Experimental Procedure for Synthesis, Delamination, Phosphate Uptake & Characterization

Synthesis & Delamination

In a typical synthetic procedure 80 ml of 1M solution of divalent metal ion and trivalent metal ion (nitrate salts) were mixed in a ratio 2:1; HMT in a molar ratio of [M(II)+M(III)]:[HMT] of 1:1.5 (16.8 g) and 120 ml of deionised water was added to this solution. The solution was mixed thoroughly, nitrogen gas was purged for 30 min and was kept in an oil bath sharply at 80 ^{o}C (very subtle temperature variations affected the phase purity; see below) for four days with out stirring. The resulting material was filtered, washed with deionised water several times and dried in vacuum at room temperature (yield – 7 g). In whole process we have used CO_2 free Milli-Q water (18 ohm resistivity). Soon after the synthesis (pH of this slurry is around 5.0) we have washed the material to neutral pH (6.5 to 7.0).

Delamination in water was done by taking 2.5 g of wet-LDH cake immediately after filtration in to a Teflon lined stainless steel reactor to which 50 ml of deionised water was added and kept at 120 ^{o}C for 12 h in nitrogen atmosphere. (pH after the hydrothermal treatment was 6.4, probably due to release of nitrate ions from the interlayers). The undelaminated material was removed after centrifuging at 2000 rpm for 30 min. The actual dispersion degree was obtained by drying the samples under vacuum at room temperature both before and after hydrothermal treatment and computed from their difference. The value reported here is an average value of 2.5 g/L with a variation of around ± 1 g/L.

Calculation of dispersion degree in water

Weight of LDH present in 2.5 g of wet cake is 0.283 g

Weight of unexfoliated LDH remained after centrifuging at 2000 rpm is 0.211 g

Weight of material exfoliated is 0.072 g

Dispersion degree of the delaminated material is (0.072/0.283)*100 = 25%

Total delamination study

Total delamination of synthesised LDHs was done by taking 0.050 g of dried LDH powder and 50 cm^3 of formamide (Aldrich) in a 100 ml conical flask, which was sealed after purging nitrogen gas and vigorously agitated by a mechanical shaker at a speed of 150 rpm for two days; the colloidal suspension was then centrifuged at 2000 rpm for 30 min; no residue was seen.

Phosphate uptake study

Phosphate uptake studies were done using 100 mgP/L solution of KH_2PO_4 (pH of study is 6.2); both dry powder and water delaminated LDHs were stirred with the solution in the ratio of 1 g/L for 4 h under nitrogen. Phosphate uptake was measured using molybdenum blue method.

Sample characterization

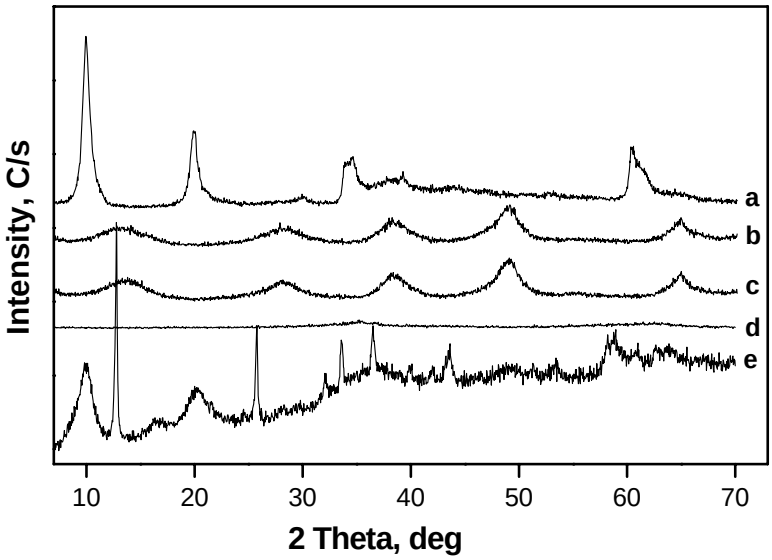
Powder X-ray diffraction (PXRD) measurements were carried out on a Philips X'Pert MPD system using Cu Kα radiation. The operating voltage and current were 40 kV and 30 mA, respectively. The step size was 0.04˚ with a step time of 2 second for dried samples and for glue like materials 0.02^o step size and 1 second step time. FT-IR spectra were recorded in a Perkin-Elmer Spectrum-GX instrument, using KBr pellets; 64 spectra (recorded with a nominal resolution of 4 cm^{-1}) were accumulated and averaged to improve the signal-to-noise ratio. Transmission electron microscope (TEM) analysis was done using JEOL, JEM-2100 microscope at 200 kV using carbon coated copper grids. Atomic Force Microscope (AFM) was done in Innova SPM with scan rate of 1Hz to know the shape and size of the delaminated LDH platelets. 0.1 g/L of LDH dispersion was deposited on a freshly cleaved mica substrate and images were obtained using tapping mode. A RTESPA tip with 10 nm radius was used to achieve high resolution.

