered by decantation and resuspended in distilled water to remove remaining ions. This washing was repeated three times, thereafter the solids were dried at 60 °C during 36 h.

2.2. Ammonia intercalation

Ammonia 99.999% was bubbled through a plastic rubber at a rate of 180 mL min^{-1} at room temperature into 15 mL of the freshly precipitated ZHC and ZHN suspensions. The products were labeled as ZHC-NH$_3$ and ZHN-NH$_3$, respectively. The final pH for ZHC-NH$_3$ was 10, while the sample of ZHN-NH$_3$ was bubbled up to pH$=$8 because zinc oxide is formed above this pH (personal observations). The samples were washed with water and dried at 60 °C for 24 h.

2.3. Amino acid intercalation assays

Amino acid intercalation was attempted by anion exchange and co-precipitation. Ion-exchange reactions were performed in 25 mL of aqueous solution containing the amino acids cysteine (Cys), aspartic acid (Asp) or glycine (Gly). The aspartic acid solubilization was improved in a mixture of 8 mL of acetone and 17 mL of water. Solutions were adjusted to pH$=$8 with NH$_4$OH 7% and then 0.2 g of the layered compounds (ZHN or LDH) were added and stirred at room temperature for 12 h. Solutions for ZHC were adjusted to pH$=$10.

Co-precipitations were conducted in 40 mL of water containing a metal salt and the amino acid with the amounts listed in Table 1. The addition of 8 mL of acetone was required to dissolve aspartic acid. NH$_4$OH was used to precipitate the solids. The washings were done with water for three times.

Table 1
Amount of reagents in solution to co-precipitate layered compounds with amino acids.

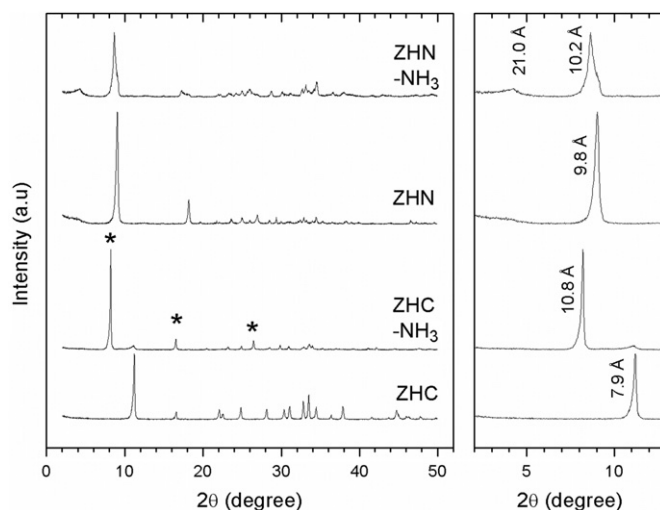| Attempted compound	$ZnCl_2$	$Zn(NO_3)_2 \cdot 6H_2O$	$Al(NO_3)_3 \cdot 9H_2O$	Cys	Asp	Gly
ZHC-Cys	0.552	–	–	0.108	–	–
ZHN-Cys	–	0.649	–	0.998	–	–
LDH-Cys	–	0.609	0.256	0.105	–	–
ZHC-Asp	0.537	–	–	–	0.112	–
ZHN-Asp	–	0.651	–	–	0.066	–
LDH-Asp	–	0.751	0.299	–	0.068	–
ZHC-Gly	0.608	–	–	–	–	0.167
ZHN-Gly	–	0.647	–	–	–	0.072
LDH-Gly	–	0.585	0.246	–	–	0.102

Fig. 1. X-ray diffraction patterns of ZHN and ZHC precipitated with NaOH solution and the products after bubbling ammonia into suspensions of these powders (ZHC-NH$_3$ and ZHC-NH$_3$).

2.4. Characterization

X-ray diffraction analyses were performed in a Philips X'pert-MDP diffractometer with CuKα radiation (1.5404 Å); the powder samples were placed on a glass holder and scanned at a step of 0.2° (2Θ) and 2 s of collection per step. Fourier-transformed infrared (FTIR) spectra were obtained with a Bruker Tensor 27 spectrometer in the transmittance mode. The samples were mixed with KBr to prepare pellets and collect the spectra in the transmittance mode with 32 scans and 4 cm^{-1} resolution. Simultaneous thermogravimetry and differential scanning calorimetry (TG/DSC) profiles were obtained in a TA instrument SDT Q600 under air atmosphere at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Matrix preparation and the effect of gaseous ammonia

The ZHC and ZHN precipitated with NaOH solution corresponded to the crystalline phases of $Zn_5(OH)_8Cl_2 \cdot 2H_2O$ (ICDD card 07-0155) and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (ICDD card 24-1460) (Fig. 1).

