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Supporting Information

Rapid, Efficient Phase Pure Synthesis of Ca_2AlNO_3 Layered Double Hydroxide

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1. General details

Powder X-ray Diffraction (XRD). Powder X-ray diffraction patterns were recorded on a PANalytical X'Pert Pro instrument using a Cu anode and K-alpha 1 λ=1.540598 and K-alpha 2 λ=1.544426 with a K-alpha 2/K-alpha 1 ratio of 0.5. The generator voltage was set to 40 kV and the tube current to 40 mA at 0.01 ^{o} s^{-1} from 3 to 70^{o} with a slit size of 1^{o}. Samples were ground in powder form and loaded onto stainless steel sample holders.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was carried out using a Mettler Toledo TGA/DSC 1 System. Around 20 mg of the sample was heated in a crucible from 25 to 700 °C at a rate of 5 °C per minute, and then left to cool.

Dynamic Light Scattering (DLS). A Malvern Zetasizer Nano ZS in the Begbroke Science Park was used to carry out the dynamic light scattering analysis. A small amount of the sample in paste form was fully dispersed in about 10 mL of dionised water using a sonicator for 5 minutes, this dispersion was then pipetted into a plastic cuvette to the suggested level and inserted into the instrument.

Transmission Electron Microscopy (TEM). Transmission electron microscopy images were obtained at Harwell Science and Innovation Campus using a JEOL 2100 microscope with an accelerating voltage of 200 kV to view the samples. A small amount of the LDH sample in paste form was dispersed in ethanol in a sonicator for about 3 minutes, and then cast onto copper grids coated with Formvar film.

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectra were recorded on a Nicolet iS5 Spectrometer equipped with the iD3 ATR (attenuated total reflection) accessory, measuring in the range of 400-4000 cm^{-1} with 50 scans at 4 cm^{-1} resolution.

Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{27}Al DPMAS and ^{13}C CPMAS Solid state NMR spectra were obtained by Dr. Nicholas Rees (University of Oxford) at 104.2 and 100.5 MHz respectively (9.4 T) on a Bruker Avance IIIHD spectrometer. For ^{27}Al NMR spectroscopy, in order to obtain quantitative MAS spectra, a single pulse excitation was applied using a short pulse length (0.15 μs). 7000 scans were acquired with a 0.1 s delay and a MAS rate of 40 kHz using 1.9 mm O.D zirconia rotors. The ^{27}Al NMR spectroscopy chemical shift is referenced to an aqueous solution of $Al(NO_3)_3$. ^{13}C CPMAS NMR spectra were measured using 4mm O.D zirconia rotors and a MAS rate of 10 kHz using a cross-polarization sequence with a variable X-amplitude spin-lock pulse and spinal64 proton decoupling. 1500 transients were acquired using a contact time of 1.0 ms, an acquisition time of 12.5 ms (1024 data points zero filled to 16 K) and a recycle delay of 5

s. All ^{13}C NMR spectra were referenced to adamantane (the upfield methine resonance was taken to be at $\delta = 29.5$ ppm on a scale where $\delta(TMS) = 0$) as a secondary reference.

Scanning Electron Microscopy (SEM). SEM images were obtained at Harwell Science and Innovation Campus using a JEOL JSM 6610 scanning microscope.

Brunauer-Emmett-Teller Surface Area Analysis (BET). BET Surface area analysis was carried out by Dr. Chunping Chen and Dr. Alexander Kilpatrick (University of Oxford). The gas adsorption isotherm for nitrogen adsorption onto the LDH surface was measured using a Tristar II plus 3030. The samples were degassed at 110 °C overnight using a VacPrep degas machine. The Brunauer-Emmett-Teller (BET) method was then used to calculate the surface area.

Synthesis of Ca_2AlNO_3-LDH. 7.56 g of $Ca(NO_3)_2$ and 6.00 g of $Al(NO_3)_3$ (to give a 2:1 Ca:Al ratio of cations) were dissolved in 50 mL of deionised and degassed water (purged with N_2 for two hours to remove any carbonate ions), to give a 0.64 M solution of calcium ions and a 0.32 M solution of aluminium ions. 4.40 g of NaOH pellets were dissolved in another 50 mL of deionised and degassed water to give a 2.2 M solution of NaOH. The colloid mill was first washed with water, and then dionised water three times. The two solutions mentioned above were then poured into the mill for a mixing time of 90 s, the rotor speed was set to 2000 rpm. After mixing the product was collected, washed using deionised and degassed water 4 times using a centrifuge at 9000 rpm for 5 minutes. The sample was then collected, ~0.5 g was dried in a vacuum oven for characterisation, the rest was stored in a fridge at 8 °C.