Table S1

Elemental composition and formula of the synthesized materials

Materials synthesized	**M(II)/M(III)**		**Formula**
	Solution	**Solid**	
CoAl-NO_3-HT	2.00	2.02	$[Co_{0.66}Al_{0.34}(OH)_2]\ (NO_3)_{0.34}.0.32\ H_2O$
NiAl-NO_3-HT	2.00	2.00	$[Ni_{0.66}Al_{0.34}(OH)_2]\ (NO_3)_{0.34}.0.51\ H_2O$

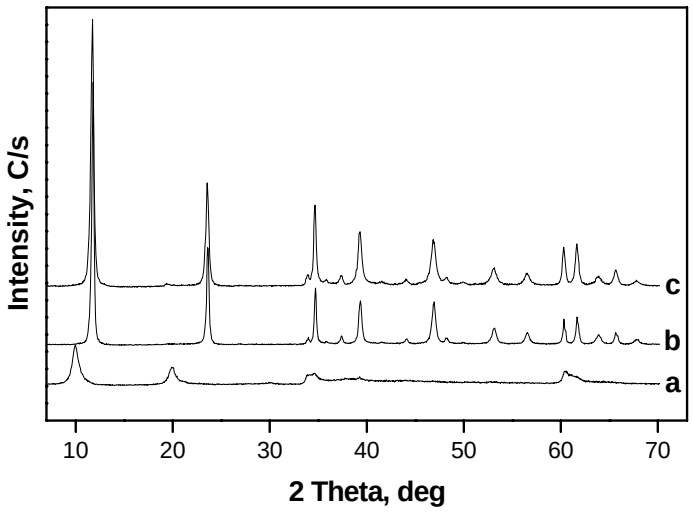
Fig. S1 PXRD pattern of all synthesized materials other than CoAl and NiAl-LDHs



a) ZnAl-LDH, b) MgAl-LDH, c) CaAl-LDH, d) CoFe-LDH, e) CuAl-LDH.

Fig. S1 clearly shows different phases obtained after hexamine synthesis. MgAl, CaAl and CoFe failed to form LDH phase. CuAl formed mixed LDH like phase and ZnAl formed NO_3-LDH.

