

Efficient Synthesis of Ordered Organo-Layered Double Hydroxides

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Electronic Supporting Information

1. SEM Comparison Samples – Synthetic Method

Co-precipitation

Co-precipitated TA-LDHs were prepared by combining two aqueous solutions both held at 70 °C (all chemicals from Aldrich). The first solution contained Mg(NO₃)₂ and Al(NO₃)₃ (70 ml, 0.15 M) with the required Mg:Al ratio. The second solution contained aqueous NaOH (70 ml, 2.00 M). The solutions were combined together through a Pyrex glass T-piece, then dropping into a third aqueous solution also at 70 °C containing terephthalic acid (8.3 g, 0.05 moles) and NaOH (0.05 moles). During addition, the pH was held close to 7.0 by adjusting the flow rate of base. After the solutions were added, the mixture was aged in the mother liquor at 70 °C for 30 min and filtered.

Sol-gel

Sol-gel LDHs were prepared using a similar method to coprecipitated LDHs using a method adapted from the literature.¹ Variations from the coprecipitation method were that base solution was 70 ml of 2.25 mol dm⁻³ NaOH and 0.25 mol dm⁻³ NaHCO₃, the pH was held between 11.4 and 11.6 and here the mixture was aged in the at 70 °C for 3 h before washing with copious amounts of distilled water and filtering. To intercalate the terephthalate ion, sol gel LDH (0.5 g) was calcined (450 °C in a Carbolite MTF tube furnace under flowing air (space velocity 30,000 h⁻¹) for 4 h) and then suspended in distilled water containing terephthalic acid (0.1 g, 0.6 mmol) and NaOH (0.02 g, 0.06 mmol) under inert conditions and heated with stirring for 2 h before filtering and drying.

Urea hydrolysis

LDHs were prepared by urea hydrolysis using a method adapted from the literature.² Typically, a 200 ml solution containing Mg(NO₃)₂, Al(NO₃)₃ and urea was prepared with the required Mg:Al ratio to a total metal ion concentration of 0.18 M for Mg:Al of 2:1 and 0.24 M for Mg:Al of 5:1 with a urea concentration of 0.8 M. The solution was stirred and heated

to 90 °C until a white precipitate appeared. After cooling, the resulting slurry was filtered, washed with distilled water and dried at 70 °C before calcining at 450 °C in a Carbolite MTF tube furnace under flowing air (space velocity 30,000 h⁻¹) for 4 h. The calcined clay (0.50 g) was then rehydrated under inert conditions in deionised water (50 ml) containing terephthalic acid (0.10 g, 0.6 mmol) and NaOH (0.02g, 0.6 mmol) by heating for 2 h at 90 °C and then stirring for 24 h before filtering and drying.

References

1. T. Lopéz, P. Bosch, E. Ramos, R. Gómez, O. Novaro, D. Acosta and F. Figueras, *Langmuir*, 12 (1996) 189.
2. U. Constantino, F. Marmottini, M. Nocchetti and R. Vivani, *Eur J. Inorg. Chem.*, 10 (1998) 1439.

