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## ARTICLE

## Insight on the synthesis of LDH with urea method: morphology and intercalated anion control

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Layered double hydroxides (LDH) are a class of layered solids applied in many application fields. The study on synthetic methods able to control the interlayer composition and morphology of LDH is an open issue. The urea method, that exploits the thermal decomposition of urea, is known for yielding highly crystalline LDH in carbonate form. This form is highly stable and, to replace carbonate ions with more easily exchangeable anions, a second step is required. In this work, we modified the urea method to obtain MgAl and ZnAl LDH in chloride or nitrate form through a one-step synthesis. The effect of the urea/(Al+M(III)) molar ratio (R), reaction time and metal salt concentrations were deeply investigated. We found that LDH in chloride and nitrate forms can be prepared from solutions of metal salts not exceeding 1M by adjusting R and maintaining the reaction time at 48 hours. The morphology of these products was found to depend on the R value and on the metal salts used in the synthesis. High R value and nitrate salts favoured the formation of sand-rose crystals, while chloride salts induced the formation of plate-like crystals. The crystal growth mechanism and the parameters influencing the morphology are discussed with reference to ZnAl LDH by monitoring the synthesis over time.

## Introduction

Layered double hydroxides (LDH) are a fascinating class of lamellar solids characterized by the general formula  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A_{x/n}^{n-} \cdot mH_2O]$ , where M(II) and M(III) are divalent and trivalent metal cations, respectively, and  $A^{n-}$  are anionic species.<sup>1-3</sup>  $x$  can be defined as the M(III)/[M(II)+M(III)] molar ratio in the solid, and its value is generally in the 0.20 - 0.33 range. The LDH properties can be tuned by changing the nature of metal cations and of the intercalated anions, thus enabling their use in

various application areas such as catalysis, biomaterials,<sup>1,4-6</sup> energy storage and conversion,<sup>7</sup> polymer composites,<sup>8</sup> environmental pollution control.<sup>9-11</sup>

The design of materials for a specific application requires not only the preparation of compounds with an appropriate chemical composition, but also with suitable textural properties (i.e., surface area, micro- and/or meso-porosity), particle size, thickness and morphology, and selected intercalated anions.<sup>12</sup> In this connection, the development of new synthetic methods to obtain LDH with suitable dimensions and morphology of crystallites, and a desired intercalated anion, represents an open challenge to increase the potentiality of these materials. The most common synthetic route used to prepare LDH is the so-called co-precipitation method. This procedure was first investigated by Miyata<sup>13</sup> and consists in the simultaneous precipitation of the metal cations in hydroxide form, following the slow addition of a basic solution, such as  $NaHCO_3/Na_2CO_3$  buffer (precipitation at constant pH value) or NaOH solution (precipitation at variable pH). Furthermore, the precipitation may be carried out at low or high supersaturation degree according to the solution concentration and the rate of addition of the precipitating reagent. After complete precipitation, the solid is aged in the mother solution for a certain time, ranging from a few hours to several days. Poorly crystalline samples are generally obtained, unless a low degree of supersaturation and a relatively high temperature are maintained during the precipitation.<sup>1</sup> Aggregates of microcrystals with a plate-like

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† Supplementary Information available: [Details on the synthesis parameters of ZnAl LDH samples (Tables S1-S2). Crystallographic data and refinement details for ZnAlCO<sub>3</sub>, ZnAlNO<sub>3</sub> and ZnAlCl with added corundum as internal standard for the evaluation of the amount of the amorphous fraction (Tables S3-S6). Rietveld plot of the last refinement cycle for ZnAlCO<sub>3</sub>, ZnAlNO<sub>3</sub> and ZnAlCl (Fig. S1-S3). FT-IR of ZnAlCO<sub>3</sub> and ZAN/1 in the 4000-1500 cm<sup>-1</sup> spectral region of samples recovered at increasing times (Fig. S4). SEM images of ZACl/1, ZnAlCO<sub>3</sub> and ZAN/1 after 0, 2, 4 h of reaction (Fig. S5). EDX analysis on different points of ZACl/1, ZnAlCO<sub>3</sub> and ZAN/1 crystals collected after 6, 48 and 120 h of reaction (Fig. S6-S8). Details on the synthesis parameters of MgAl LDH samples (Tables S7-S8). XRPD patterns of MgAl LDH samples]. See DOI: 10.1039/x0xx00000x



morphology are commonly formed. However, LDH are obtained in carbonate form, except when the synthesis is carried out in a nitrogen atmosphere. In this case, LDH in chloride or nitrate form can be prepared.

Syntheses that include separate nucleation (formation of seeds) and aging (crystal growth) steps (SNAS)<sup>14-16</sup> or the precipitation in reverse micellae<sup>17-20</sup> were proposed to obtain LDH nanocrystals having dimension of 50 - 250 nm and plate-like morphology. These methods allow the insertion of transition metals,<sup>21</sup> such as Ir<sup>3+</sup>, and lanthanides<sup>22,23</sup> (i.e., Eu<sup>3+</sup>, Yb<sup>3+</sup>, Tb<sup>3+</sup> and Nd<sup>3+</sup>) in the brucite structure. The type of interlayer anion intercalated depends on the surfactant used to prepare the reverse micellae: when an anionic surfactant, like dodecylsulphate, is used, it normally remains intercalated in the precipitated LDH and it is very difficult to replace it, whereas, in the presence of a cationic surfactant, like cetyltrimethylammonium bromide, the LDHs are intercalated with bromide, an easily exchangeable anion.<sup>19</sup>

The sol-gel route allows the fabrication of LDH with the desired *x* value and different combinations of metal ions.<sup>24</sup> Recently, a new sol-gel method was proposed in which the LDH gel precursor was calcinated and the mixed metal oxide obtained were then rehydrated in water to reconstitute the LDHs structure.<sup>25,26</sup> This method produced nanoscale LDH with high specific surface area, although the crystallinity remained poor and there was no control over the intercalated anions. The crystallinity can be improved by subjecting the sample to further treatments like microwave irradiation,<sup>27</sup> sonication or hydrothermal treatments.

Other preparative routes, sometimes referred to as homogeneous precipitation, use hexamethylenetetramine (HMT),<sup>28,29</sup> or urea<sup>30-32</sup> that, upon hydrolysis, generate ammonia. The hydrolysis of HMT and urea at high temperature (60-100°C) increases the pH value, inducing the precipitation of a large amount of metal hydroxides. These methods provide well-defined hexagonal microcrystals with the required stoichiometry and generally lead to the formation of LDH in carbonate form. Rosette-like LDH microcrystals in carbonate form were obtained by a reduction of HMT (or urea) concentration,<sup>29</sup> whereas the substitution of carbonate with chloride and perchlorate anions resulted in materials having suitable anion-exchange and water permeability characteristics.<sup>33</sup> Flower-like MgAl-CO<sub>3</sub> were obtained by a solvothermal method in a mixed solution of ethylene glycol and water using urea as precipitating reagent.<sup>34</sup> A systematic decreasing of the urea concentration in a solution of nitrate salts of zinc and aluminum was

used to prepare LDH directly in nitrate form.<sup>35</sup> Table 1 shows the synthetic conditions used by several authors to prepare LDH via the urea method such as urea/(Al+M(II)) molar ratio (R), reaction time, concentration of the metal salts and temperature. Noteworthy is the prevalent formation of LDH in carbonate form despite the different synthetic conditions used. In addition, from the literature data, the comprehension of the parameters driving the synthesis towards the formation of LDH with anions other than carbonate is not straightforward. The direct synthesis of LDH with easily exchangeable anions is very advantageous for applications that imply ion-exchange reactions. Therefore, in this work, the effect of various synthetic parameters were investigated with the aim of obtaining LDH in nitrate or chloride form directly in a one pot synthesis. The evolution of the samples over time was investigated to determine the crystalline phases, the composition and the morphology of the solids. Interestingly, different morphologies were obtained according to the salt type, chloride or nitrate, used.