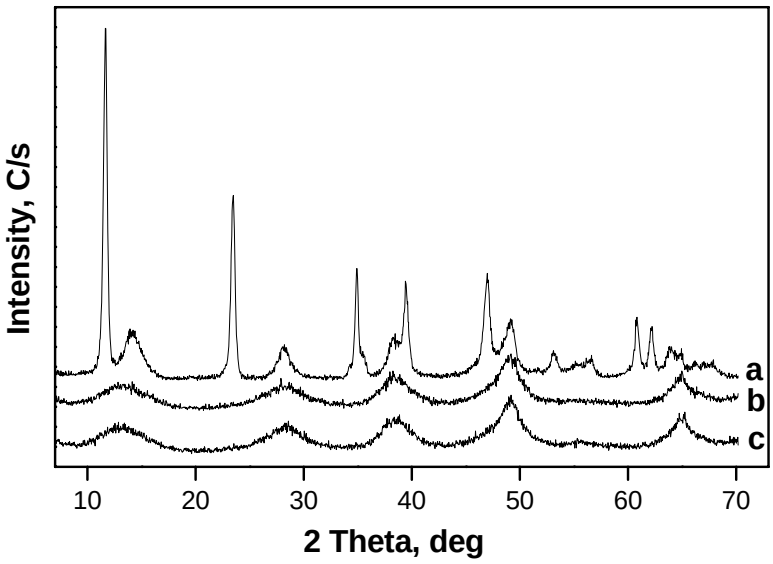
Fig. S2 PXRD of ZnAl-LDHs



a) ZnAl-80 ^{o}C, b) ZnAl-100 ^{o}C, c) ZnAl-80 ^{o}C repeated

Fig. S2 shows the PXRD patterns of ZnAl-LDHs synthesized at different temperatures. Results showed that the final phase is highly sensitive to temperature. Some results are not reproducible.

Fig. S3 PXRD of MgAl-LDHs synthesized at different conditions

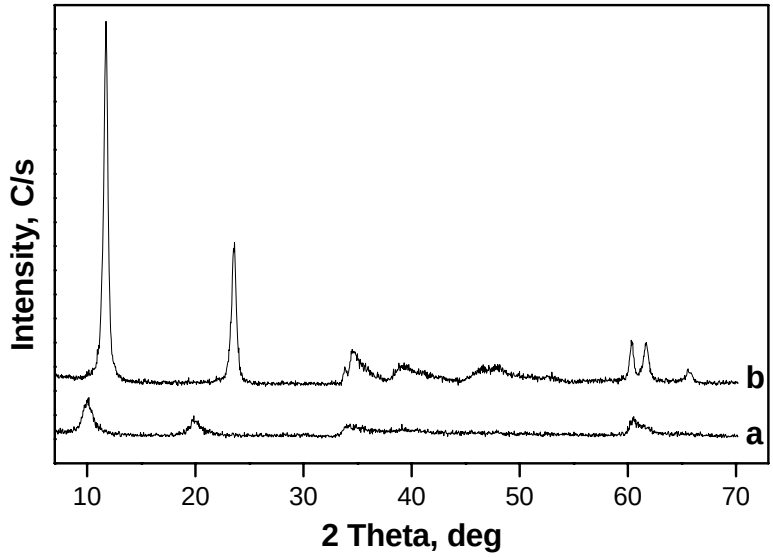


a) MgAl-115 ^{o}C, b) MgAl-80 ^{o}C,

c) MgAl-80 ^{o}C prepared by taking double the concentration of hexamine

Fig. S3 shows PXRD patterns of MgAl-LDHs synthesized at different temperatures and hexamine concentration. At higher temperature, we have obtained carbonate containing LDH phase along with an unknown impurity phase.

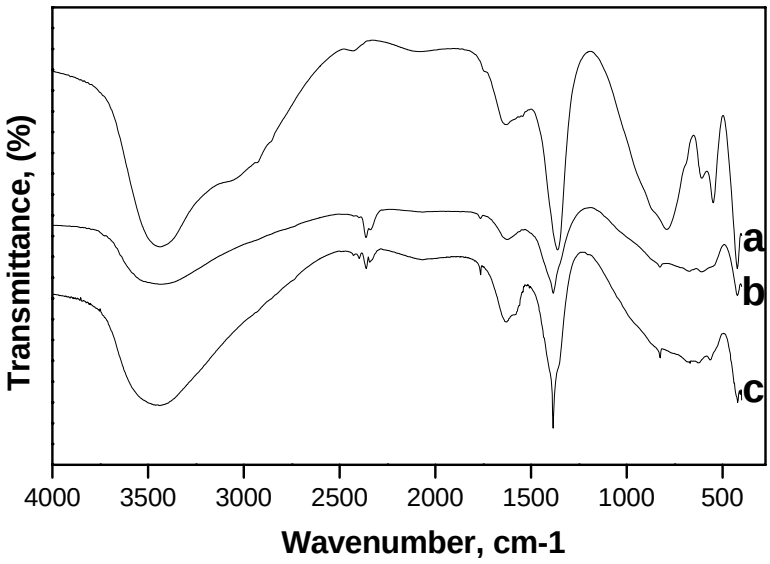
Fig. S4 PXRD of CoAl-LDHs synthesized at different temperatures