The products obtained from treatment with ammonia presented XRD profiles with basal spaces different from those of the pristine compounds precipitated with NaOH solution (Fig. 1). The increment in basal space had been previously observed in LDH

structures when precipitated with gaseous ammonia, and the reason was the intercalation of ammonium ions and ammonia molecules into the interlayer space [11]. A similar observation was made here: in ZHC the basal space increased from 7.9 Å to 10.8 Å with the ammonia treatment.

The XRD profile of ZHC-NH$_3$ is typical of a layered structure where the basal reflection appears at the lowest angle with the highest intensity and the reflections marked with asterisk correspond to interplanar distances with multiple values of the basal reflection [14]. Besides the basal reflection of the ZHC-NH$_3$ product a weak peak at 11.1° (2Θ) which matches with the most intense reflection of ZHC indicates a small amount of unreacted ZHC. The new compound evidences the ability of ammonia to diffuse through the ZHC layers and produce an intercalation compound.

The NaOH-precipitated ZHN showed a basal space of 9.8 Å, which after the ammonia treatment formed two crystalline phases: the main and unaltered phase with a basal distance of 9.8 Å and a secondary phase of very low intensity with a basal distance of 21.0 Å (see profile of ZHN-NH$_3$ in Fig. 1). Ammonia treatment of this ZHN-NH$_3$ was softer than for ZHC-NH$_3$, i.e. less amount of ammonia was bubbled because the nitrate structure is stable up to pH=8. If more ammonia is introduced, the pH increases and ZnO is formed; alternately, ZHC-NH$_3$ tolerates up to pH=10; thus more ammonia was introduced to increase the pH and also more molecular ammonia would be in the solution improving the intercalation into the ZHC matrix. The intercalated ZHC-NH$_3$ crystals are well-organized owing the narrow reflections of the XRD pattern.

To confirm the presence of ammonia in the intercalated products, the compounds were analyzed by FTIR spectroscopy. The ZHC matrix (Fig. 2) presented signals of Zn–O lattice vibrations at 519 cm^{-1}. The bands at 994, 876 and 704 cm^{-1} are associated to vibrational modes involving O–H moieties as evidenced earlier with deuterium (dashed lines in Fig. 2) [8].

All compounds presented an intense band around 3500 cm^{-1} corresponding to stretching modes of OH groups. The band is broad because the hydroxyls take part in hydrogen bonds with water molecules, counter-ions and probably hydroxyls in defect sites. Besides one sharp band is present at 3567 cm^{-1}; this is very intense in ZHC and weak in the other compounds. The sharpness indicates the stretching mode has a specific vibrational frequency,

and it can be associated to OH groups not involved in hydrogen bonds which are found in well-organized layered crystals like clays [15].

After the ammonia treatment, N–H vibrational modes appeared in three regions: a broad band from 3200 to 3000 cm^{-1}, at 1630 cm^{-1} (overlapped with water modes) [16,17] and at 1420 cm^{-1} [18] (solid lines in Fig. 2). Ammonia molecules in the interlayer space of ZHC-NH$_3$ promotes formation of hydrogen bonds with OH groups in the lattice widening and shifting the bands below 1000 cm^{-1}, while the band at 3500 cm^{-1} became broader and overlapped the N–H band at 3200 cm^{-1} and O–H at 3567 cm^{-1}.

Regarding the spectrum of ZHN, vibrations were also present at similar wavelength as those found in ZHC (dashed lines in Fig. 2); the most intense sharp band belongs to the stretching mode of the nitrate ion at 1384 cm^{-1}. The expositions to ammonia molecules produced the poorly intercalated compound (evidenced by XRD), despite this the FTIR spectrum of ZHN-NH$_3$ showed intense ammonia vibrations (solid lines), which can be explained with adsorbed ammonia molecules on the crystallites surface.

In this section, XRD and FTIR evidenced the intercalation of ammonia molecules and ammonium ions in the hydroxide salts, which was more efficient in the ZHC matrix. Considering that the intercalation in a LDH with nitrate is possible [11], the restriction to intercalate ammonia in ZHN is not limited by the nitrate ion, it rather depends on the chemical stability against pH like ZHC and the LDH, which can be treated with ammonia up to pH 10.