## Experimental

### Materials

Urea (Percent Purity, 98+%), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Percent Purity, 98%), ZnO (Percent Purity 99.5+%), Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Percent Purity, 98%), MgCl<sub>2</sub>·6H<sub>2</sub>O (Percent Purity, 98+%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Percent Purity, 98+%) and AlCl<sub>3</sub>·6H<sub>2</sub>O (Percent Purity, 98%) were purchased from Thermo Fisher Scientific and were used without further purifications. All the other reagents were supplied by Sigma-Aldrich.

### Synthesis of ZnAl and MgAl LDH with different urea/(Al+M(II)) molar ratio

ZnAl LDH were prepared starting either from solution of nitrate or chloride metal salts. As far as the preparation of zinc chloride solution, ZnO was used. Specifically, to prepare a solution 0.5 M of ZnCl<sub>2</sub> 40.7 g of ZnO were suspended in 500 mL of deionized water and concentrated hydrochloric acid was added under stirring to dissolve almost all the solid (80 mL). The complete dissolution of ZnO was performed by adding, under stirring, 1 M HCl and monitoring the pH of the solution that has to be in the range of 4.2 to 4.3. Finally, the solution was brought to 1 L with deionized water adjusting the pH above reported.

**Table 1.** Synthetic conditions used to prepare LDH with the urea method.

Salt	R	M(II)	Reaction time (h)	[M(II)+M(III)]	phase	T(°C)	Ref.
NO <sub>3</sub>	0.58-4	Mg	24	0.15	CO <sub>3</sub>	140 <sup>(c)</sup>	29
NO <sub>3</sub>	3-10	Mg	18-48	1	CO <sub>3</sub>	90-100	31
NO <sub>3</sub>	2.5	Mg	20	0.5	CO <sub>3</sub> /NO <sub>3</sub>	90	36
NO <sub>3</sub>	7	Zn	24	0.15	CO <sub>3</sub>	100	37
NO <sub>3</sub>	4	Mg	96	0.01-0.5	CO <sub>3</sub>	90-120 <sup>(c)</sup>	38
NO <sub>3</sub>	3.3-3.5 <sup>(a)</sup>	Zn	10-124	0.5	NO <sub>3</sub>	90	35
NO <sub>3</sub>	5 <sup>(b)</sup>	Mg	6	-	CO <sub>3</sub>	160 <sup>(c)</sup>	34
NO <sub>3</sub>	2.3-9.2	Mg, Zn, Ni	30	0.9	CO <sub>3</sub>	95	39
Cl	2-3.5	Mg	24	0.5	CO <sub>3</sub>	120 <sup>(c)</sup>	40
Cl	4	Zn	24	0.6	Cl	100	41

<sup>(a)</sup>The synthesis was carried out in the presence of 1 M NH<sub>4</sub>NO<sub>3</sub>. <sup>(b)</sup>Solvent: ethylene glycol: H<sub>2</sub>O = 9:1. <sup>(c)</sup>In a closed vessel.



Volumes of 0.5 M aqueous solutions of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solutions were mixed in order to obtain an  $\text{Al}/(\text{Al}+\text{Zn})$  molar ratio in solution ( $\gamma$  in the following) equal to 0.30. Finally, solid urea was added to the previous solution in order to reach an  $\text{urea}/(\text{Al}+\text{Zn})$  molar ratio ( $R$  in the following) equal to 3, 1.8, 1.2 (the samples were labelled as: ZAN/3, ZAN/2, ZAN/1). The synthesis was carried out under magnetic stirring at reflux temperature in an open flask for 24 h. Additional samples with  $R=1.8$  and 1.2 were precipitated from a solution containing 0.5 M  $\text{KNO}_3$ ; these samples were named ZAN/2s and ZAN/1s.

The previous procedure was repeated by using 0.5 M aqueous solutions of  $\text{ZnCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  and  $R=1.2$  (ZACI/1).

MgAl LDH were prepared as follows: starting from 0.5 M aqueous solutions of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) and  $R=1.8$ , samples named MAN/2 and MACI/2 were prepared. The syntheses were carried out under magnetic stirring, at reflux temperature and in an open flask for 48 h.

The solids were separated by centrifugation (5000 rpm for 10 min), washed with water until the neutrality of the washing water (at least  $3 \times 100$  mL) and dried under vacuum at 75% of relative humidity (RH).

The reaction time and the amount of salts and urea used to prepare about 5 g of the LDH described in this paragraph are reported in Table S1.

#### Synthesis of ZnAl and MgAl LDH with different concentration of metal salts

The synthesis of ZAN/1 and MAN/2 were carried out by using concentration of metal salts equal to 1, 2, and 2.5 M and refluxing the solution in an open vessel for 48 h. The recovered samples were named ZAN/1-M and MAN/2-M (with  $M=1, 2, 2.5$ ). The solids were separated by centrifugation (5000 rpm for 10 min), washed with water until the neutrality of the washing water (at least  $3 \times 100$  mL) and dried under vacuum at 75% RH.

The volumes of metal solutions used to prepare about 5 g of the LDH described in this paragraph are reported in Table S2.

#### Synthesis of ZAN/1, ZACI/1 and $\text{ZnAlCO}_3$ at different reaction times

$\text{ZnAlCO}_3$  was prepared as previously reported.<sup>30</sup> Briefly, volumes of 0.5 M  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solutions were mixed in order to obtain a  $\gamma$  value equal to 0.30 and solid urea was added in order to obtain  $R=3$ . The volumes of metal solutions used to prepare about 5 g of  $\text{ZnAlCO}_3$  are equal to those used for ZAN/3, Table S1. The final solution was kept under magnetic stirring at reflux temperature in an open flask for 72 h.

The syntheses of ZAN/1, ZACI/1 and  $\text{ZnAlCO}_3$  were repeated and the precipitating solutions were maintained at reflux temperature in an open flask for 5 days. Small samples were taken at set times of 0, 2, 4, 6, 20, 24, 28, 48, 120 hours after the beginning of the precipitation process, which was assumed to start when the mixed solution became cloudy ( $t=0$ ). The mother liquors were filtered, and the pH was monitored by a pH-meter provided with a glass electrode.