a) CoAl-LDH-80 ^{o}C b) CoAl-LDH-90 ^{o}C

Fig. S4 clearly shows the temperature dependence. When the temperature is increased to 90 ^{o}C, a highly crystalline carbonate containing LDH phase was obtained through Leuckart reaction (see scheme given below).

Fig. S5 FT-IR spectra of synthesized materials



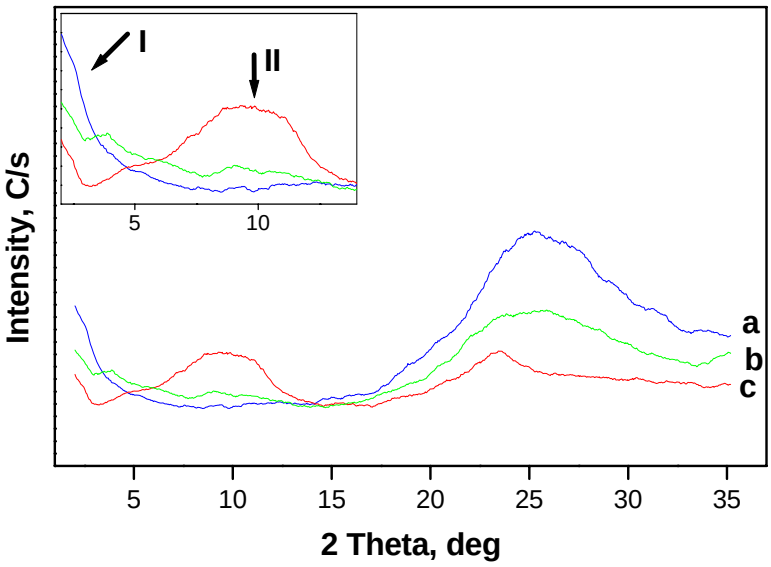
(a) CoAl-CO_3 LDH, (b) CoAl-NO_3 LDH, (c) NiAl-NO_3 LDH.

Fig. S5 shows an intense absorption band around 1384 cm^{-1} attributed to N-O stretching vibration mode of NO_3^- ions and the absence of band at 1360 and 790 cm^{-1} confirms the absence of carbonate in the interlayer.

Fig. S6 Before and after centrifuging at 15000 rpm

ICP analysis of the glue-like residue (dried in a microwave oven) obtained after centrifugation at 15000 rpm was done. No significant variation in the M(II)/Al ratio was found between the parent sample and the centrifuged residue, which supports against the possibility of dissolution of the LDHs.

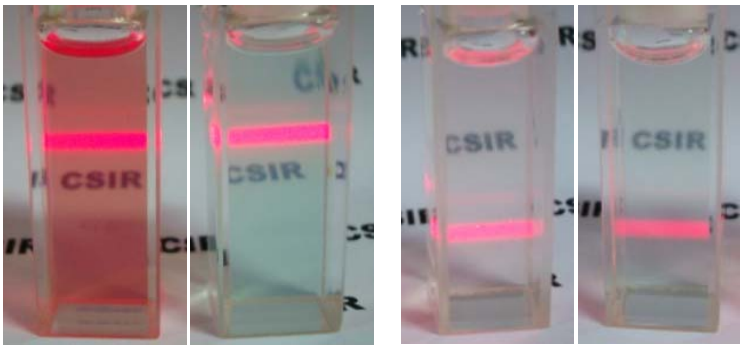
Fig. S7 Total delamination of NiAl-LDH in formamide



a) Delaminated LDH, b) 'a' after one day c) 'a' after 4 days

Inset is the expanded region for clarity. Broad reflection indicated by arrow (I) at 2θ = 1.5-3.5^{o} is due to aggregates of exfoliated nano sheets, 2θ = 7-15^{o} indicated by arrow (II) is the crystallized LDH phase and broad reflection in the 2θ range 20 – 30^{o} is due to scattering of liquid formamide.