Effect of storage time. The Ca_2AlNO_3-LDH paste sample was left in the lab fridge at 8 °C. Small amounts of the sample were extracted and tested after 1 week, and then after 4 weeks.

Effect of storage temperature. Three different Ca_2AlNO_3-LDH paste samples were left for 1 week at different temperatures. One was left at room temperature, 23 °C, one in the fridge, 8 °C, and one at -20 °C in the lab freezer. The samples were tested after this week.

2. Characterising data CaAl-NO_3 layered double hydroxide as prepared

2.1 X-ray diffraction

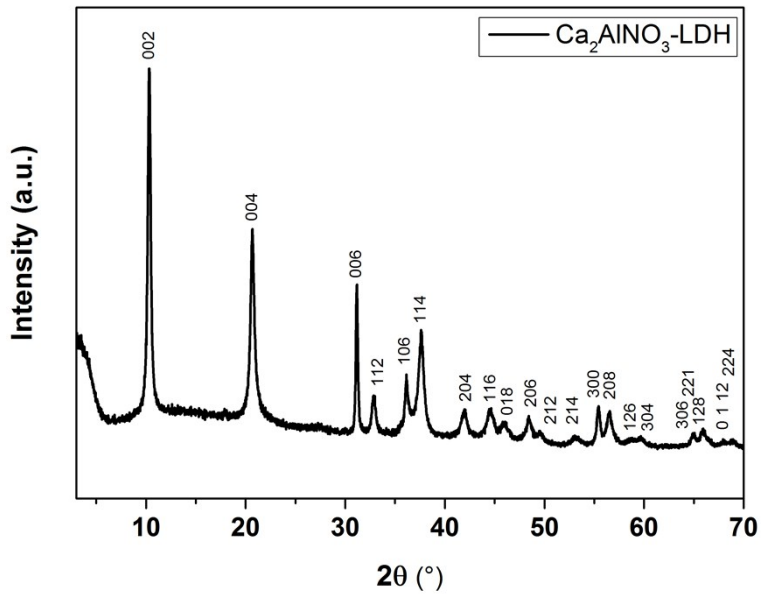

Fig. S1: Diffraction pattern for Ca_2AlNO_3-LDH synthesised using the rapid mixing method in a colloid mill with a rotor speed of 2000 rpm and for a mixing time of 90 s (2k-90s).

2.2 Infra-red spectroscopy

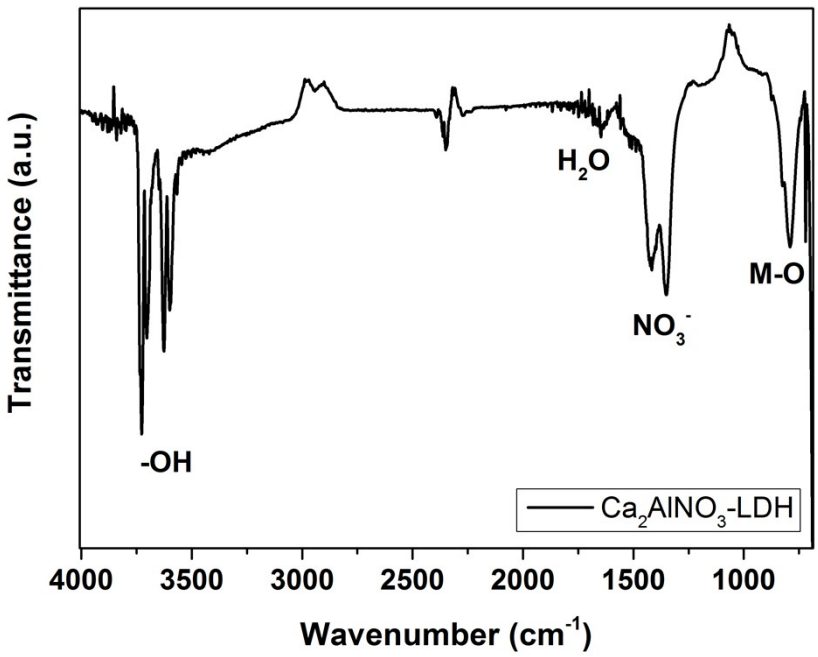

Fig. S2: FTIR transmission spectrum for Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s.