Each sample was separated by centrifugation (5000 rpm for 10 min), washed with water until the neutrality of the washing water (at least  $3 \times 100$  mL) and dried under vacuum at 75% RH.

#### Analytical Procedures

XRPD patterns were recorded by a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) in Bragg-Brentano geometry, equipped with a Lynxeye XE-T position sensitive detector,  $\text{CuK}\alpha$  radiation operating at 40 kV and 40 mA, with a step size  $0.0170^\circ 2\theta$ , and step scan 20 s. The phase identification was performed by using the Bruker DIFFRAC.EVA V5 software equipped with COD database. Quantitative phase analyses were performed with the Rietveld method with the help of the GSAS-II<sup>42</sup> and Bruker-AXS TOPAS V6.0 software packages.

Metal analyses were performed by ICP with a Varian Liberty Series spectrometer. 20 mg of ZnAl LDH, or MgAl LDH, was first dissolved in concentrated  $\text{HNO}_3$  and de-ionized water until a final volume of 100 mL. The solution, properly diluted, was analyzed by ICP.

The morphology of the samples was investigated with a transmission electron microscope (TEM, Philips 208) and with a scanning electron microscope (SEM, FEG LEO 1525). For the TEM images, a small drop of the aqueous dispersion was deposited on a copper grid precoated with a Formvar film and then evaporated in air at room temperature. SEM micrographs were collected after depositing the dry samples on a stub and sputter coating with chromium (8 nm of thickness). Measurements were performed with an acceleration voltage of 15 kV and a working distance from 3 to 1.5 mm using an In-lens detector. The images were collected at different magnification, from  $\times 10\text{K}$  to  $\times 100\text{K}$ . The elemental mapping of samples was carried out by using energy-dispersive X-ray spectroscopy (EDX) supported by a field emission scanning electron microscope. Measurements were performed with an acceleration voltage of 15 kV and a working distance of 8 mm using a secondary electron detector. The images were collected at different magnification, from  $\times 10\text{K}$  to  $\times 80\text{K}$ .

Nitrogen adsorption and desorption isotherms were performed using a Micromeritics ASAP 2010 analyser. Prior the analysis, the samples were degassed overnight under vacuum at  $80^\circ\text{C}$ . Brunauer-Emmett-Teller (BET) analysis of the data was used to calculate specific surface area.

FT-IR of different samples, dispersed in KBr pellets, were recorded at room temperature using a Bruker IFS113V spectrometer. Typically, each spectrum was obtained at a resolution of  $1\text{ cm}^{-1}$  in the  $370\text{--}5000\text{ cm}^{-1}$  spectral region.

#### Results and discussion

The urea method was properly modified to prepare ZnAl and MgAl LDH directly in nitrate or chloride form. With this aim, some synthetic parameters, i.e. the  $\text{urea}/(\text{Al}+\text{M}(\text{II}))$  molar ratio, the reaction time and the concentration of the metal salts, were finely tuned. In the following, the effect of each parameter on the composition and morphology of ZnAl LDH will be mainly discussed. Some preliminary results for MgAl LDH systems will be also outlined.



### Effect of the urea/(Al+Zn) molar ratio

Syntheses of ZnAl LDH were carried out by using the nitrate salts of the metals and varying R. The total concentration of metal ions was set at 0.5 M, the  $\gamma$  value was kept at 0.30 and the reflux time was 24 h. Table 2 shows the R value, the presence of added  $\text{KNO}_3$ , the Al/(Al+Zn) molar ratio in the solid (F), and the phases formed as detected by XRPD. From these data it is clear that the R value affects the anionic form of the LDH obtained: high R values favour the formation of the carbonate form, while low R values tend to produce the nitrate or chloride forms, depending on the metal salt used for the synthesis. Furthermore, the presence of added  $\text{KNO}_3$  does not seem to affect this trend.

The compounds consisting of a single phase at XRPD analysis, were characterized for their Al content; the found F values fell in the 0.2–0.33 range, which is typical of a pure LDH phase. Rietveld refinements of these phases (entries 1, 5, and 6 in Table 2) based on literature structural model<sup>43</sup> confirmed our attribution. Furthermore, additional quantitative analyses based on the Rietveld method, devoted to the determination of the amount of the amorphous fraction of the samples were performed. For this aim, weighed amounts of crystalline corundum, as internal standard, were added to the above samples and the fraction of the amorphous phase was determined as reported in Ref. 44. It resulted that the three samples contained a negligible amount, less than 3% w/w, of amorphous phase, and therefore they can be considered as pure crystalline phases (see SI for details for the Rietveld refinement results). For these samples it is clear that the F values coincide with x in their formula.

These experiments show that when  $R=1.2$ ,  $\text{ZnAlNO}_3$  is obtained as a pure crystalline phase after 24 h of reaction (sample ZAN/1, entry 5 in Table 2). Moreover, it was found that these synthetic conditions produce pure ZnAlCl starting from the chloride salts of the metals (sample ZACl/1, entry 6 in Table 2).

**Table 2.** Effect of R on the formation of ZnAl LDH in nitrate and chloride form. Reaction condition: 0.5 M of metal ions,  $\gamma = 0.30$ , temperature: reflux.

Entry	Sample	R	Reaction time (h)	Added salt [0.5 M]	F ( $\pm 0.01$ )	Phases <sup>(a)</sup>
1	ZAN/3	3	24	-	0.33	$\text{CO}_3$
2	ZAN/2	1.8	24	-	-	$\text{NO}_3/\text{CO}_3$
3	ZAN/2s	1.8	24	$\text{KNO}_3$	-	$\text{NO}_3/\text{CO}_3$
4	ZAN/1s	1.2	24	$\text{KNO}_3$	0.40	$\text{NO}_3$
5	ZAN/1	1.2	24	-	0.32	$\text{NO}_3$
6	ZACl/1	1.2	24	-	0.32	Cl

<sup>(a)</sup>Crystalline phases observed by XRPD

### Effect of the concentration of metal salts

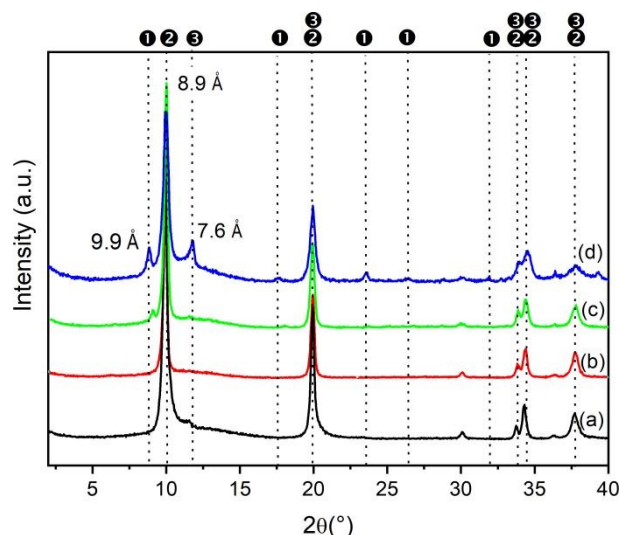
It was also interesting to study the effect of the concentration of metal salts on the formation of LDH containing anions other than carbonate. Increasing the metal concentration opens up the

possibility to prepare large quantities of LDH in small volumes of solution. In this connection, the phases formed in the synthesis of  $\text{ZnAlNO}_3$  were investigated at increasing concentrations of metal nitrate salts. Fig. 1 shows the XRPD patterns of the solids obtained by using Zn(II) and Al(III) solutions at different concentrations and keeping fixed the R value (as reported for ZAN/1) and the reaction time at 48 h.