A last observation from the XRD profiles is the narrow reflections indicating the higher crystal quality of chloride salts (ZHC and ZHC-NH$_3$) than nitrate salts.

3.2. Amino acid intercalation

Intercalation studies with amino acids were performed considering the easiness to introduce molecules with carboxylic or carboxylate functional groups into layered compounds with hydroxylated layers [19], with the possibility to functionalize layers or at least, the ionized carboxylate form would remain close to the layers [12,13,20].

The attempts to intercalate amino acids into the layered structures were evaluated by comparing the basal distances of ZHC, ZHN and LDH matrices determined from the X-ray diffraction patterns with those of the products obtained by anion-exchange and co-precipitation.

The anion-exchange experiments in Gly and Asp solutions did not produce intercalated products; the XRD profiles of the powders contained the same diffraction profiles of the matrices, whereas the powders separated from the Cys solution corresponded to ZnO (zincite structure).

The restriction to intercalate Gly and Asp amino acids by anion exchange seems to be a steric matter. For example, succinic, glutaric and adipic acids were easily intercalated into ZHN by anion exchange [21]. The difference between the structure of succinic acid (HOOC(CH$_2$)$_2$COOH) and aspartic acid is the amino group in the alpha position. This group increases the volume of the molecule and requires greater expansion of the interlayer distances in ZHC, ZHN and LDH to be intercalated, i.e. higher activation energy is necessary to intercalate Asp than succinic acid.

Even with short molecules like Gly, intercalation was not possible under similar experimental conditions in which larger molecules like succinic, glutaric and adipic acids were intercalated [21]. Thus, steric restriction is a feasible explanation for the lack of intercalation of Asp and Gly into the three layered hosts.

To avoid the problem of the high energy needed to separate the layers of ZHC, ZHN and LDH, the co-precipitation method was followed because the formation of layers occurs in the presence of
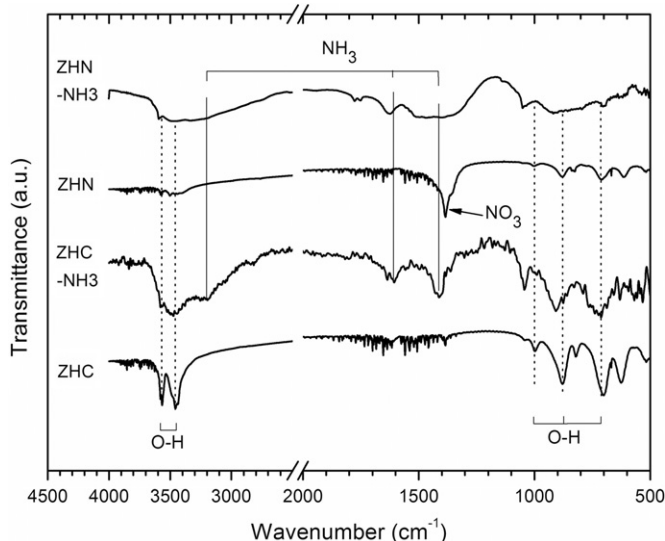

Fig. 2. FTIR spectra of ZHN and ZHC precipitated with NaOH solution and the products after bubbling ammonia into suspensions of these powders (ZHC-NH$_3$ and ZHN-NH$_3$).

amino acids and these could be trapped between the layers. This might be the reason why amino acid intercalation into LDHs has been done by co-precipitation [12] or by reconstruction [20].

The powders precipitated in Cys solutions corresponded to non-intercalated matrices with low crystal quality since the reflections of XRD profiles (not shown) were broad. For Cys intercalation, at least with LDH structures, the layers must be composed of Mg^{2+}/Al^{3+} cations [22]. The LDH containing zinc was not able to precipitate in Cys solution under the conditions employed in this study.

With respect to co-precipitation experiments with Asp, the products presented basal distances of 17.2 Å in ZHC, 17.5 Å in ZHN and 13.8 Å in LDH (Fig. 3). The maximum interlayer space available for the Asp molecule was determined by subtraction of the layer thickness (4.8 Å) from the basal distance [19] giving values of 12.3 Å, 12.7 Å and 9.0 Å for ZHC, ZHN and LDH, respectively, which is enough to allocate Asp. The LDH structures with Zn/Al composition are prone to allocate carboxylate ions in the interlayer space without functionalization [13], giving preference to the formation of organic monolayers, i.e. the ionized dicarboxylate remains hydrated between the layers [13] and for this reason the LDH product presented the lowest basal distance.