2.3 High-resolution TEM

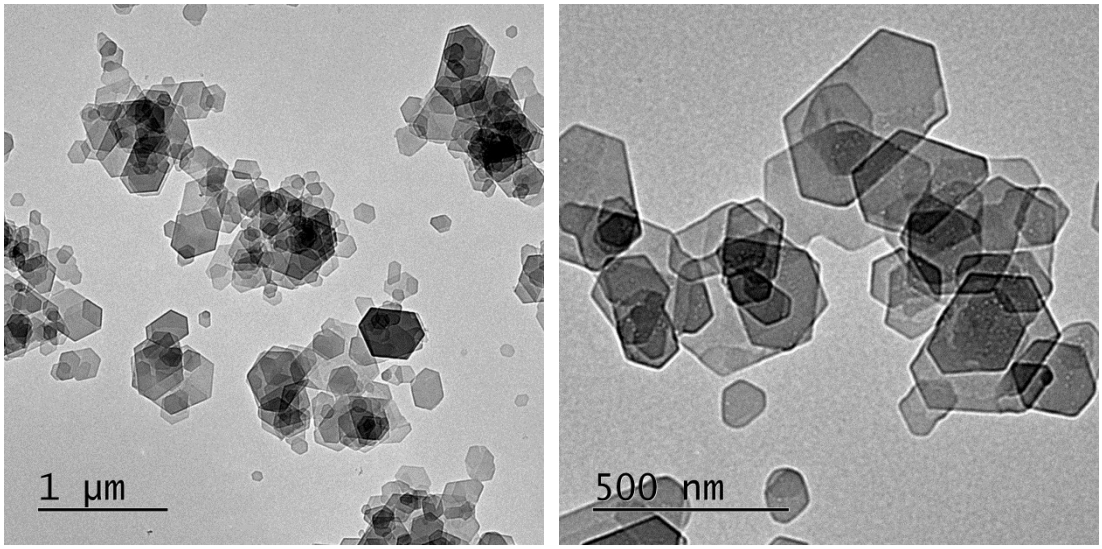

Fig. S3: TEM images for Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s.

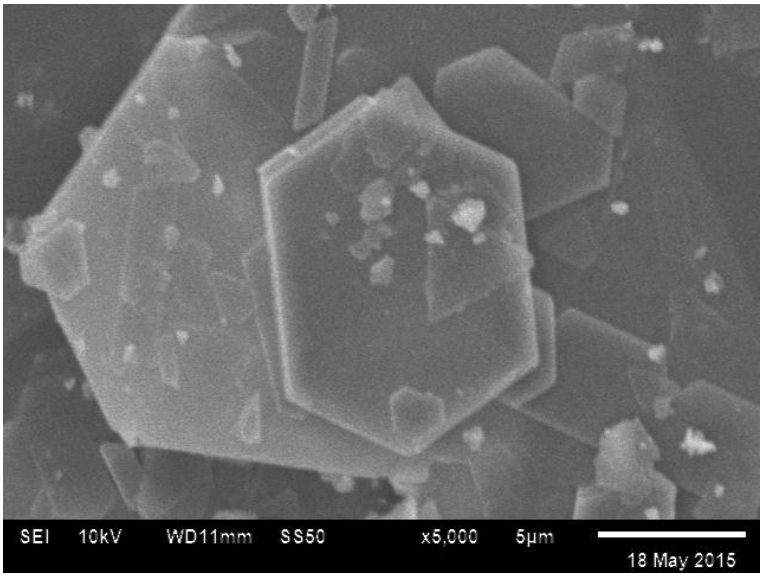

Fig. S4: SEM image for Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s.