ZnAl compounds precipitated from solutions with the concentration of metals ranging from 0.5 to 1 M consisted of a single phase with an interlayer distance of 8.9 Å that can be attributed to the nitrate phase. In contrast, when the metal concentration exceeded 2 M, reflections of a new phase (first reflection at 9.9 Å) appeared next to the nitrate phase at XRPD analysis. By comparison with the literature data, this phase can be attributed to  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (COD ID: 2106442) and could not be converted back into LDH phase even when the reaction time was increased (data not shown).

The composition of the samples consisting of a pure phase was determined by ICP and is shown in Table 3. For metal salt concentrations equal to 0.5 M and 1 M, (samples ZAN/1 and ZAN/1-1) the F values, 0.29 and 0.33, respectively, are typical of an LDH phase, and are close to the aluminum molar fraction in solution ( $\gamma$ ). Summarizing the results of these experiments, the best conditions to obtain a pure crystalline  $\text{ZnAlNO}_3$  phase with a high yield were: ion concentration 1 M,  $R = 1.2$ , time 48 h under reflux.

The effect of the concentration of metals was also evaluated in terms of surface area of the pure LDH samples. Table 3 reports the surface areas of the solids degassed at 80°C overnight. Changes in the synthetic parameters did not lead to major modifications in the measured surface areas.



**Fig. 1** XRPD patterns of ZnAl LDH synthesized by using  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  salts with concentrations: 0.5 M (a); 1 M (b); 2 M (c); 2.5 M (d).  $R=1.2$ , reaction time 48 h at reflux temperature. ①  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , ②  $\text{ZnAlNO}_3$ , ③  $\text{ZnAlCO}_3$ .

**Table 3.** Effect of the concentration of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  salts on the formation of LDH in nitrate form.  $R = 1.2$ ,  $\gamma = 0.30$ , reflux time: 48 h.



Sample	[Zn+Al] in solution	F	B.E.T. surface area (m <sup>2</sup> /g)	Phase <sup>(a)</sup>
ZAN/1	0.5	0.29	12	NO <sub>3</sub>
ZAN/1-1	1	0.33	10	NO <sub>3</sub>
ZAN/1-2	2	-	-	Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O/NO <sub>3</sub>
ZAN/1-2.5	2.5	-	-	Zn <sub>5</sub> (OH) <sub>8</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O/NO <sub>3</sub> /CO <sub>3</sub>

<sup>(a)</sup>Crystalline phases observed by XRPD

### Mechanism of ZnAl LDH formation: effect of the reaction time on the sample composition and morphology

#### Structural and chemical composition

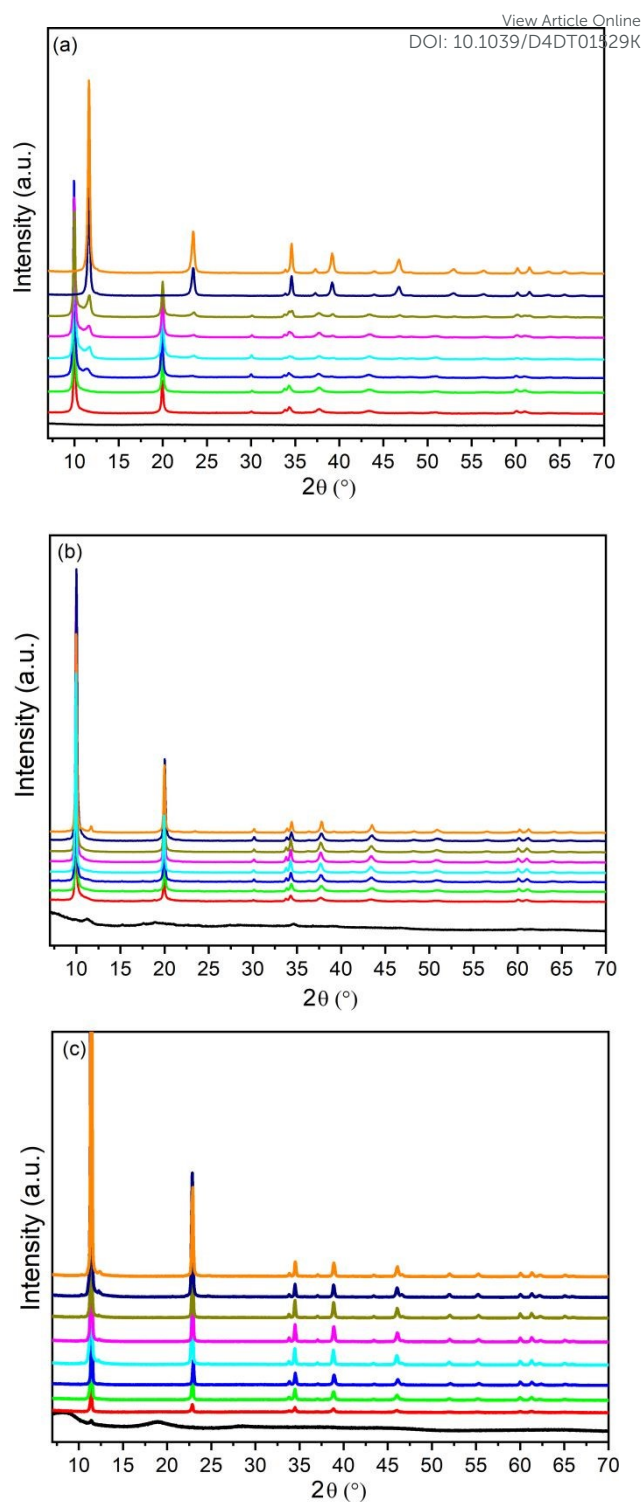
The effect of reaction time on the composition of ZAN/1 and ZACI/1 samples was investigated. These results were compared with that of ZnAlCO<sub>3</sub> prepared by the classical urea method (R = 3) from nitrate metal salts. Samples of ZnAlCO<sub>3</sub>, ZAN/1 and ZACI/1, recovered at increasing intervals, were characterized by XRPD, FT-IR and ICP.

Fig. 2 shows the evolution over the time of the XRPD patterns of the solids obtained during the synthesis of ZnAlCO<sub>3</sub>, ZAN/1 and ZACI/1. The moment the solution turned into a white colloidal dispersion was set as 0 h. The three series show very different behaviors.

