Supporting Information

# Insight into the synthesis of LDH using the urea method: morphology and intercalated anion control

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**Table S1.** Reaction time and amount of salts and urea used to prepare about 5 g of LDH in nitrate and chloride form. The aluminium molar fraction: $y = 0.30$, temperature: reflux. The reactions were carried out in a 250 mL round flask equipped with a reflux condenser.

| Sample | R | $M(II)(NO_3)_2$ or $M(II)Cl_2$ 0.5 M (mL) | $Al(NO_3)_3$ or $AlCl_3$ 0.5 M (mL) | $KNO_3$ (g) | Urea (g) | Time (h) |
|---|---|---|---|---|---|---|
| ZAN/3 | 3 | 59.0 | 26.4 | - | 7.92 | 24 |
| ZAN/2 | 1.8 | 59.0 | 26.4 | - | 4.75 | 24 |
| ZAN/2s | 1.8 | 59.0 | 26.4 | 4.31 | 4.75 | 24 |
| ZAN/1s | 1.2 | 59.0 | 26.4 | 4.31 | 3.17 | 24 |
| ZAN/1 | 1.2 | 59.0 | 26.4 | - | 3.17 | 24 |
| ZACl/1 | 1.2 | 63.4 | 28.4 | - | 3.41 | 24 |
| MAN/2 | 1.8 | 78.0 | 35.0 | - | 6.36 | 48 |
| MACl/2 | 1.8 | 86.1 | 38.6 | - | 6.95 | 48 |

**Table S2.** Volumes of salt solutions, with different concentration, used to prepare about 5 g of LDH in nitrate form. The aluminium molar fraction: $y = 0.30$, temperature: reflux, reaction time: 48 h. The reactions were carried out in a round flask (100 ml when 1 M salt solutions were used; 50 mL when 2 M and 2.5 M salt solutions were used) equipped with a reflux condenser.

| Sample | $M(II)(NO_3)_2$ 1 M (mL) | $Al(NO_3)_3$ 1 M (mL) | $M(II)(NO_3)_2$ 2 M (mL) | $Al(NO_3)_3$ 2 M (mL) | $M(II)(NO_3)_2$ 2.5 M (mL) | $Al(NO_3)_3$ 2.5 M (mL) |
|---|---|---|---|---|---|---|
| ZAN/1-1 | 29.5 | 13.2 | - | - | - | - |
| ZAN/1-2 | - | - | 14.8 | 6.6 | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| ZAN/1-2.5 | - | - | - | - | 11.8 | 5.3 |
| MAN/2-1 | 43.1 | 19.3 | - | - | - | - |
| MAN/2-2 | - | - | 21.6 | 9.7 | | |
| MAN/2-2.5 | - | - | - | - | 17.2 | 7.7 |

**Table S3.** Crystallographic data for $ZnAlCO_3$, $ZnAlNO_3$, and ZnAlCl

| | $ZnAlCO_3$ | $ZnAlNO_3$ | ZnAlCl |
|---|---|---|---|
| Formula sum | $Zn_{0.67}Al_{0.33}(OH)_2(CO_3)_{0.165}\cdot 0.52H_2O$ | $Zn_{0.67}Al_{0.33}(OH)_2(NO_3)_{0.33}\cdot 0.55H_2O$ | $Zn_{0.67}Al_{0.33}(OH)_2Cl_{0.33}\cdot 0.75H_2O$ |
| FW / g $mol^{-1}$ | | | |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space-group | *C2/m* | *C2/m* | *C2/m* |
| *a*/ Å | 5.3253(4) | 5.3324(2) | 5.3383(2) |
| *b*/ Å | 9.2170(6) | 9.2359(4) | 9.2467(2) |
| *c*/ Å | 7.7816(6) | 9.0832(6) | 7.9712(3) |
| *β*/ deg. | 103.030(7) | 101.192(8) | 102.752(4) |
| Volume/$Å^3$ | 372.11(5) | 438.83(4) | 383.76(2) |
| *Z* | 8 | 8 | 8 |
| Calc. d. /g·$cm^{-3}$ | 2.68 | 2.45 | 2.65 |
| 2$\theta$ range /deg | 8-130 | 8-130 | 8-130 |
| 2$\theta$ step /deg | 0.010 | 0.010 | 0.013 |
| % $R_p$ [a] | 6.31 | 5.34 | 4.88 |
| % $R_{wp}$ [b] | 8.51 | 7.33 | 6.76 |
| wt% st | 24.70 | 31.80 | 30.20 |
| wt% st $_{(exp)}$ | 24.9(1) | 32.5(2) | 30.4(1) |
| wt% amorphous [c] | 0.8(6) | 2.9(8) | 1.1(7) |