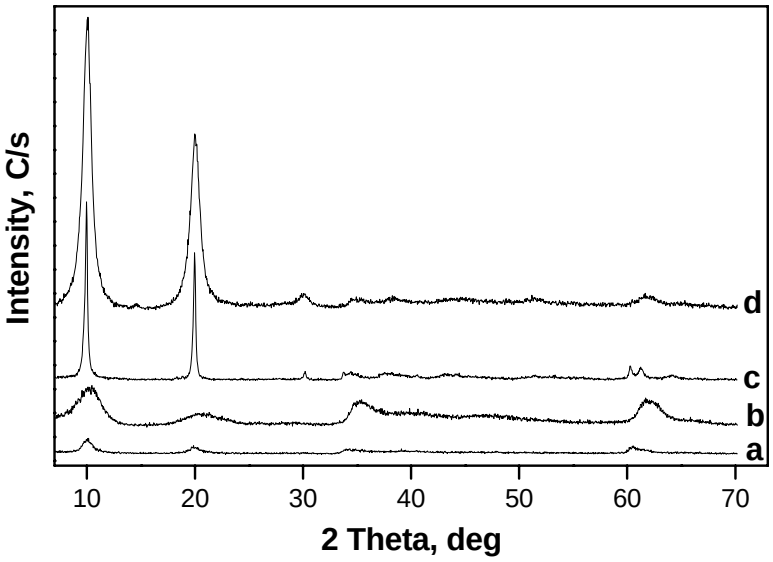
Fig. S8 Tyndall effect of delaminated LDH



CoAl and NiAl LDHs delaminated in formamide	CoAl and NiAl LDHs delaminated in water

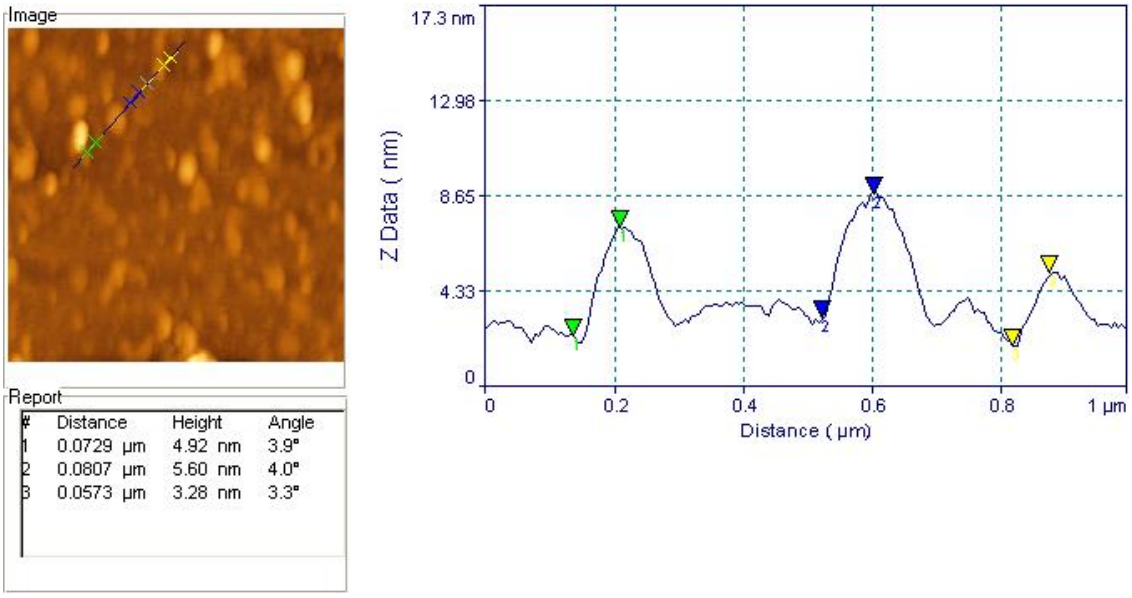
The variation in the color between the colloidal suspension of LDH in formamide and water is a consequence of the different physical properties of the solvents.