For as concerns the synthesis of ZnAlCO<sub>3</sub> (starting from nitrate salts, and R = 3, Fig. 2a), the first precipitate (time 0) consisted in an amorphous material (black line in Fig. 2a), while the diffraction peaks characteristic of LDH in nitrate form ( $d = 8.9 \text{ \AA}$ ) appeared after 2 hours and became sharper over time, indicating an increase in crystallinity. Starting from about 6 h of reaction, a second basal peak at  $d = 7.6 \text{ \AA}$ , that was attributed to the LDH in carbonate form, appeared. The intensity of this peak increased, while that relating to the nitrate form decreased over time, indicating that first, LDH precipitated by incorporating the nitrate anions of the starting metal salts, then the pristine nitrate phase gradually converted into the carbonate one as the carbonate concentration in solution increased due to the degradation of urea. The  $a$  and  $b$  lattice parameters of nitrate and carbonate phases were found in good agreement with the literature data<sup>43</sup> over time, indicating that very likely, the molar fraction of metals remained unchanged, as also confirmed by ICP analysis (Table 4).

When the synthesis conditions of ZAN/1 were used, a small peak ascribed to the carbonate phase appeared only after 120 h of reaction (Fig. 2b). However, in the first 6 h, the F value, obtained by ICP, was found much larger than 0.33, the characteristic  $x$  value of an LDH phase, suggesting the presence of aluminum-rich amorphous phases. The pure nitrate phase was observed between 24 and 48 h (Table 4).

Fig. 2 (c) shows the time evolution of the XRPD patterns for the ZACI/1 system. In this case, the pure chloride phase ( $d = 7.76 \text{ \AA}$ ) was obtained and maintained throughout the duration of the synthesis. As with ZAN/1, after 120 hours of reaction, a very low reflection appears, due to the carbonate phase. The broadening of diffraction peaks was found to reduce with time, suggesting a progressive increase in crystal size and/or a reduction in lattice defects in the sample.



**Fig. 2** XRPD of ZnAlCO<sub>3</sub> (R=3) (a); ZAN/1 (b) and ZACI/1 (c) samples recovered at the increasing times (0 h, black ; 2 h, red line; 4 h, green line; 6 h, blue line; 20 h, cyan line; 24 h, pink line; 28 h, olive line; 48 h, navy line; 120 h, orange line). Reaction conditions: concentration of metal ions 0.5 M,  $y = 0.30$ , temperature: reflux.

At time 0, the precipitate was completely amorphous and the high F value suggests the presence of aluminum rich phases, that were present up to 4 h of reaction. After 6 h, F reached the value of 0.33



and the unit cell parameters were consistent with literature data,<sup>43</sup> indicating the formation of the pure LDH phase. By prolonging the contact of the precipitate with the mother liquor, both unit cell parameters and *F* remained unchanged and only an improvement of crystallinity of the sample occurred. These results confirm that the urea method could be used to obtain LDH with a good crystallinity and containing anions other than carbonate in the interlayer region directly from the synthesis.

In order to get more information on the evolution of the samples during the synthesis, FT-IR spectra were collected (Fig. 3). In the first precipitate (0 h) of all the samples, three broad bands centred at 966, 740 and 584  $\text{cm}^{-1}$  are detected and can be attributed to AlOH deformations and AlOH translations, attesting the presence of amorphous oxohydroxides of alumina.<sup>45</sup> Moreover, multiple bands are observed in the 1300-1500  $\text{cm}^{-1}$  region that can be assigned to both nitrate (at around 1390  $\text{cm}^{-1}$ ) and carbonate anions (between 1450 and 1300  $\text{cm}^{-1}$ ). The position of the carbonate bands depends on the environment surrounding the anions.<sup>46</sup> The bending mode of hydrogen bonded water ( $\nu_2$ ) with carbonate and nitrate is displayed at 1650  $\text{cm}^{-1}$  in Fig. 3 (a) and (b); this mode is shifted towards lower wavenumbers, about 1635  $\text{cm}^{-1}$ , in the sample precipitated from the chloride salts (Fig. 3 (c)) given the contribute of weak hydrogen bonds between the water molecules and the chloride anions.<sup>1</sup>

Over time, in the 800-400  $\text{cm}^{-1}$  region, the bands of amorphous aluminum compounds are replaced by several Al-OH and Zn-OH translation modes,<sup>47</sup> positioned at about 427, 551, 612 and 697  $\text{cm}^{-1}$ , that suggest the formation of LDH as observed by XRPD. The region 1300 and 1500  $\text{cm}^{-1}$  of FT-IR spectra provides information on the composition of the interlayer region during the synthesis. Regarding the  $\text{ZnAlCO}_3$  samples recovered after 6-24 h of reaction, this region (Fig. 3 (a)) reveals the presence of three superimposed bands, one sharp and two broad. The first is ascribable to  $\nu_3$  mode of nitrate (1384  $\text{cm}^{-1}$ ) and the others to the  $\nu_3$  mode of carbonate that is split in two bands at 1354 and 1434  $\text{cm}^{-1}$ . This splitting is due to a decrease in the symmetry of the

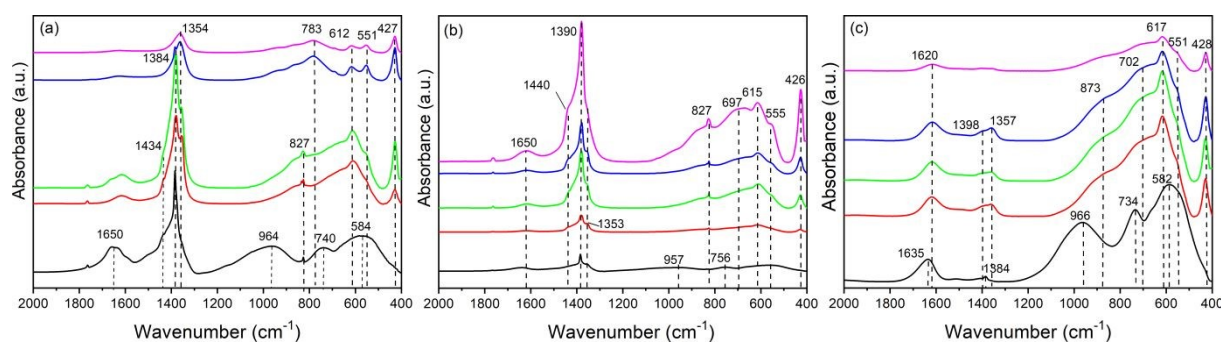
reaction time exceeds 48 h, the  $\nu_2$  and  $\nu_3$  modes of nitrate disappear and the  $\nu_3$  mode of carbonate is centred at 1354  $\text{cm}^{-1}$ . In ZAN/1 (Fig. 3 (b)) the nitrate bands are always more intense ( $\nu_3$  mode at 1390  $\text{cm}^{-1}$  and  $\nu_2$  mode at 827  $\text{cm}^{-1}$ ); these signals may be due to either LDH in nitrate form or zinc hydroxide nitrate ( $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ), the latter can precipitate in the first stage of the synthesis (see after). The bands at 1353  $\text{cm}^{-1}$  and 1440  $\text{cm}^{-1}$  are related to the traces of carbonate most likely adsorbed on the surface up to 48 h, after that, as observed by XRPD, the incorporation of carbonates also involves the interlayer region.