[a] $R_p = \Sigma\,|I_o\text{-}I_c| \,/\, \Sigma\, I_o$; [b] $R_{wp} = [\Sigma\, w(I_o\text{-}I_c)^2 \,/\, \Sigma\, wI_o^2]^{1/2}$; [c] wt% amorphous = 100 / (100 - wt% st) × (1 - wt% st / wt% st $_{(exp)}$)

**Table S4.** Atomic coordinates for $ZnAlCO_3$.*

| Atom | Site mult. | x/*a* | y/*b* | z/*c* | Occ. |
|---|---|---|---|---|---|
| Zn | 4 | 0 | 0.3321 | 0 | 1 |
| Al | 2 | 0 | 0 | 0 | 1 |
| O1 | 8 | 0.8892 | 0.1386 | 0.1108 | 1 |
| O2 | 4 | 0.3292 | 0 | 0.1212 | 1 |
| C | 8 | 0.8397 | 0.6365 | 0.5116 | 0.125 |
| O11 | 8 | 0.9184 | 0.5127 | 0.4623 | 0.125 |
| O12 | 8 | 0.5962 | 0.6478 | 0.5163 | 0.125 |
| O13 | 8 | 0.9841 | 0.7539 | 0.5096 | 0.125 |
| Ow1 | 2 | 0.5 | 0 | 0.5 | 0.2184 |
| Ow2 | 4 | 0 | 0.1246 | 0.5 | 0.4144 |

**Table S5.** Refined atomic coordinates for $ZnAlNO_3$.*

| Atom | Site mult. | x/*a* | y/*b* | z/*c* | Occ. |
|---|---|---|---|---|---|
| Zn | 4 | 0 | 0.3411(5) | 0 | 1 |
| Al | 2 | 0 | 0 | 0 | 1 |
| O1 | 8 | 0.886(2) | 0.1531(7) | 0.1170(8) | 1 |

| | | | | | |
|---|---|---|---|---|---|
| O2 | 4 | 0.348(2) | 0 | 0.109(1) | 1 |
| N | 8 | 0.631(4) | 0.640(2) | 0.570(2) | 0.25 |
| O3 | 8 | 0.747(6) | 0.593(4) | 0.475(3) | 0.25 |
| O4 | 8 | 0.464(5) | 0.572(4) | 0.610(2) | 0.25 |
| O5 | 8 | 0.674(8) | 0.763(3) | 0.614(3) | 0.25 |
| Ow1 | 2 | 0.5 | 0 | 0.5 | 0.1 |
| Ow2 | 4 | 0 | 0.243(7) | 0.5 | 0.5 |

**Table S6.** Refined atomic coordinates for ZnAlCl.*

| Atom | Site mult. | x/*a* | y/*b* | z/*c* | Occ. |
|---|---|---|---|---|---|
| Zn | 4 | 0 | 0.3340(3) | 0 | 1 |
| Al | 2 | 0 | 0 | 0 | 1 |
| O1 | 8 | 0.8892 | 0.1386 | 0.1108 | 1 |
| O2 | 4 | 0.3292 | 0 | 0.1212 | 1 |
| Cl | 8 | 0.874(2) | 0.6134(6) | 0.499(1) | 0.25 |
| Ow1 | 2 | 0.5 | 0 | 0.5 | 0.3 |
| Ow2 | 4 | 0 | 0.12462 | 0.5 | 0.6 |

* Structural model from "Marappa, S.; Kamath, P. V., *Ind. Eng. Chem. Res.* **2015**, *54*, 11075–11079". The parameters without esds were not refined.