2.4 Thermogravimetric analysis

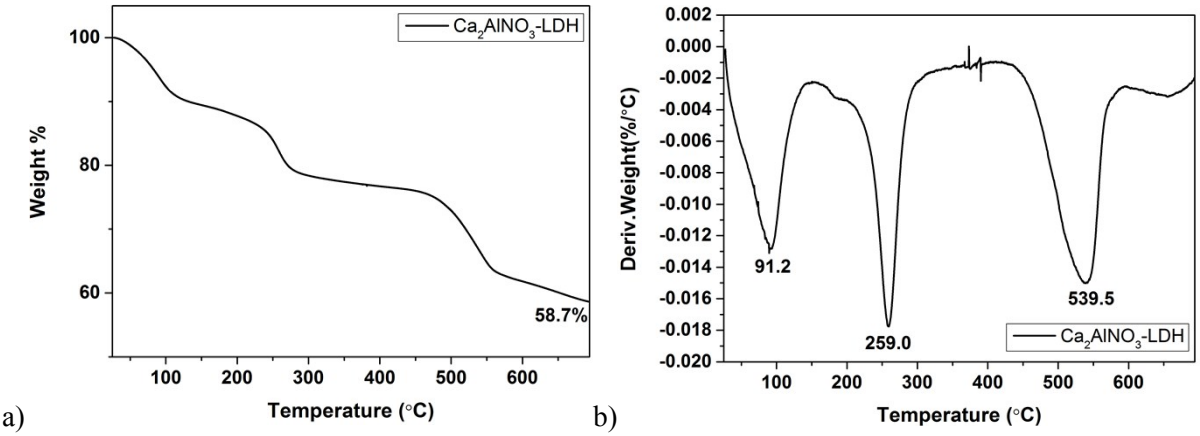

Fig. S5: (a) TGA curve for Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s and (b) TGA derivatives

2.5 Adsorption measurement

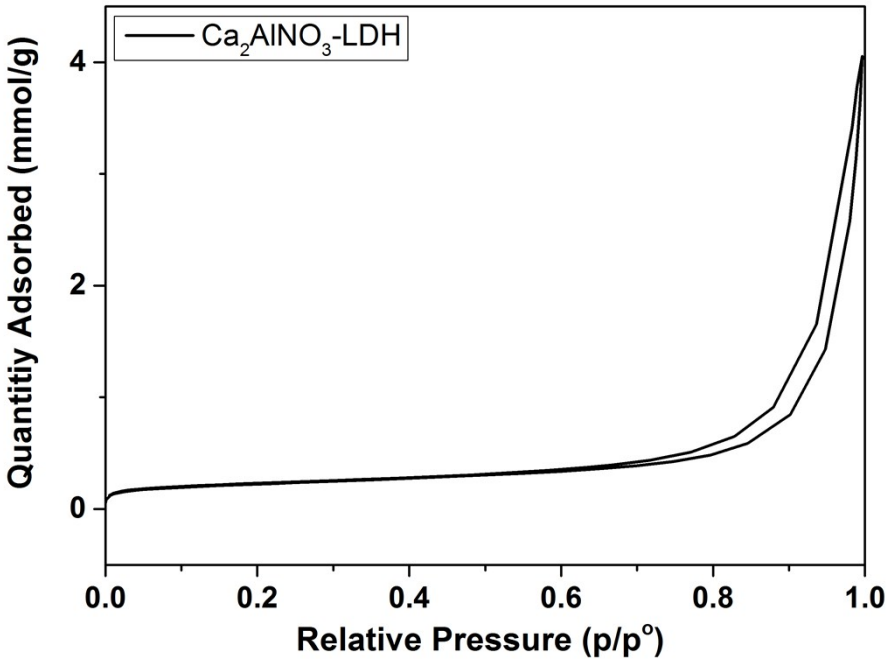

Fig. S6: BET isotherm for Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s.