When LHS like ZHC and ZHN are intercalated with dicarboxylates, one carboxylic extreme could functionalize a layer while the other extreme would remain free and solvated with water [13]. In the present results, the interlayer space around 12.7 Å in ZHC and ZHN gives room to allocate two layers of Asp because the length of this amino acid is 5.6 Å; thus, a plausible arrangement comprises a bilayer of Asp molecules. Co-precipitation in Asp solutions seems to affect the crystal size of the three matrices regardless the intercalation. The XRD profiles in Fig. 3 have broader basal reflections (except for ZHC precipitated in Gly solution) than the profiles in Fig. 1, whereas the high angle reflections are not seen. The broadening related to reduction of crystal size is in agreement with the Scherrer equation.

The FTIR spectra of the Asp co-precipitation products (Fig. 4) presented an intense broad band at around 1550 and 1470 cm^{-1} of the carboxylate asymmetric and symmetric stretching modes typically reported for carboxylate-intercalated layered compounds [21,23,24], which rose due to ionization of the carboxylic groups. The carboxylate band at 1550 cm^{-1} is broad because near to this wavelength appear the water (1630 cm^{-1}) and N–H (1600 cm^{-1}) stretching modes [18], which also forms the wide
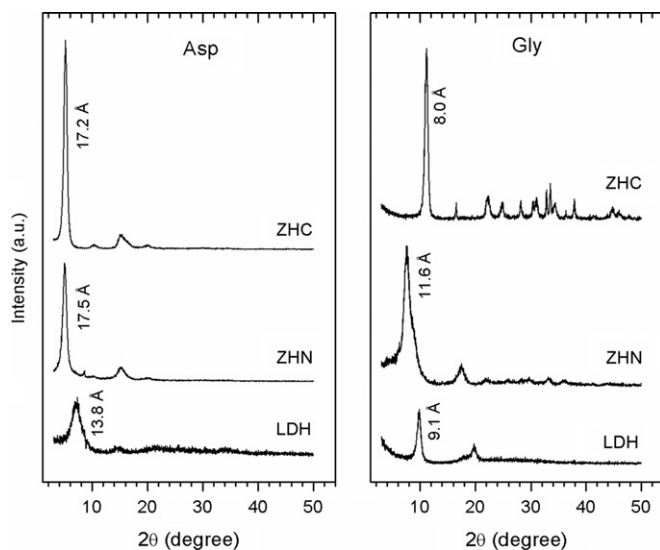

Fig. 3. XRD profiles of ZHC, ZHN and LDH derivatives co-precipitated in Asp and Gly solutions.
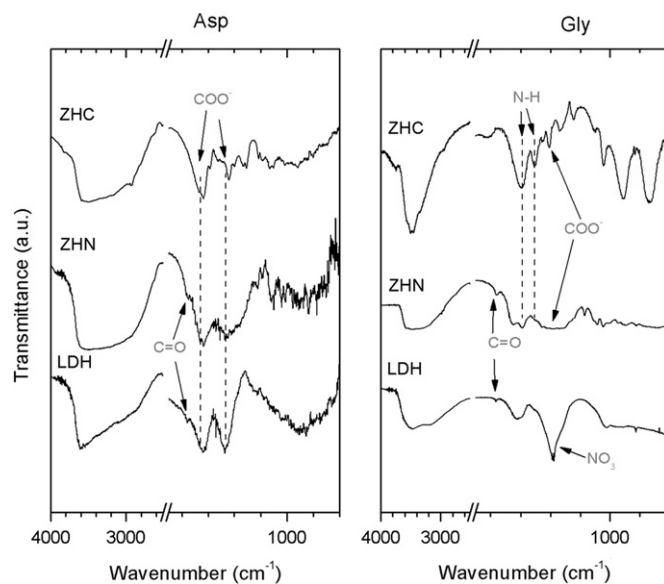

Fig. 4. FTIR spectra of ZHC, ZHN and LDH derivatives co-precipitated with Asp and Gly solutions.

band in the 2800–3100 cm^{-1} region [18] overlapping with the OH vibrations around 3400 cm^{-1}.

The Asp molecule has two carboxylic groups with pK_a of 2.1 and 3.86 so that the co-precipitation pH (8–10) was enough to deprotonate them. However, in the ZHN and LHD derivatives appeared a weak but detectable band at 1762 cm^{-1}, which is a value for the C=O stretching. For the carboxylate protonation to occur, the protonated $-NH_3^+$ group whose pK_a is 9.6 could be involved in the mechanism. The co-precipitation pH of ZHN and LDH was 8, thus is possible to find protonated amino groups and the further proton transfer to a neighboring carboxylate groups.