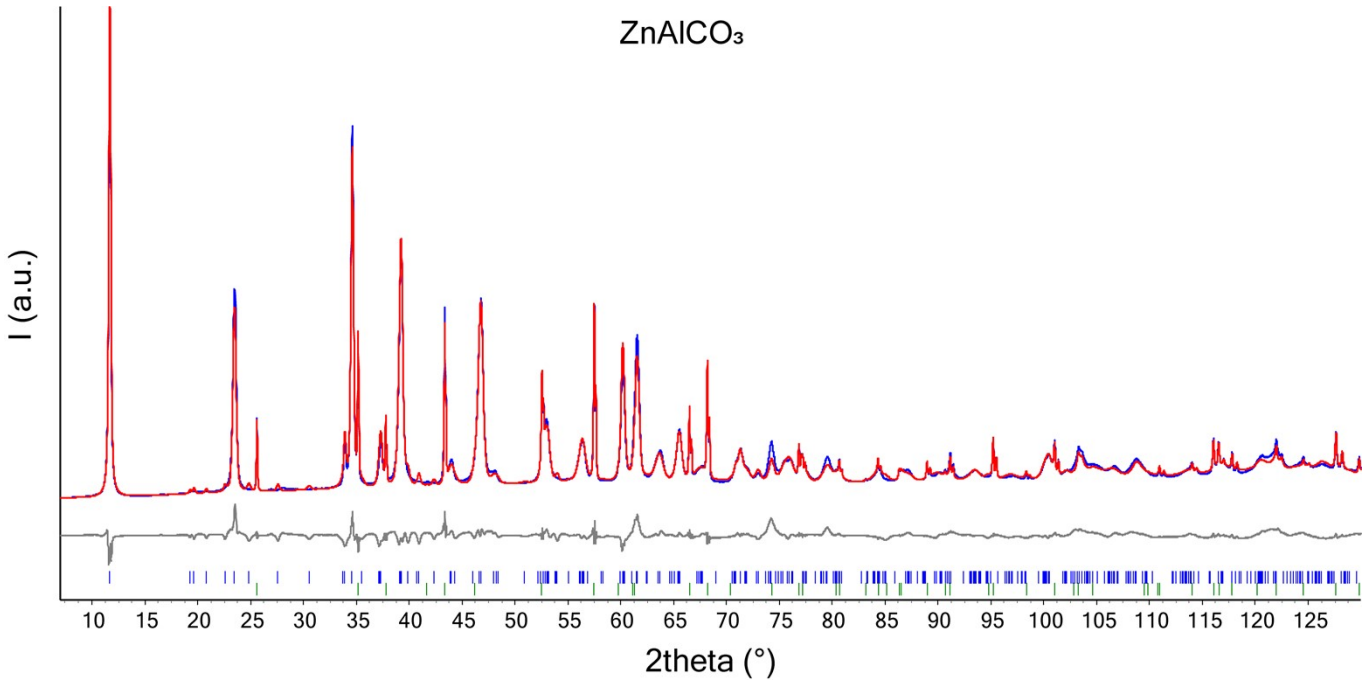



**Fig. S1.** Rietveld plot of the last refinement cycle for $ZnAlCO_3$ (reaction time: 120 h, blue marks) containing 24.70% w/w of corundum (green marks) as internal standard. Calculated profile (red), experimental pattern (blue) their difference (grey).