Fig. S9 NiAl and CoAl-LDHs delaminated in water and then dried in microwave oven (for 8 minutes with full power; domestic oven, 2.45 GHz, 800 W)

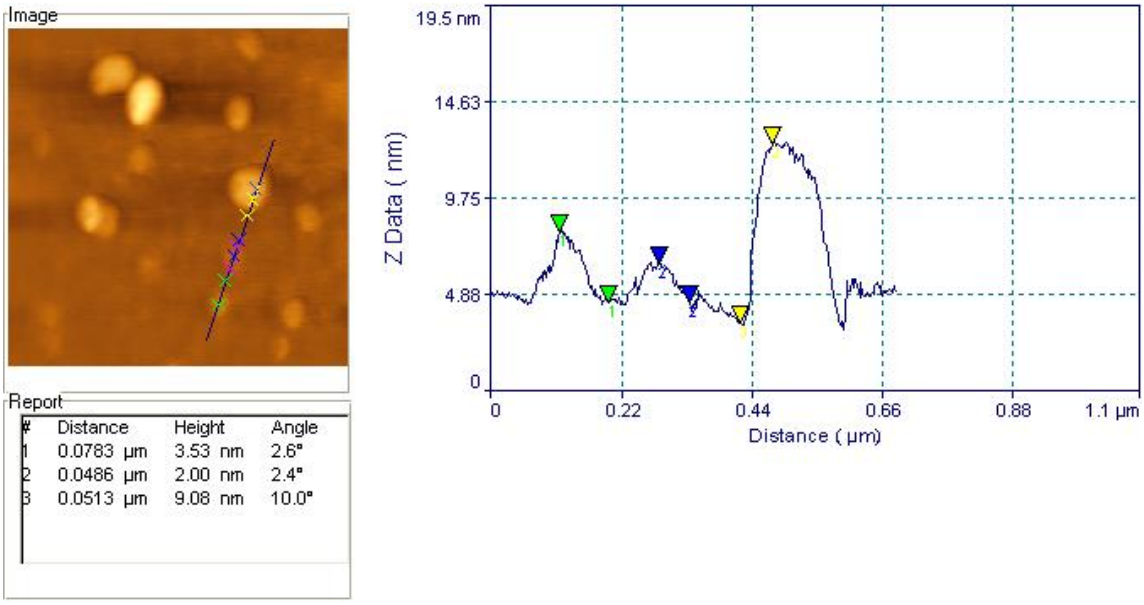


a) $CoAlNO_3$-LDH, b) $NiAlNO_3$-LDH, c) 'a' delaminated and microwave dried, d) 'b' delaminated and microwave dried.