2.6 Solid-state NMR spectroscopy

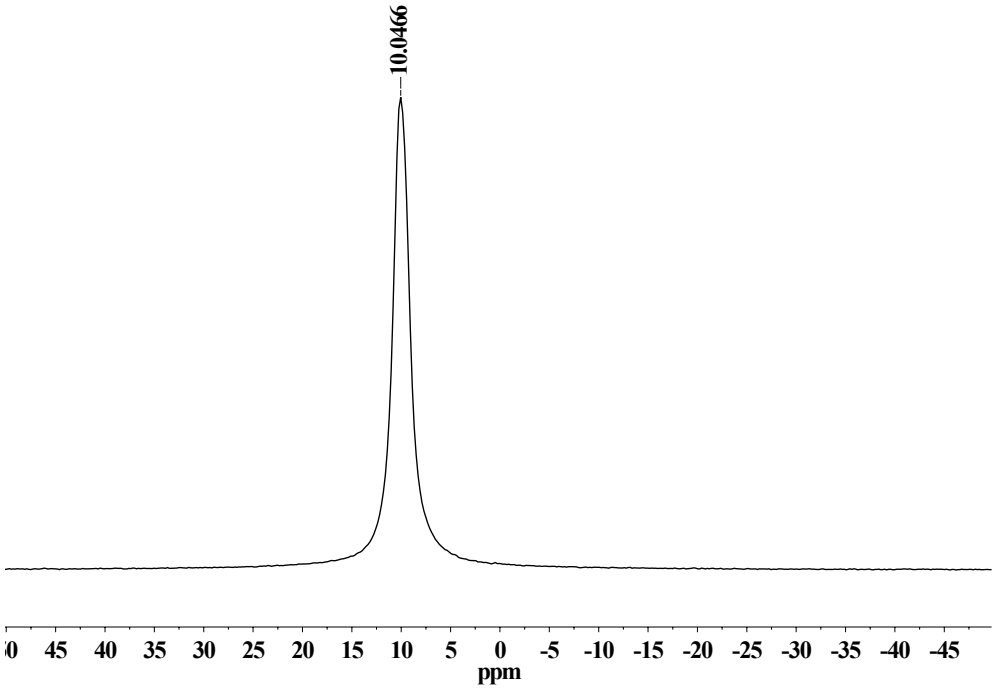

Fig. S7: ^{27}Al NMR spectrum for the Ca_2AlNO_3-LDH synthesised with the parameters 2k-90s.

3. Characterising data for CaAl-NO_3 layered double hydroxide stored over time and temperature

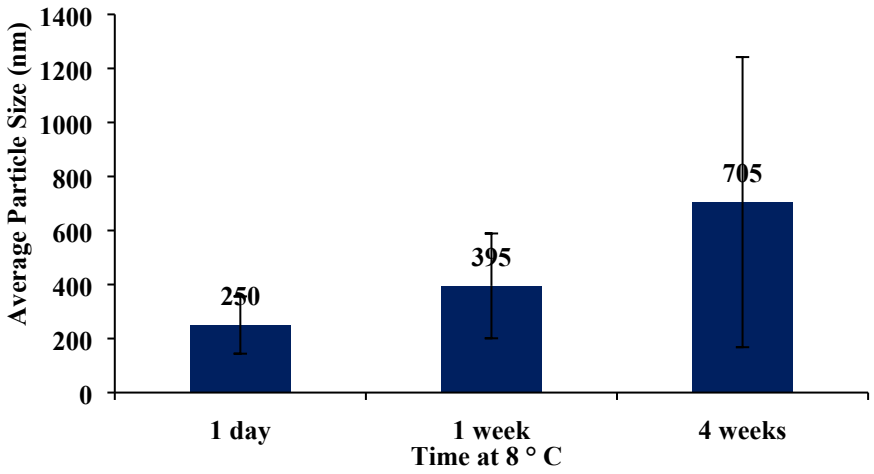

Fig. S8: Average particle size for Ca_2AlNO_3-LDH particles after storage at 8 °C.

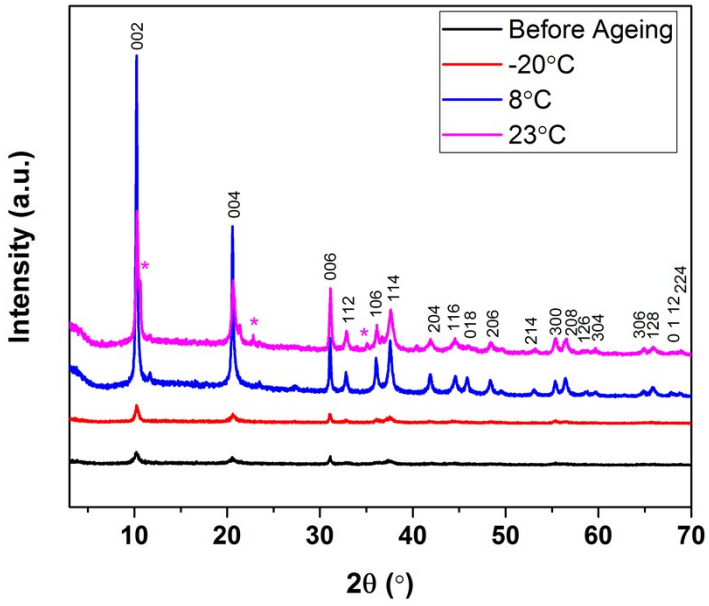

Fig. S9: XRD spectra for Ca_2AlNO_3-LDHs after storage for 1 week at different temperatures.