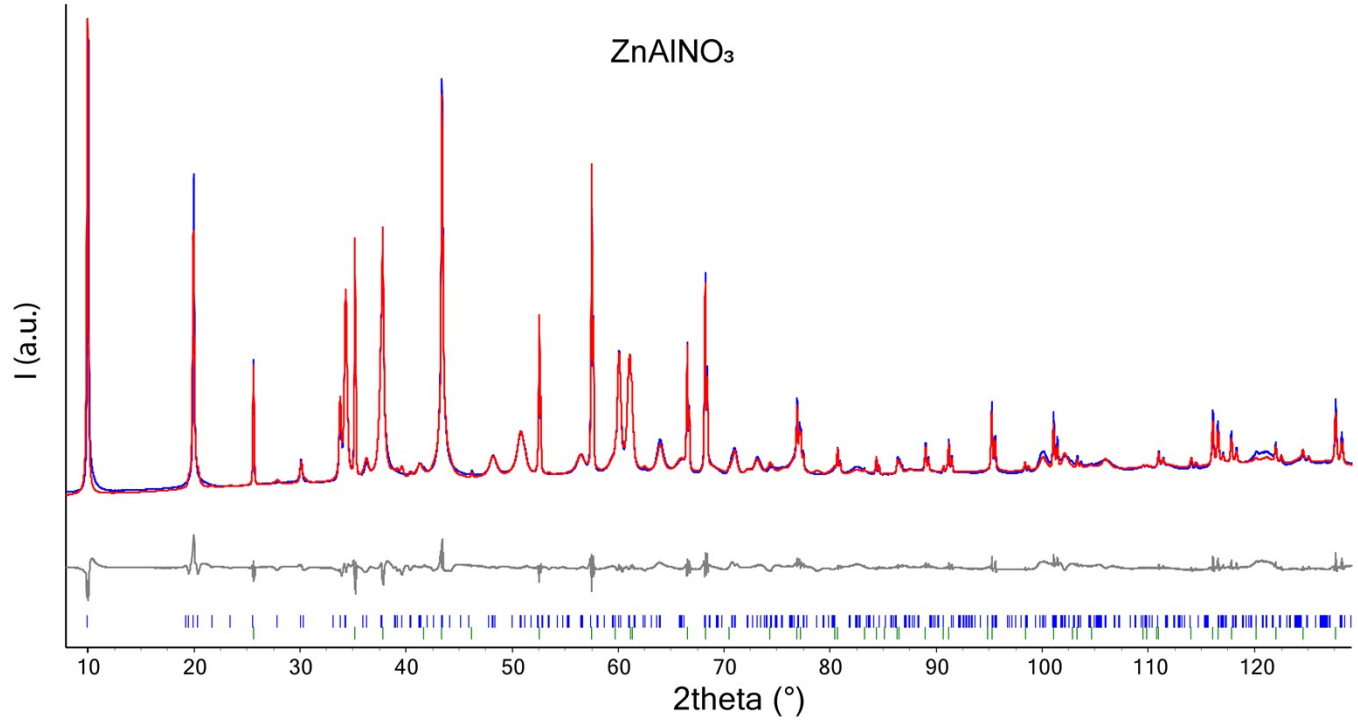



**Fig. S2.** Rietveld plot of the last refinement cycle for $ZnAlNO_3$ (sample ZAN/1, reaction time: 48 h, blue marks) containing 31.80% w/w of corundum (green marks) as internal standard. Calculated profile (red), experimental pattern (blue) their difference (grey).

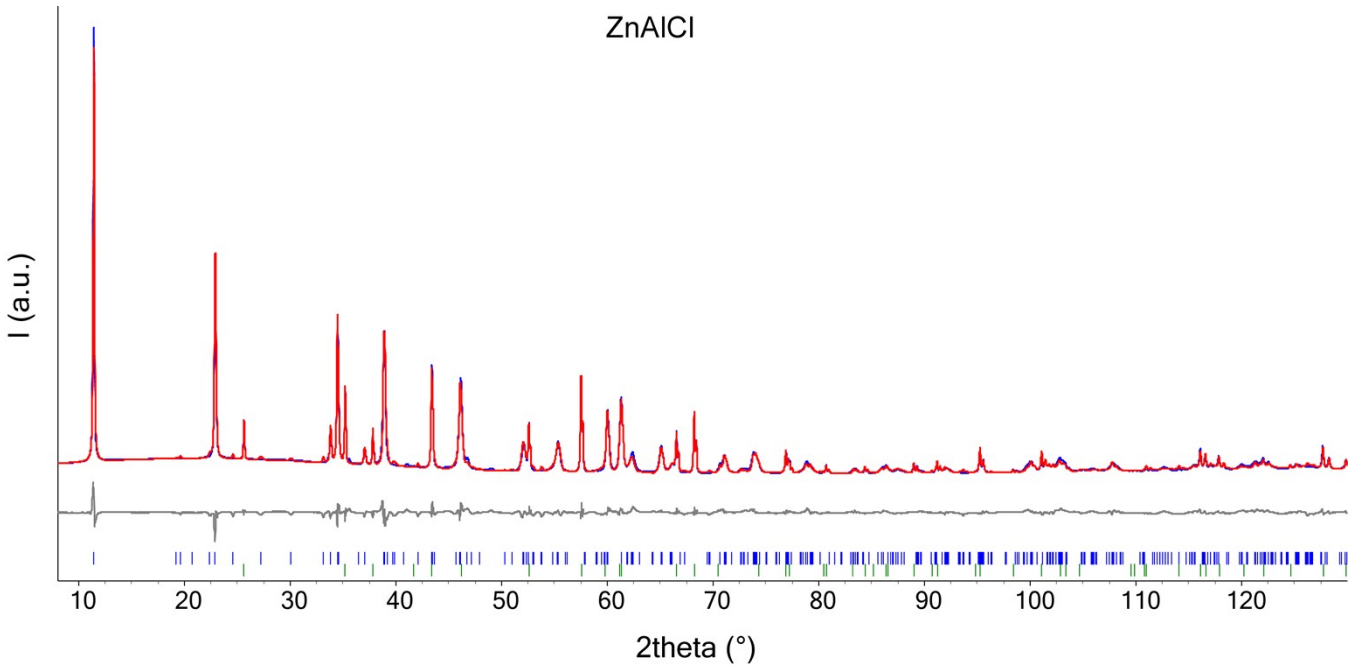



**Fig. S3.** Rietveld plot of the last refinement cycle for ZnAlCl (sample ZACl/1, reaction time: 48h, blue marks) containing 30.20% w/w of corundum (green marks) as internal standard. Calculated profile (red), experimental pattern (blue) their difference (grey).