In the ZHC derivative, where the co-precipitation pH was 10 (since this compound tolerates higher pH conditions), the probability to find deprotonated amino groups is higher, reducing the possibilities to neutralize the carboxylates. This fact is congruent with the absence of the sharp band at 1762 cm^{-1} in the FTIR spectrum of ZHC with Asp (Fig. 4).

Gly was intercalated by co-precipitation only in ZHN resulting in a compound with a basal distance of 11.6 Å (Fig. 3). In LDHs, the intercalation of short amino acids seems to be difficult or does not produce evident enlargement of the interlayer space [25–27] as in the present experiment with the LDH. The unsuccessful intercalation of Gly in ZHC could be a result of a higher thermodynamic stability of the layers with chloride as the counter-ion than with Gly. This stability could be responsible for the high crystal quality of ZHC and ZHC-NH₃. Although Gly was not intercalated into ZHC, the FTIR spectrum showed bands at 1630, 1445 and 1380 cm^{-1} corresponding to the amino and carboxylate group of Gly in the ZHC structure (Fig. 4). These signals are explained by the adsorption of Gly molecules in the outer surfaces of ZHC crystallites. The adsorption of Gly also occurred on the LDH structure, but here the stretching band of the nitrate ion was more intense since this is the major component in the interlayer space in agreement with the basal distance determined by XRD. The FTIR spectrum of the Gly-intercalated ZHN presented very intense signals of ammonia and carboxylate vibrations since this product contains more Gly than in ZHC and LDH.

The identification of the protonated (–COOH) and ionized (–COO⁻) forms of the carboxylic group in intercalated amino acids is important to design further applications. Specifically for the Asp derivatives, both forms are possible if the co-precipitation pH is

controlled. The ionized state could be tested for immobilization of enzymes with preference for ionized surfaces, since layered materials can be used for this purpose [28,29]. The presence of carboxylic and amino groups in hybrid hydroxide salts seems also interesting to study the effects on compatibilization when these compounds are mixed in polymers to reinforce the mechanical properties [7].

Thermal analyses were done for Asp-intercalated ZHC, ZHN and LDH. As reference, it is known that the thermal decomposition of ZHC comprised two endothermic events [8,9], one between 150 and 200 °C involving dehydroxylation of the layers and the second around 500 °C for hydrolysis from $ZnCl_2$ to ZnO. These endothermic events have also been also seen in the decomposition of ZHN [21] and LDH. The Asp-intercalated hydroxide salts presented two additional exothermic peaks associated to combustion of organic matter once the analyses were conducted in air atmosphere. In the ZHC matrix Asp burns at 375 and 452 °C, while in ZHN the peaks appeared at 272 and 366 °C (Fig. 5).

At first sight, the temperatures were higher in the ZHC derivative. Taking into account the high crystallinity detected for ZHC products in comparison with ZHN or LDH, the ZHC layers would require more thermal energy to break the crystalline order and then decompose.

In the LDH structure the combustion of the Asp moiety produced an intense exothermic peak in the DSC profile with a simultaneous mass loss at 276 °C. This uncommon profile was repeated in this compound analyzed in triplicate. Regardless the reason of the abrupt burn the important observation concerning this study is the higher thermal stability of the Asp-intercalated ZHC retarding the combustion of the organic moiety up to 452 °C, which represents 176 °C more than the LDH derivative.

4. Conclusions

The ZHC and ZHN structures precipitated with NaOH solution at room temperature and atmospheric pressure were identified to have the compositions $Zn_5(OH)_8Cl_2 \cdot 2H_2O$ and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$. Of these layered structures, ZHC showed a higher crystal quality, which could be related to greater thermodynamic stability in the crystalline form. The ZHC product of ammonia (ZHC-NH$_3$) retained the crystal quality and was stable at pH=10, whereas ZHN resisted up to pH=8. ZHC presented differentiated intercalation properties. Ammonia was easier to intercalate in ZHC than in ZHN.

Intercalation of amino acids by anion-exchange was restricted by the amino group, which increases the volume of one extreme of the molecule and therefore, it requires more energy to expand the interlayer space in comparison with linear carboxylic acids, therefore co-precipitation was the best method to intercalate amino acids in ZHC, ZHN and LDH.