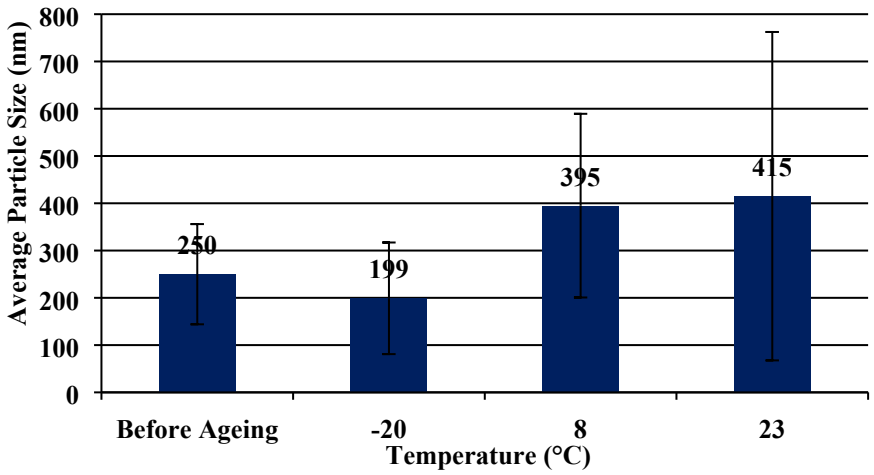

Fig. S10 Average particle sizes of Ca_2AlNO_3-LDH samples stored at different temperatures for 1 week, measured from TEM images.

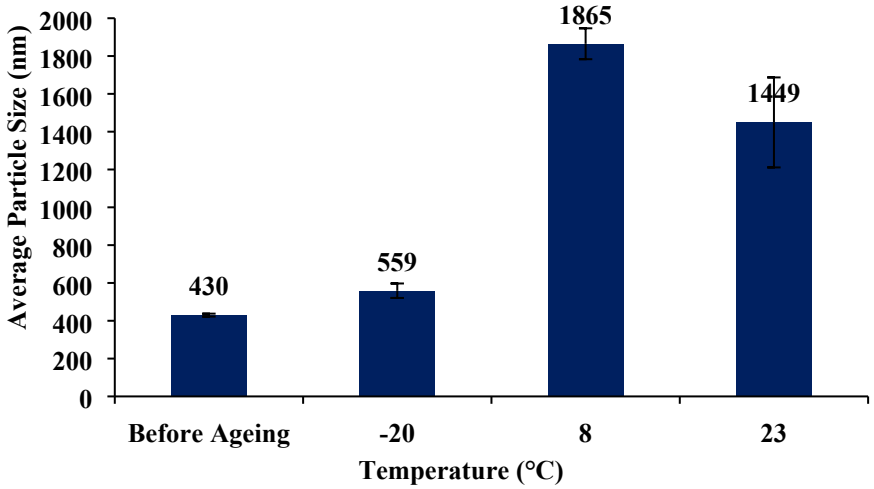

Fig. S11 Average particle size of the Ca_2AlNO_3-LDH particles after storage at different temperatures, measured using DLS.

Table S1: Crystalline Domain Lengths (CDLs)* for Ca_2AlNO_3-LDHs after different storage time at 8 °C.

Storage Time	**Intensity of *002* reflections (a.u.)**	**CDL along *c*-axis using *002* reflection FWHM (Å)**	**CDL along *a*- and *b*-axes, using *300* reflection FWHM (Å)**
1 day	931.0	146.6	106.7
1 week	4245.3	448.0	177.8
4 weeks	11871.0	733.2	251.9

*Calculated using the Scherrer equation.

Table S2: TGA data after different storage times at 8 °C.

Storage Time	**Temperature (°C)**		
	T1	**T2**	**T3**
1 day	90.3	258.0	539.5
1 week	105.5	273.3	565.4
4 weeks	100.2	275.4	576.7

Table S3: Crystalline Domain Lengths (CDLs)* of Ca_2AlNO_3-LDHs after 1 week storage at different temperatures.

Storage Temperature (°C)	**Intensity of *002* reflections (a.u.)**	**CDL along *c*-axis using *002* reflection FWHM (Å)**	**CDL along *a*- and *b*-axes, using *300* reflection FWHM (Å)**
Before storage	931.0	146.6	106.7
– 20	221.2	187.6	177.9
+ 8	4245.3	448.0	177.9
+ 23	1725.5	310.2	177.9

*Calculated using the Scherrer equation.

Table S4: TGA data for Ca_2AlNO_3-LDHs after storage at different temperatures.

Storage Temperature (°C)	**Temperature (°C)**		
	T1	**T2**	**T3**
Before storage	90.3	258.0	539.5
- 20	111.8	271.7	551.0
+ 8	102.2	272.7	568.3
+ 23	115.4, 149.3	275.2	565.8