2. Fourier Transform Infra Red Spectroscopy Analysis

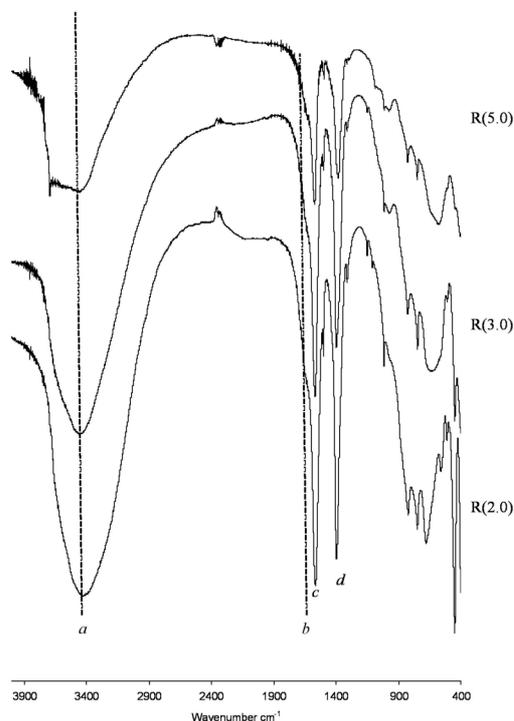


Fig S1. FTIR spectra of MgAl(TA) LDHs, R(2.0), R(3.0) and R(5.0). Major absorptions: *a* = H-bonded OH stretch, *b* = H₂O bend, *c* = COO⁻ anti-symmetric stretch and *d* = COO⁻ symmetric stretch.

A broad H-bonded OH stretching vibration absorbance at 3450 cm⁻¹ indicates that the terephthalic acid has dissociated and is present within the interlayer as the anion species. This shifts to higher frequency as R increases. The sharp absorbance at *circa* 3700 cm⁻¹ in the R(5.0) spectra is due to discrete OH stretches from brucite, the presence of which is known from the powder XRD patterns. The other major bands, *c* and *d*, are due to the anti-symmetric and symmetric carboxylate stretching vibrations respectively. The anti-symmetric stretch shifts almost imperceptibly to higher wave numbers as R increases. Conversely, the symmetric stretch shifts to slightly lower wave numbers as R increases from (3.0) to (5.0). The finger print region shows some interesting peaks with large shifts dependent on R, e.g. ~700 cm⁻¹ which may be due to OH vibrational modes.^{1,2} The 1,4-di-substituted benzene C-H out of plane bends are usually strong possibly accounting for the peaks at around 750 cm⁻¹ and 825 cm⁻¹, while the in-plane bending is very weak and may account for the peak at 1018 cm⁻¹.

1. M. J. Hernandez-Moreno, M. A. Ulibarri, J. L. Rendon and C. J. Serna, *Phys. Chem. Mater.* 1985, **12**, 34-38.
2. W. Kagunya, R. Baddour-Hadjean, F. Kooli and W. Jones, *Chem. Phys.* 1998, **236**, 225-234.

3. Interlayer Arrangements in Terephthalate LDHs.

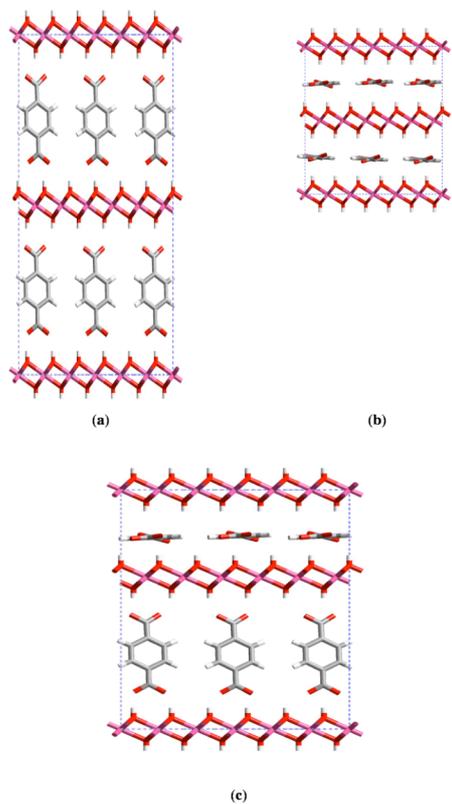


Fig. S2 Schematic to show the possible interlayer arrangements in terephthalate intercalated LDHs. The interlayer arrangement are generally described as (a) expanded, when the terephthalate is perpendicular to the LDH sheet, (b) collapsed when the terephthalate is parallel with the LDH sheet, and (c) interstratified when an alternating sequence of collapsed and expanded layers are observed.