As regard the ZACI/1 sample, Fig. 3 (c) shows that the solids contains mainly chloride anions with very low amount of carbonate anions (bands at 1384, 1357 and 1398  $\text{cm}^{-1}$ ). The bending mode of water ( $\nu_2$ ) at 1620  $\text{cm}^{-1}$  attests the presence of water weakly bonded due to the formation of less hydrogen bonds.

In the 4000-1500  $\text{cm}^{-1}$  spectral region of the  $\text{ZnAlCO}_3$  and ZAN/1 samples, reported in Fig. S4, some bands with very low intensity are detected; these signals are ascribable to intermediate products formed during the urea hydrolysis like cyanate, isocyanate, biuret and carbamate.<sup>52,53</sup> In particular the band at 2212  $\text{cm}^{-1}$  in the  $\text{ZnAlCO}_3$  until 24 h can be assigned to isocyanate  $\text{N}=\text{C}=\text{O}$ <sup>54</sup> that decomposes to carbonate after 48 h. Bands in the region 2200-2500  $\text{cm}^{-1}$  can be assigned to physisorbed  $\text{CO}_2$ .<sup>55</sup>

From FT-IR it can be inferred that after 48 h of reaction all the samples are constituted by pure LDH in carbonate, nitrate or chloride form depending on the synthetic parameters selected. An in-depth analysis on the composition of the samples coupled with the XRPD and FT-IR data allowed further insights into the mechanism of LDHs formation.

Fig. 4 shows the trend of the pH of the mother liquor and of Al molar fraction in the solid during the different syntheses. In each case, the sample at 0 h contained mainly Al, and by comparing this result with the XRPD and IR spectra, it can be deduced that the solids were mainly constituted by amorphous aluminum hydroxide,<sup>29,36</sup> the percentage of which increased as follows: ZAN/1 <  $\text{ZnAlCO}_3$  < ZACI/1. The higher is the amount of aluminum hydroxides precipitated at 0



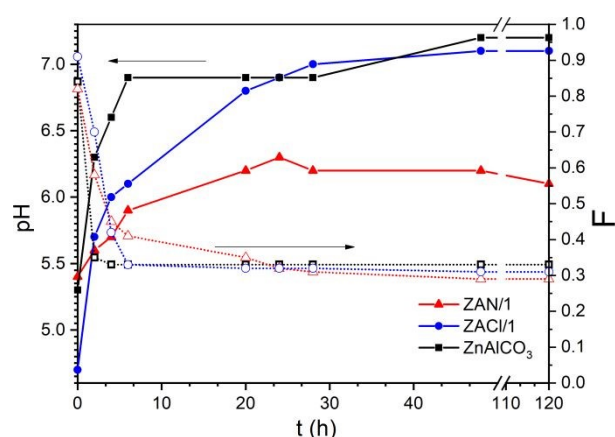
**Fig. 3** FT-IR spectra of  $\text{ZnAlCO}_3$  (R=3) (a); ZAN/1 (b) and ZACI/1 (c) samples recovered at increasing times (0 h, black line; 6 h, red line; 24 h, green line; 48 h, blue line; 120 h, magenta line). Reaction conditions: concentration of metal ions 0.5 M,  $\gamma = 0.30$ , temperature: reflux.

carbonate ion upon the interactions with water molecules.<sup>48,49</sup> Moreover, the samples also show the  $\nu_2$  mode of nitrate<sup>50</sup> at 827  $\text{cm}^{-1}$ . From the initial stage (time 0), the intense adsorption band of nitrate (1384  $\text{cm}^{-1}$ ) is progressively replaced by the absorption band of carbonate ions (1354  $\text{cm}^{-1}$ ), as proved by XRPD.<sup>28,47</sup> When the

h, the lower is the pH of the solution due to the higher consumption of  $\text{OH}^-$  groups. However, while the pH of  $\text{ZnAlCO}_3$  and ZACI/1 increased very quickly with a change of 1.9 and 2.4 pH units in 48 h, respectively, ZAN/1 showed a slow pH increase with a change of only 0.9 units.







**Fig. 4** pH of the reaction solution (solid lines) and F (Al/(Zn+Al) molar fraction in the solid, dashed lines) collected during the synthesis for the indicated samples.

Concerning the composition, after a few hours of reaction, the solids were clearly enriched in Zn ions, achieving the molar fraction typical of LDH. Note that an Al molar fraction,  $F$ , compatible with the existence of pure LDH ( $0.2 \leq x \leq 0.33$ ), for all the samples, was obtained when the pH of the mother liquor was greater than 6.1. This value, in the case of  $\text{ZnAlCO}_3$  and  $\text{ZACl/1}$ , was reached in 4 and 6 h respectively, from the beginning of the reaction; whereas  $\text{ZAN/1}$  reached pH 6.3 in a longer time (20 h) and maintained this value for the whole duration of the synthesis. This value is one unit lower than the pH recorded in the  $\text{ZACl/1}$  and  $\text{ZnAlCO}_3$  preparation. These findings suggest that the formation of LDH requires a pH higher than 6 and that the rate at which the system reaches this value depends on the concentration of urea and on the metal salt used: chloride or nitrate. In  $\text{ZnAlCO}_3$ , the high urea concentration caused an increase in the urea hydrolysis rate with a consequent increase in pH. The  $\text{ZAN/1}$  and  $\text{ZACl/1}$  samples were prepared with the identical urea concentration but different salts, nitrate and chloride respectively. The different trend of the pH value during the synthesis should be sought in the nature of the anion. Another important parameter to consider is the amount of precipitated metals. The content of Zn and Al was also determined in the mother liquor; these analyses confirmed the data shown in Fig. 4.  $\text{Al}^{3+}$  precipitated very quickly and, at time 0, was already absent in the solution. As a consequence, only the percentage of Zn in the mother liquor at different times was determined. These data indicate that after 6 h the  $\text{Zn}^{2+}$  precipitated in  $\text{ZAN/1}$  is higher than that precipitated in  $\text{ZACl/1}$ : very likely, the formation of amorphous zinc hydroxide nitrate occurs and maintains the pH around 6. It was reported that freshly prepared  $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  has buffering properties, maintaining the pH of the solution at 6.1, in agreement with the pH value found during the synthesis of  $\text{ZAN/1}$ .<sup>56</sup> During the time, both aluminum hydroxide and zinc hydroxide nitrate were converted in LDH. After 28 hours, the amount of  $\text{Zn}^{2+}$  in solution