Fig S10 AFM images of the delaminated CoAl-LDH in formamide and water

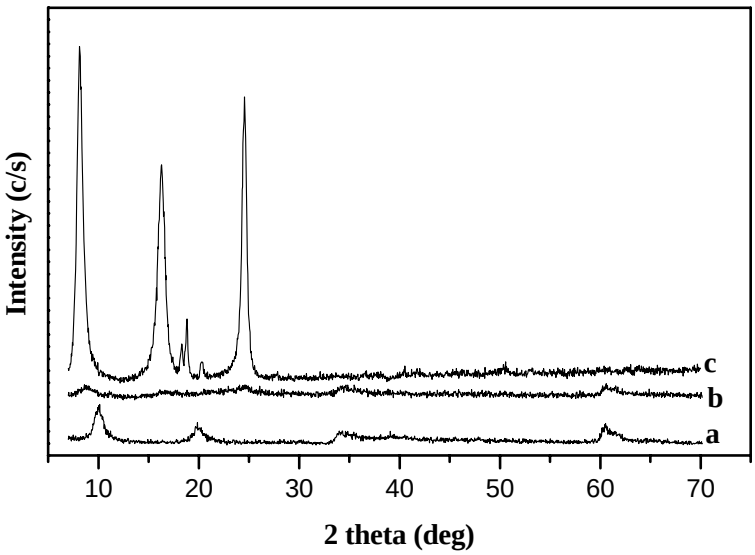


Formamide delaminated LDH



Water delaminated LDH

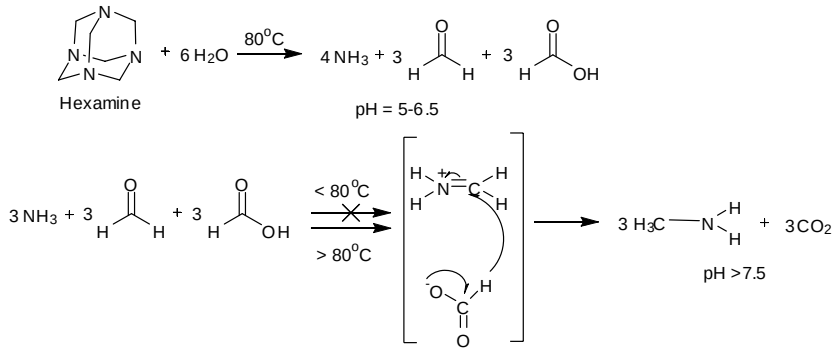
Fig. S11 PXRD of $CoAlNO_3$-LDH before and after phosphate uptake



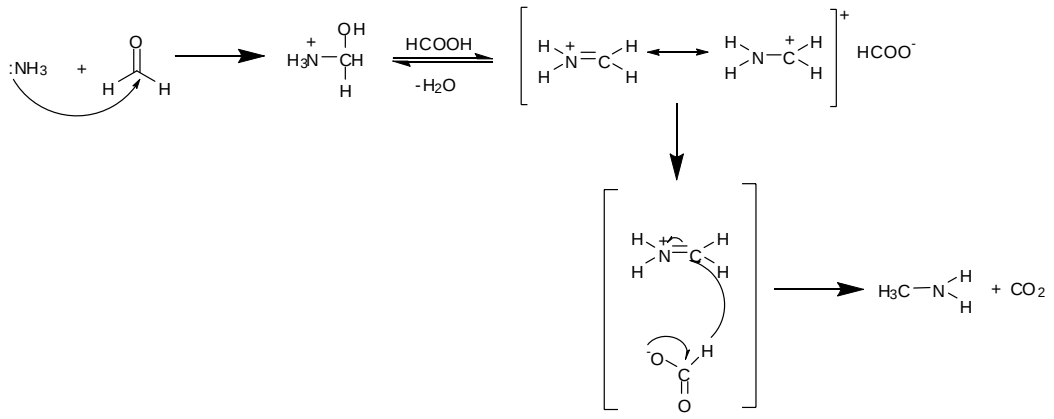
PXRD patterns of (a) $CoAlNO_3$-LDH, (b) 'a' after phosphate uptake and (c) CoAl-delaminated LDH after phosphate uptake (dried on glass plate)

Reflection at $2\theta = 8.08^o$, 16.3^o and 24.5^o confirms the intercalation of phosphate and other reflections at $2\theta = 18.8^o$ might be due to intercalation of different hydrated phosphate anions (A. Legrouri, M. Badreddine, A. Barroug, A. Deroy, J. P, Besse, J. Mater. Sci. Lett., 18 (1999) 1077).

Scheme 1



Mechanism



***** Source of nitrate in LDH is from precursor only

Hexamine on hydrolysis yield ammonia and formaldehyde/formic acid. Thus formed, ammonia increases the pH, resulting in the precipitation of metal ions. The excess ammonia present in the system undergoes the Leuckart reaction when the temperature is higher.