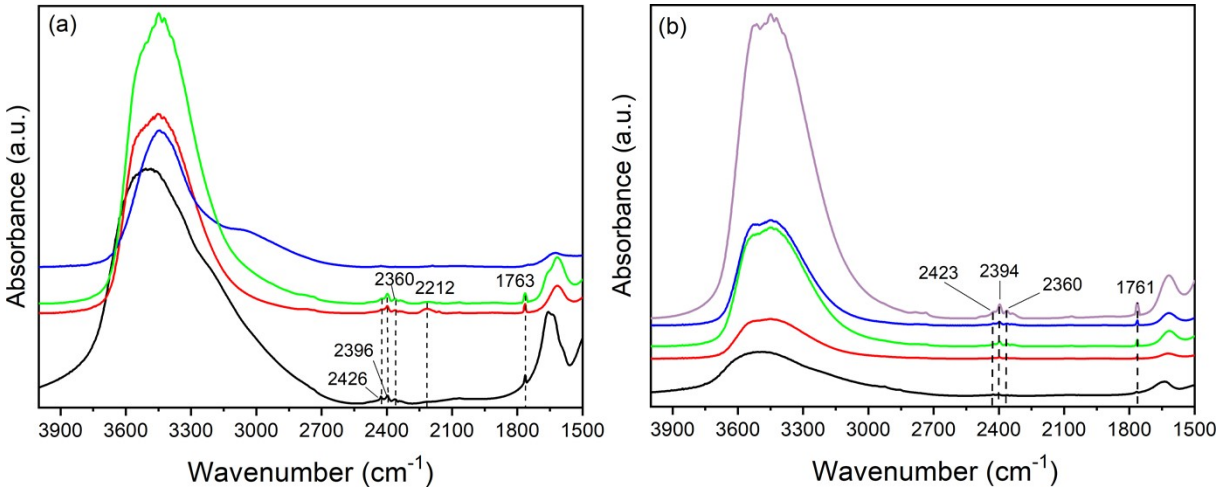



**Fig. S4.** FT-IR of $ZnAlCO_3$ (a) and ZAN/1 (b) in the 4000-1500 $cm^{-1}$ spectral region of samples recovered at increasing times (0 h, black line; 6 h, red line; 24 h, green line; 48 h, blue line; 120 h, pink line).