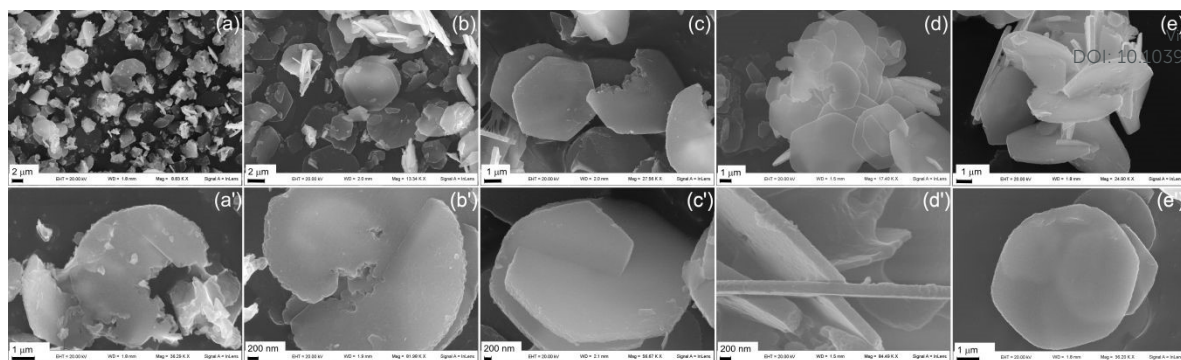
was very low and maintained a constant value. At this time, LDH had a stable composition, while the crystallinity, in terms of size and order of crystals, was increased by prolonging the contact time with the mother liquors.

#### LDH morphology

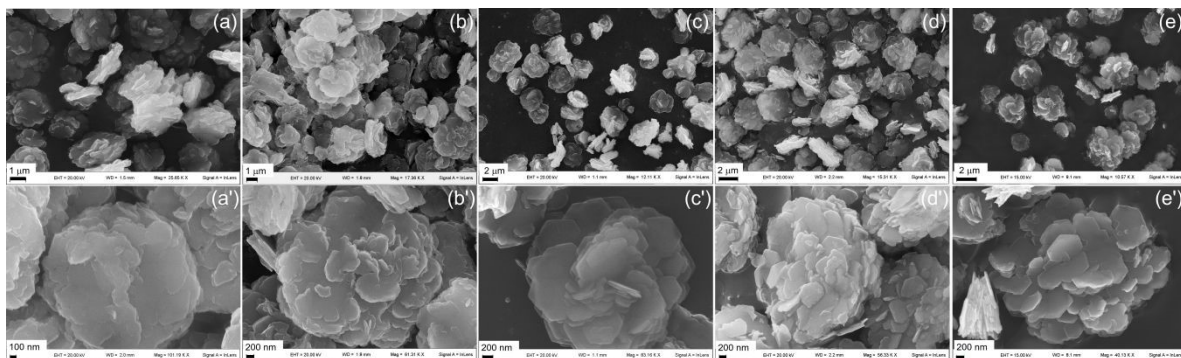
The samples recovered at increasing reaction times were investigated by SEM and TEM. XRPD, FT-IR and ICP data indicated that the first precipitate, at 0 h, for all the investigated series ( $\text{ZnAlCO}_3$ ,  $\text{ZAN/1}$  and  $\text{ZACl/1}$ ), consisted mainly of amorphous aluminum hydroxide, suggesting that it acted as crystallization seed, in agreement with literature data.<sup>29,37,57</sup> SEM images of samples at 0 h are reported in Fig. S5 (a,b,c) and show the presence of amorphous aggregates. At time 2 and 4 h in  $\text{ZACl/1}$  no formation of definite particles is detected (Fig. S5 d,g), even if the XRPD showed the presence of chloride phase of LDH. Conversely, in  $\text{ZnAlCO}_3$  and  $\text{ZAN/1}$  flower-like particles appeared with the largest size of about 3–5  $\mu\text{m}$  (Fig. S5 e,h and f,i), in the latter, the flower-like crystals were combined with platelet particles with dimension of about 200 nm. As the reaction time increased, a different crystal growth was observed in the systems investigated, that requires a separate discussion.

Fig. 5 displays the evolution of  $\text{ZACl/1}$  crystals which resemble those found by Okamoto et al.<sup>29</sup> Flat semi-circular crystals, covered by some smaller crystals, appeared after 6 h of reaction. Punctual EDX elemental analysis (reported in Fig. S6 (a,b)) showed that  $F$  of the larger crystals was about 0.43–0.45, which is a higher value than that to of an ideal LDH indicating an excess of  $\text{Al}^{3+}$  in the structure. Conversely, in smaller crystals the  $F$  ranged from 0.25 to 0.33 suggesting, in some crystals, the presence of an excess of  $\text{Zn}^{2+}$ . With the time, some semi-circular crystals grew to give single hexagonal platelets with 5–7  $\mu\text{m}$  size (Fig. 5 e'), while other fused together to form aggregates of hexagonal platelets (Fig. 5 c',d',e). According to Okamoto, the growth starts from seeds of aluminum hydroxides, that act as LDH crystallization sites. The  $\text{Zn}^{2+}$  ions coming from the solution are adsorbed on aluminum hydroxides<sup>58</sup> and deplete the seeds with the formation of the LDH structure having chloride anions in the interlayer region and leaving a hole at the site of the seeds. Very likely, when the crystallization process starts from the same seed, the development of geminated flat crystals occurs (Fig. 5 b',c',d'). The formation of geminated crystals is expected to be favoured by a high ratio between zinc ions and aluminum hydroxide seeds. This situation is verified after 20 h, since the amount of precipitated zinc is 90% of the initial value, the pH of the solution is close to the maximum value reached by this system and supplies enough  $\text{OH}^-$  ions. By prolonging the reaction time, no more zinc ions precipitate and the growth of the crystals can be justified by a dissolution-reprecipitation mechanism. Indeed,  $F$ , determined by EDX (Fig. S6 (c-e)) in different point of the crystals collected after 48 and 120 h, is constant and ranges between 0.30 and 0.32.





**Fig. 5** SEM images at different magnification of ZACl/1 recovered after 6 (a,a'), 20 (b,b'), 28 (c,c'), 48 (d,d'), 120 (e,e') h of reaction.



**Fig. 6** SEM images at different magnification of ZnAlCO<sub>3</sub> recovered after 6 (a,a'), 20 (b,b'), 28 (c,c'), 48 (d,d'), 120 (e,e') h of reaction.

When the synthetic conditions of ZnAlCO<sub>3</sub> are applied, sand rose aggregates of the hexagonal platelets are observed, and this morphology is retained throughout the synthesis, also regarding the size of the aggregates (Fig. 6). In this case, due the high urea concentration, the pH of the solution increases to 6.9 in 6 h, leading to a massive precipitation of zinc ions that are adsorbed on the aluminum hydroxide and crystallize as LDH. The ratio between zinc ions and the aluminum hydroxide seeds is very high and several crystals can be formed from a single seed, yielding multiple geminated crystals. *F* values determined in different zones of the crystals collected during after 6, 48 and 120 h are always low and range from 0.26 to 0.29 (Fig. S7). These crystals consist in small flat hexagonal specimens of 500 nm, arranged in aggregates of 2-3 μm. Over time (after 28 h), the small crystals that form the sand rose aggregates take on a more definite hexagonal shape due to a crystallization process.