Unlike Cys and Gly, Asp was intercalated in ZHC and the product presented higher thermal stability than the ZHN and LDH derivatives. The combustion of Asp intercalated in ZHC occurred at 452 °C, while the highest exothermic event in ZHN was 366 °C and the single combustion event in the LDH occurred at 276 °C.

ZHC is recommendable as intercalation matrix owing to the good quality of the crystals, chemical stability and thermal resistance.

Acknowledgments
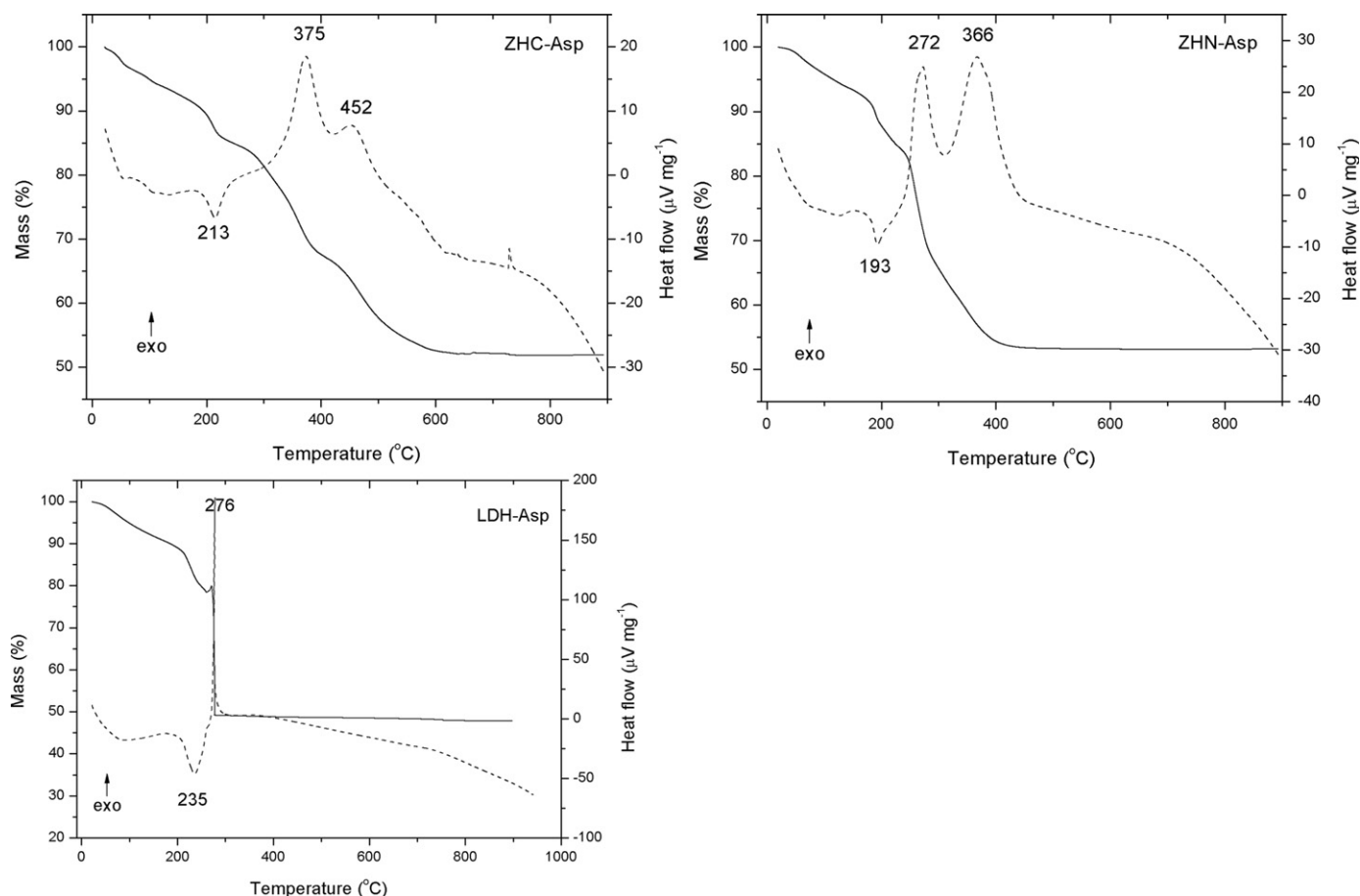
Fig. 5. TG (solid line) and DTA (dashed line) profiles of the Asp intercalation products in ZHC, ZHN and LDH.

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