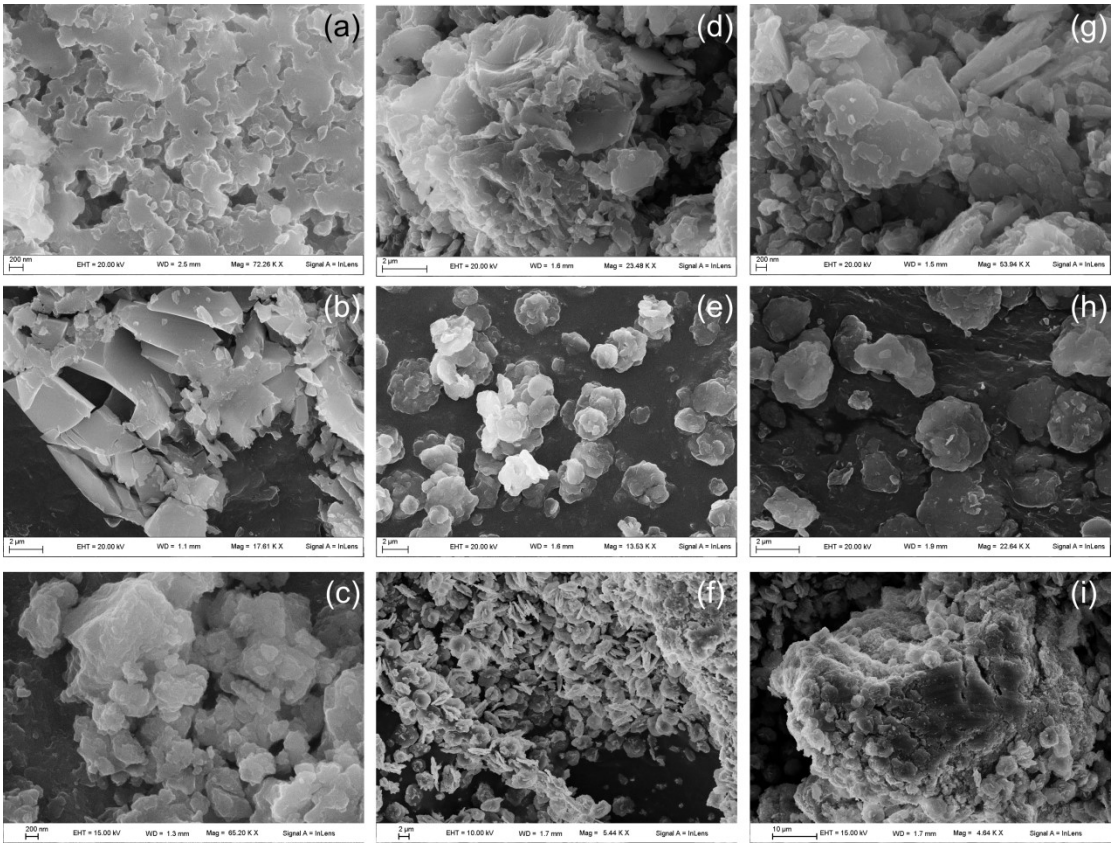
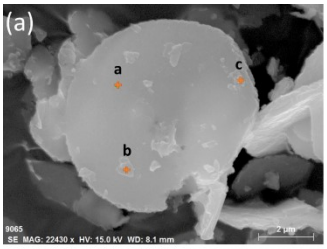
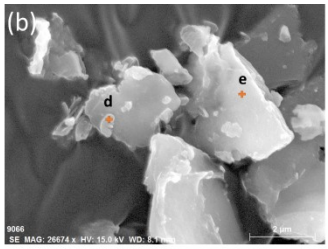
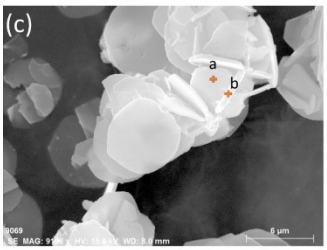


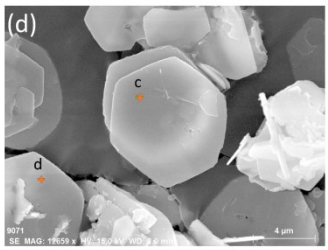

**Fig. S5.** SEM images of ZACl/1, $ZnAlCO_3$ and ZAN/1 after 0 (a,b,c), 2 (d,e,f), 4 (g,h,i) h of reaction.



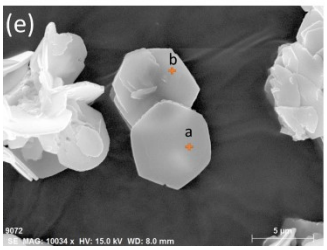




| Point | F |
|---|---|
| a | 0.45 |
| b | 0.25 |
| c | 0.33 |
| d | 0.28 |
| e | 0.43 |