ZAN/1 shows a different behaviour: after 6 h, the formation of zinc hydroxide nitrate is assumed, beside the aluminum hydroxide. Fig. 7a and 7a' show the presence of flower-like particles of about 5 mm of diameter covered by small particles. Punctual EDX analysis (see Fig. S8 (a,b)) performed on the small particles show that they are richer in zinc ( $F=0.17-0.22$ ) while in the flower-like particles *F* ranges between 0.3 and 0.33, in agreement with the ICP data. The corresponding TEM image (Fig. 7a'') shows uniform particles. After 20 h the small particles are partially dissolved assuming a "C" shape as if they were consumed from the center (Fig. 7b and b'). The different texture of the small particles is highlighted by TEM in Fig. 7b'' and reflects the different chemical composition. The "C" shaped particles appear fibrous and some voids are present near them. After

28 h the morphology is similar to the previous one, the number of voids increase and the "C" shaped particles are decrease (Fig. 7 c,c,c'). Over 48 h, flower-like particles with lacy edges and holes on the surface are obtained (Fig. 7 d,d,d''), *F* is 0.29 (Fig. S8). Finally, after 120 h, combined flat crystals are formed, but smaller (2.5 μm) and more irregular than in the ZACl/1 case.

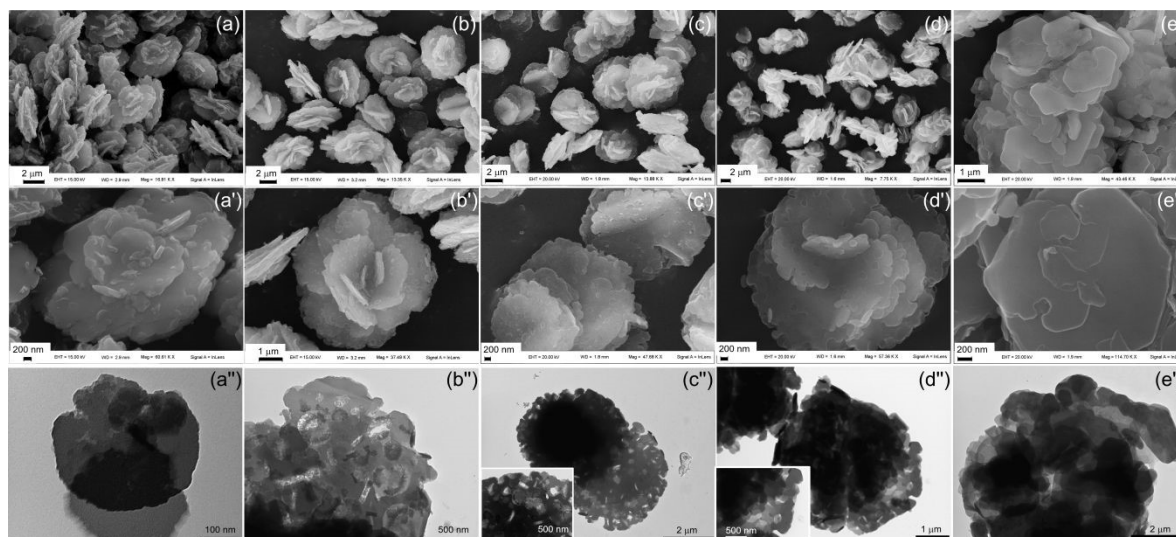
These findings suggest that both the aluminum hydroxide and zinc hydroxide nitrate phase are converted into LDH. The first acts as a crystallization seed, adsorbing the zinc ion deriving from the solution and the zinc hydroxide nitrate that dissolves during the synthesis. The ability of zinc hydroxide nitrate to release Zn<sup>2+</sup> or [Zn(OH)<sub>3</sub>]<sup>-</sup> under weakly acidic or basic conditions respectively, was reported in a recent work.<sup>56</sup> Upon the dissolution of the zinc hydroxide nitrate, particles holes are formed on the surface of LDH.

#### MgAl system

As far as MgAl LDH is concerned, the synthetic conditions used for ZnAl LDHs were not suitable to obtain LDHs in nitrate or chloride form; indeed, the low amount of urea used yielded quite amorphous materials after 24 h of reaction and the samples required longer reaction times to be converted into crystalline materials in carbonate form. Therefore, to prepare MgAlNO<sub>3</sub> and MgAlCl from nitrate and chloride salt solutions, respectively, it was necessary to increase the *R* value up to 1.8, and the reaction time up to 48 h (sample MAN/2 and MACl/2 of Table S7). This was probably due to the different solubility of zinc and magnesium hydroxides. Compared to the coprecipitation method, wherein NaOH is the alkaline agent and the pH of the solution is immediately very high (around 10), in



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**Fig. 7** SEM and TEM images at different magnification of ZAN/1 recovered after 6 (a,a', a''), 20 (b,b',b''), 28 (c,c',c''), 48 (d,d',d''), 120 (e,e',e'') h of reaction.

homogeneous syntheses, the hydrolysis of urea produces a slow OH<sup>-</sup> release. Therefore, the precipitation of M(II) and Al(III) hydroxides is not simultaneous and the formation of the LDH structure occurs through an intermediate step that involves the precipitation of aluminum hydroxide species.<sup>59,60</sup> Then, as the pH raises, divalent cations diffuse onto the aluminum hydroxide agglomerates and are adsorbed and incorporated on the surface, leading to the final LDH, either through surface growth or dissolution-reprecipitation mechanisms.<sup>31</sup> In this second phase, the solubility of the M(II) hydroxide species is crucial and, since the suitable pH for the precipitation of Mg(OH)<sub>2</sub> is higher than that of Zn(OH)<sub>2</sub>, more urea is required to assist the synthesis.<sup>61</sup>

Preliminary experiments (see SI) to elucidate the dependence of reaction time and salt concentration on this system have been carried out. From them, the best experimental conditions to obtain a crystalline MgAlNO<sub>3</sub> phase were the following: ion concentration 1 M, R = 1.8, time 48 h, under reflux, although the experimental analysis on the obtained solids showed the concomitant formation of a certain amount of amorphous phase (see SI for further detail). A deeper investigation will be required on the MgAl system.

## Conclusions

In this work, the reaction time, urea/(Al+Zn) molar ratio, and metal concentration were finely adjusted to obtain ZnAl LDH in a single step with the required anions in the interlayer region. In addition, the parameters affecting the morphology of the ZnAl in carbonate, nitrate and chloride form have been studied. The micrographs obtained showed two different morphologies: sand rose

aggregates, that are favoured by a high R value, and the presence of nitrate anions, while hexagonal platelet, that were obtained with low R values and the presence of chloride anions. In the future, similar studies will be applied to deeply investigate the MgAl LDH system.

## Author contributions

Conceptualization, M.N. and R.V.; Data curation and Methodology, M.N., R.V. A.D.M. and F.C. Validation, M.N., R.V; A.D.M. and F.C.; Investigation, M.N., M.B., E.B. and A.D.M.; Writing—original draft, M.N.; Writing—Review, M.N., R.V., A.D.M., E.B. and F.C.; Editing, M.N. and R.V.

## Conflicts of interest

There are no conflicts to declare.

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