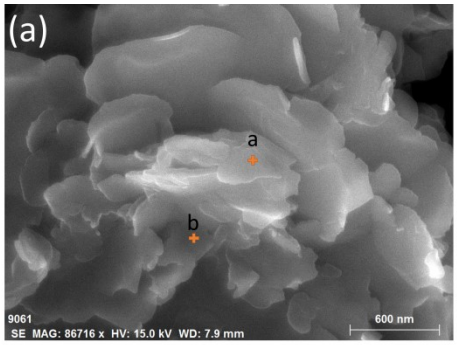



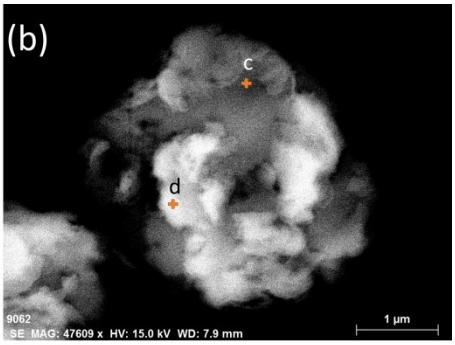

| Point | F |
|---|---|
| a | 0.30 |
| b | 0.31 |
| c | 0.29 |
| d | 0.30 |

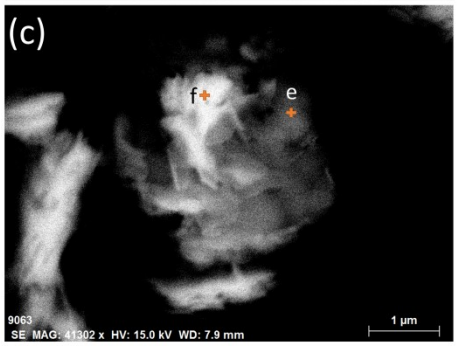



| Point | F |
|---|---|
| a | 0.30 |
| b | 0.31 |

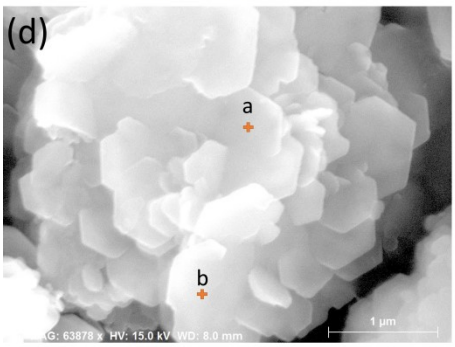
**Fig. S6.** SEM images of ZACl/1 collected after 6 (a, b), 48 (c, d) and 120 h (e) of reaction. The images show the points chosen to perform the EDX analysis, and the data obtained are reported on the right. F=Al/(Zn+Al) molar ratio.



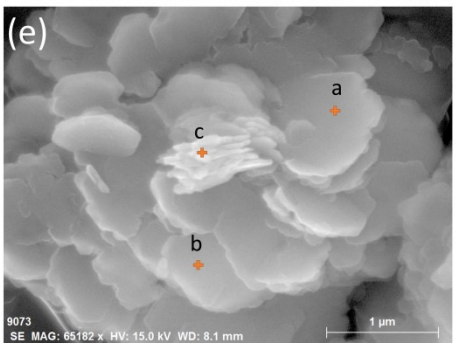




| Point | F |
|---|---|
| a | 0.23 |
| b | 0.29 |
| c | 0.20 |
| d | 0.28 |
| e | 0.29 |
| f | 0.26 |

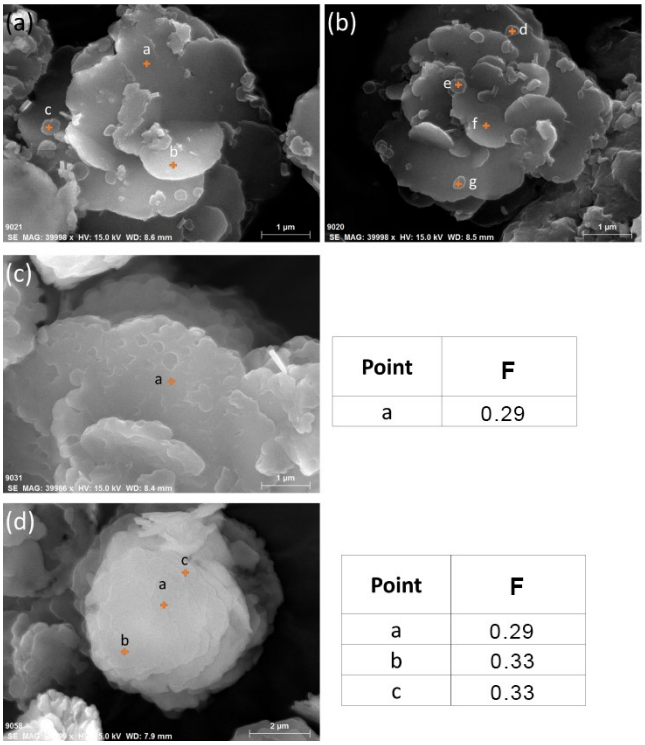



| Point | F |
|---|---|
| a | 0.30 |
| b | 0.29 |




| Point | F |
|---|---|
| a | 0.30 |
| b | 0.29 |
| c | 0.31 |

**Fig. S7.** SEM images of $ZnAlCO_3$ collected after 6 (a, b, c), 48 (d) and 120 h (e) of reaction. The images show the points chosen to perform the EDX analysis, and the data obtained are reported on the right. F=Al/(Zn+Al) molar ratio.




| Point | F |
|---|---|
| a | 0.33 |
| b | 0.31 |
| c | 0.17 |
| d | 0.22 |
| e | 0.20 |
| f | 0.30 |
| g | 0.18 |

| Point | F |
|---|---|
| a | 0.29 |

| Point | F |
|---|---|
| a | 0.29 |
| b | 0.33 |
| c | 0.33 |

**Fig. S8.** SEM images of ZAN/1 collected after 6 (a, b), 48 (d) and 120 h (e) of reaction. The images show the points chosen to perform the EDX analysis, and the data obtained are reported on the right. F=Al/(Zn+Al) molar ratio

**MgAl system**

**Table S7.** Al molar fraction (F) and phases observed by XRPD of MgAl LDH in nitrate and chloride form. Reaction condition: R=1.8, 0.5 M of metal ions, $y$ = 0.30, temperature: reflux, reaction time= 48h.

| Sample | F | Phase[(a)] |
|---|---|---|
| MAN/2 | 0.36 | $NO_3$ |
| MACl/2 | 0.38 | Cl |

[(a)]Crystalline phases observed by XRPD

The effect of the salt concentration on the formation of $MgAlNO_3$ was investigated at increasing concentrations of nitrate salts. Fig. S9 shows the XRPD patterns of the solids obtained by using Mg(II) and Al(III) solutions at different concentrations and keeping fixed the R value at 1.8 and the reaction time at 48 h. MgAl compounds were characterized by a single crystalline phase ascribable to $MgAlNO_3$ LDH throughout the range of concentrations investigated, however all XRPD patterns show a high background level, which can be related to the incoherent scattering produced by an amorphous phase.

The composition of the samples consisting of a single crystalline phase was determined by ICP and is shown in Table S8. In all samples the F value is greater than the $x$ value typical of an LDH phase (0.33), suggesting the formation of amorphous phases ascribable to aluminum hydroxides. The amount of the fraction of the amorphous phase appears to increase with increasing metal salt concentration in solution, as

suggested by the F values, by the increase of the background level shown in their XRPD patterns, and finally by the slight increase in surface area.

Summarizing the results of these experiments, the best conditions to obtain $MgAlNO_3$ were: ion concentration 1 M, R = 1.8, time 48 h under reflux, even if this crystalline phase appears to be accompanied by a certain amount of amorphous phase.

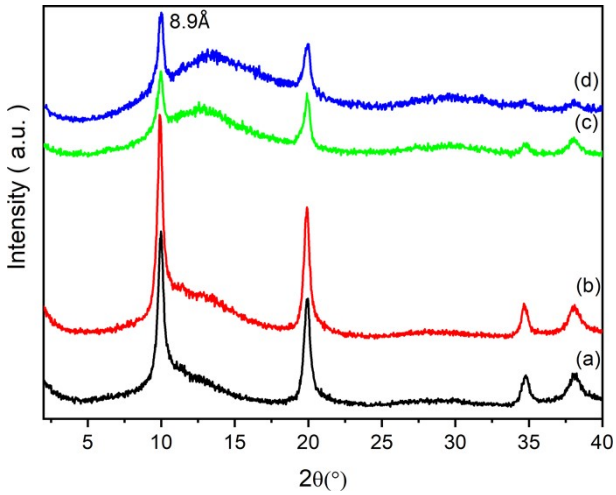



**Fig. S9** XRPD patterns of MgAl LDH synthesized by using $Mg(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ salts with concentrations: 0.5 M (a); 1 M (b); 2 M (c); 2.5 M (d). R=1.8, reaction time and temperature: 48 h and reflux.

**Table S8.** Effect of metal salt concentration on the formation of LDH in nitrate form. R = 1.8, $y$ = 0.30, reflux time: 48 h.

| Sample | [Mg+Al] in solution | F | B.E.T. surface area ($m^2/g$) | Phase[(a)] |
|---|---|---|---|---|
| MAN/2 | 0.5 | 0.36 | 28 | $NO_3$ |
| MAN/2-1 | 1 | 0.37 | 42 | $NO_3$ |
| MAN/2-2 | 2 | 0.46 | - | $NO_3$ |
| MAN/2-2.5 | 2.5 | 0.45 | - | $NO_3$ |

[(a)]Crystalline phases observed by XRPD